

Belousov–Zhabotinsky oscillations during the chemical or electrochemical generation of Ag^+ ions

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Abstract

The oscillatory Belousov–Zhabotinsky reaction has been studied in the presence of Ag^+ ions using potentiometric and amperometric methods. Amperometrically, the oscillations were followed by monitoring the anodic current at a potential of 1.0 V, which corresponds to the electrooxidation of Br^- ions. In the Ag^+ -perturbed BZ reaction we still observe anodic current oscillations due to the electrooxidation of Br^- ions more or less loosely bound in AgBr mono- or oligomers. Solid AgBr, however, has been found to be chemically and electrochemically inert in the BZ reaction. The timescale of producing electrochemically inactive AgBr precipitate is a second-order process with a rate constant of $256 \text{ M}^{-1} \text{ s}^{-1}$.

1. Introduction

The influence of silver ions in the oscillatory Belousov–Zhabotinsky (BZ) reaction has been studied by several authors. The first studies of Ag^+ -perturbed BZ systems trace back to the early work by Busse and Zhabotinsky and co-workers [1]. Most challenging was perhaps the paper by Noszticzius [2] claiming the existence of ‘non-bromide-controlled oscillations’ which questioned the validity of the Field–Körös–Noyes (FKN) mechanism [3] and the Oregonator model [4]. Even Field [5] has pointed out that ‘non-bromide controlled oscillations are the most difficult ones to rationalize within the framework of the FKN mechanism’. Ruoff [6] observed the Field and Noyes predicted [7] excitability of a reduced steady state when silver ions were added to

the BZ system. When oxygen is bubbled into an oscillatory BZ reaction with high malonic acid concentration an excitable reduced steady state is created. Continuous addition of AgNO_3 results in high frequency oscillations where the frequency increases with increasing addition rate of AgNO_3 [8–11]. Simulation of the amplitude behavior in the Ag^+ -perturbed excitable BZ reaction [10] leads to the conclusion that the platinum electrode’s potential is composed of several contributions, i.e. the $\text{Ce(III)}/\text{Ce(IV)}$ redox couple which dominates at low Ag^+ concentrations or flow rates and the contribution of HBrO_2 , HOBr and BrO_2 which dominate at higher Ag^+ addition rates.

Ganapathisubramanian and Noyes [12,13] came to the conclusion that in the presence of excess silver ions the oscillations can be explained by a competition between bromine atoms and bromate ions for HBrO_2 . The phase response of the perturbed BZ reaction provides evidence of bromide-ion-control

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without the use of a bromide-ion-detecting device [14]. Noszticzius et al. proposed on the basis of Ref. [2] a bromide-ion-free skeleton model, the so-called Explodator [15,16], in order to provide an alternative description of the oscillatory BZ reaction compared with the bromide-ion-control of the FKN mechanism. However, a test between the Explodator and Oregonator models by means of perturbation experiments was clearly in favor of the Oregonator model [17]. Furthermore, studies of the Oregonator which has been extended by a Br^- -removing reaction have shown that the FKN mechanism is able to describe the essential features of Ag^+ -perturbed BZ systems [18,19]. Treindl and Mrakovova [20] studied Ag^+ -perturbed Mn(II)/Mn(III) -catalyzed systems spectrophotometrically and also concluded that Ag^+ -induced oscillations can still be rationalized within the FKN framework. Despite the papers cited above, Noszticzius and McCormick [21] insisted on the original interpretation of the experiment [2] and on the concept of non-bromide-controlled oscillations. Spectrophotometric studies of the AgBr precipitate formation by Kshirsagar et al. [22] and reviews by Noyes et al. [23] and Ruoff et al. [24] concluded that silver ion induced oscillations are still controlled by free or lightly complexed bromide ions much as classical [25] BZ oscillations.

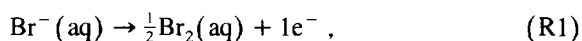
The aim of the present work was to study Ag^+ -perturbed BZ oscillations amperometrically and to measure the anodic current which corresponds to the electrooxidation of a bromide ion. We found that freshly prepared AgBr precipitate is, as expected [26], electrochemically inactive, i.e. it is not electrooxidized and does not contribute to the anodic current. Similarly, freshly prepared solid AgBr is also chemically inert in the BZ reaction and does not affect the oscillations. The formation of electrochemical inactive solid silver bromide is a second-order process with an estimated rate constant of $256 \text{ M}^{-1} \text{ s}^{-1}$.

2. Experimental

All chemicals were reagent grade and solutions were prepared from double-distilled water. The reaction course of the BZ reaction was followed potentiometrically by means of a macroscopic platinum

electrode (Metrohm, Switzerland), a Br^- -ion selective electrode (Br-ISE, Orion, USA), and voltamperometrically by measuring the anodic current, which corresponds to the electrooxidation of Br^- ions at a constant potential ($E = 1.0 \text{ V}$) against a saturated calomel reference electrode.

In these measurements we used the General Purpose Electrochemical System (GPES, EcoChemie B.V., Netherlands) in combination with a rotating (900 rpm) Pt-ring–disc electrode (Pine, USA). When all three techniques were applied simultaneously, the Pt-potential was followed at the disk, while the amperometrical measurements were performed at the ring of the rotating Pt-ring–disk electrode. The potential of $E = 1.0 \text{ V}$ was chosen, because at this potential Ce(III) and HOBr do not contribute to the anodic current. At this potential the anodic current is a linear function of the bromide ion, due to its electrooxidation at the anode (Table 1):



HOBr was prepared as described previously [27].

The generation of Ag^+ ions has been achieved either chemically by inserting a silver coil into the BZ medium, or electrochemically by using this coil as an anode against a Pt cathode. The coil was made from 30 cm 0.5 mm thick Ag-wire (99.99% Ag) and twined around a rod of 5 mm diameter. The reaction solution was stirred by a magnetic stirrer at 60 rpm.

Table 1
Amperometric calibration of bromide ion concentration in 1 M sulfuric acid ^a

Current $\times 10^6$ (A)	$[\text{Br}^-] \times 10^4$ (M)
2.95	1.1
4.66	2.2
6.48	3.3
8.32	4.4
1.02	5.5
1.24	6.6
1.49	7.7
1.69	8.8
1.87	9.9

^a Linear regression coefficient: 0.9987 with slope 0.0183 A/M ; $E = 1.0 \text{ V}$.

3. Results and discussion

We have monitored the BZ reaction with the same composition and initial concentrations as Noszticzius [2]. First the BZ reaction has been followed in the absence of Ag^+ ions and then Ag^+ -ions are generated chemically or electrochemically. Fig. 1 shows the response of the system when Ag^+ ions are generated chemically. In this case a Ag-coil was inserted and due to the corrosive BZ medium Ag^+ ions were produced. Due to the presence of Ag^+ ions higher frequency oscillations are observed (Fig. 1). Interestingly, the corresponding amperometric oscillations do not show the strong damping as the oscillations at the Br-ISE (Fig. 2).

When silver ions are produced electrochemically, the generation of Ag^+ is much faster. When we use

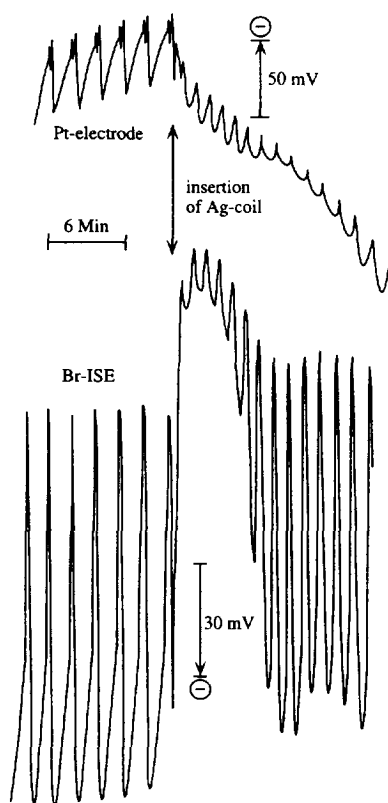


Fig. 1. Generation of high frequency oscillations when inserting the Ag-coil. Initial concentrations: $[\text{H}_2\text{SO}_4]_0 = 1.5 \text{ M}$, $[\text{Ce}(\text{SO}_4)_3]_0 = 1 \times 10^{-3} \text{ M}$, $[\text{NaBrO}_3]_0 = 4 \times 10^{-3} \text{ M}$, $[\text{malonic acid}]_0 = 0.1 \text{ M}$.

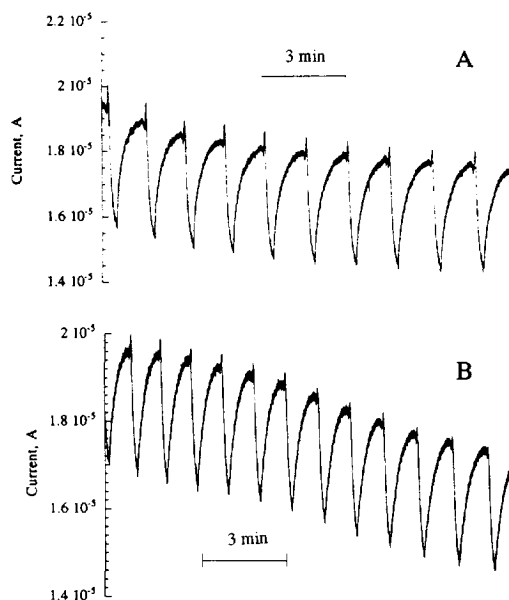
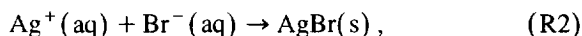


Fig. 2. A system with same initial concentrations as in Fig. 1, but the oscillations are monitored amperometrically at potential $E = +1.0 \text{ V}$. (A) Oscillations before Ag^+ ions are generated. (B) Oscillations directly after the Ag-coil has been inserted.

at least the same sensitivity of the recorder for the Br-ISE as for the Pt-electrode, we always observe oscillations at both electrodes. When the oscillations eventually die out, the amperometric oscillations, the oscillations at the Pt-electrode and the oscillations at the Br-ISE die out simultaneously (Fig. 3). From the many experiments we have performed using different Ag^+ -generation rates, we conclude that there is no indication of 'non-bromide-controlled-oscillations', i.e. the occurrence of oscillations that can only be observed at the Pt-electrode!

To better understand the amperometric response in the presence of Ag^+ ions, we investigated the formation of AgBr precipitate separately. To a $2.2 \times 10^{-4} \text{ M}$ KBr solution in $1 \text{ M H}_2\text{SO}_4$ a stoichiometric amount of AgNO_3 was added. Because solid AgBr does not contribute to the anodic current [26], a decrease of the anodic current is expected as solid AgBr is formed. Fig. 4A shows this response. The kinetics are clearly second order (Fig. 4B) according to the process



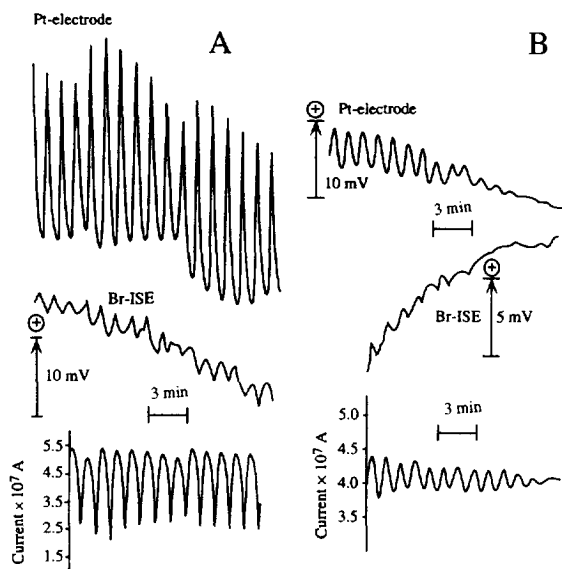
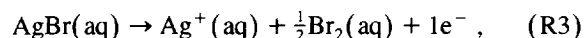


Fig. 3. (A) Oscillations approximately 15 min after the onset of the continuous electrochemical generation of Ag^+ ions and 60 min after the start of the oscillator. The generating Ag^+ current is 36 mA. (B) Same system but approximately 15 min later when the oscillations die out.

with a rate constant of $256 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. 4B). This rate constant is, as found earlier [18,19,28], considerably smaller than that expected from a diffusion-controlled process. Also in the spectrophotometric experiments by Kshirsagar et al. [22] kinetics of this timescale have been observed.

Although the initial formation of AgBr monomers in the BZ reaction is apparently a diffusion-controlled process [22], bromide ions in AgBr monomers (or oligomers) are, in contrast to solid AgBr, still electrooxidizable



and therefore also chemically active. Our amperometric findings clearly show and support the view [22] that bromide ions bound in AgBr monomers or oligomers are chemically active in the BZ medium until solid silver bromide is formed. In this view, oscillations also in the presence of excess silver ions can still be considered as bromide-ion-controlled, although bromide ions are now bound to silver ions. Further studies using the amperometric technique are being considered.

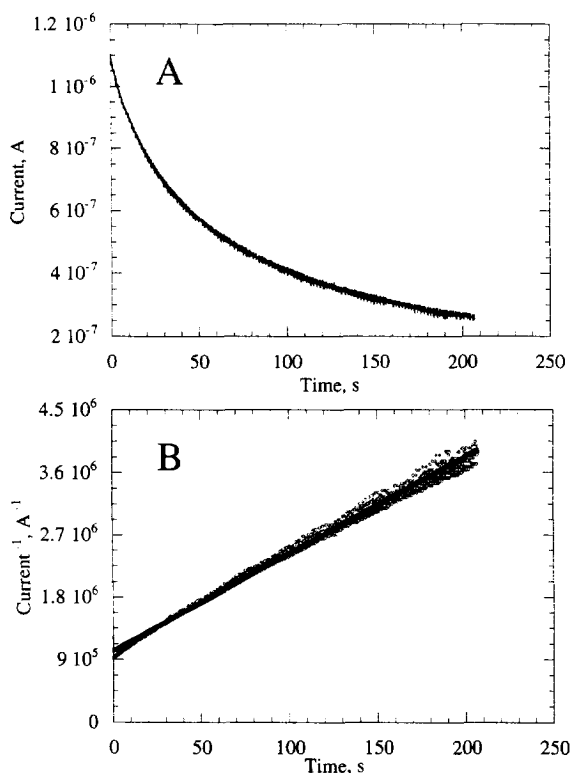


Fig. 4. (A) Decrease in amperometric current due to the formation of the electrochemically inactive AgBr precipitate. Initial concentrations: $[\text{Br}^-]_0 = [\text{Ag}^+]_0 = 2.2 \times 10^{-4} \text{ M}$ in 1 M sulfuric acid. (B) Same data as in (A) but inverse current is replotted against time. The linear relationship indicates second-order kinetics. The grey points are experimental data and the solid line is the linear regression ($r = 0.997$) with slope $1.4 \times 10^4 \text{ A}^{-1} \text{ s}^{-1}$. From the amperometric calibration curve of the bromide ion (Table 1) a rate constant of $256 \text{ M}^{-1} \text{ s}^{-1}$ is calculated.

Acknowledgements

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