Oscillation Inhibition by Bromide-Removing Reagents near the Transition to the Excitable Steady State in the Closed Stirred Belousov–Zhabotinsky Reaction

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When the oscillating state of a closed Belousov–Zhabotinsky reaction is sufficiently near the transition to the excitable steady state, addition of Br^--removing reagents leads either to excitation or to inhibition of the oscillations, depending upon where in the cycle the perturbation was applied.

Introduction

The classical[1] Belousov[2]–Zhabotinsky[3] reaction (BZR) is defined as the metal-ion-catalyzed bromination and oxidation of an organic substrate by bromate ion in acidic, aqueous media. Under suitable initial reagent concentrations, a closed BZ system may exhibit many repeated nearly unchanged concentration oscillations of the catalyst, bromide ions, and other intermediates.

The basic mechanism of the BZ oscillations is now well understood, notably from the important work of Field, Körös, and Noyes (FKN mechanism).[4,5] In this mechanism Br^- ions play the role of a control intermediate.[1] Although the FKN mechanism with its Br^- control is challenged[6–9] from time to time, recent systematically performed perturbation experiments on the closed oscillating malonic acid BZR provide further evidence of the essential validity of Br^- control in this system even without the use of a Br^--selective electrode.[10]

Recently this author observed a nonoscillatory excitable steady state where the Br^- concentration is slightly above a certain critical value (threshold). When the Br^- concentration is forced below that critical value (for example, by addition of $AgNO_3$), fully developed Ce^{IV} spikes are induced.[11] This phenomenon was originally described in a theoretical paper by Field and Noyes.[12] In relation to this excitability property, the closed, stirred BZR shows interesting analogies with biological systems.[13] Especially at the transition between oscillating and nonoscillating (excitable) states, complex behavior is observed as irregular oscillations,[14] bursts,[15,16] and apparently also turbulent behavior.[16–20] We report in this paper an observation made at the transition between the oscillating and excitable states when the closed malonic acid BZR is perturbed by addition of $AgNO_3$ and HOBr. We found that perturbations lead either to inhibition of the oscillations or to excitability, depending upon where in the (oscillatory) cycle the perturbation was applied. The results will be discussed from a mechanistic and topological point of view.

Materials and Method

In all experiments the BZR was performed in a thermostat-regulated glass container at 25 °C and 500 rpm with magnetic stirring and the reaction medium in contact with air. Potentiometric recordings with a conventional $x–t$ recorder were carried out by using a platinum electrode against a double junction Ag/AgCl reference electrode (Metrohm, sleeve type) with a satured KCl solution as the inner electrolyte and 1 M H_2SO_4 as the outer electrolyte. The platinum electrode reflects qualitatively the logarithm of the Ce^{IV}/Ce^{III} concentration ratio. Except for hydroxymalonic acid, $CH(OH)(COOH)_2$ (Merck-Schuchardt, "zur Synthese"), all other chemicals were of analytical grade. The chemicals were used without further purification. The reaction volume was 150 cm^3, and reagents were mixed as described in an earlier paper.[16] The initial reagent concentrations were $C_{H_2SO_4}$ = 1.0 M, $C_{malonic\ acid}$ = 0.28 M, C_{KBrO_3} = 0.1 M, and $C_{(NH_4)_2Ce(NO_3)_6}$ = 2.1 × 10^{-3} M.

As perturbants, aqueous solutions of $AgNO_3$ and HOBr were used. Hypobromous acid, HOBr, was prepared by adding 8.0 g of bromine to 100 cm^3 of a 0.5 M $AgNO_3$ solution which was stirred magnetically. After 10 min, the AgBr formed was removed by filtration and the solution stored at 0 °C. After 1 h, the solution

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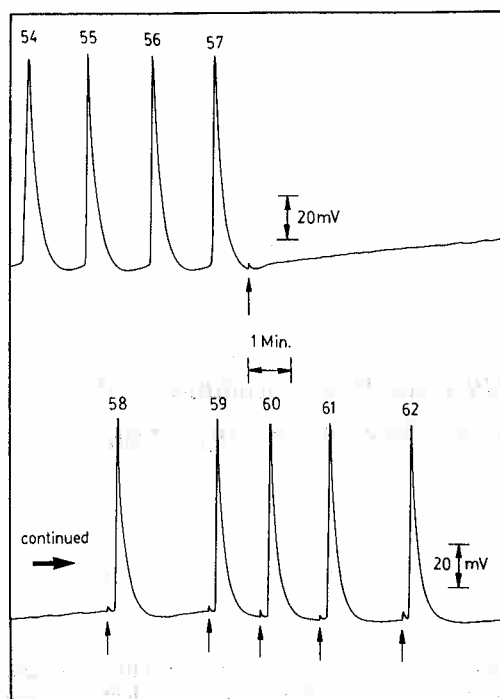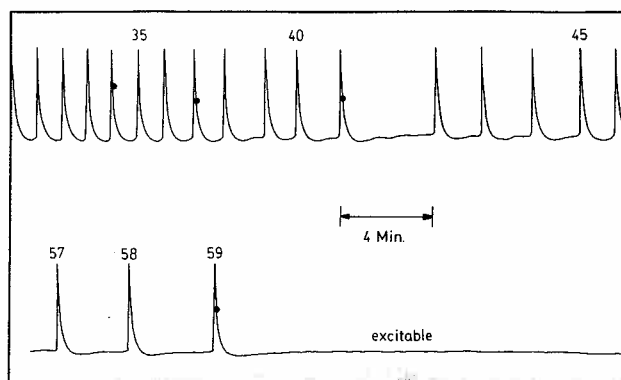
Figure 1. Inhibition of BZ oscillations and excitability by adding a single drop of the synthesized HOBr (arrows) into the reaction medium. Increasing value of the ordinate shows an increasing Ce^{IV}/Ce^{III} concentration ratio. The numbers indicate how many oscillations have taken place.

Figure 2. Temporal and complete inhibition by the addition of $AgNO_3$. The figure qualitatively shows that the inhibition effect of $AgNO_3$ grows as the oscillating system becomes closer to the border of the quiescent excitable regime. The dots indicate the addition of a single drop of a 0.25 M $AgNO_3$ solution. Increasing value of the ordinate shows an increasing Ce^{IV}/Ce^{III} concentration ratio. Numbers indicate how many oscillations have taken place.

was filtered and freed from bromine by three successive extractions using ice-cold CCl_4. Then, if necessary, the HOBr solution was filtered yet again and stored on ice. The HOBr solution was analyzed by potentiometric titration in 1 M H_2SO_4 with a 0.01 M KBr solution as titrant and a Br$^-$-selective electrode (Philips, IS 550) for determination of the endpoint. The yield of HOBr formed was 80% of the theoretical value. The perturbations were performed by adding a single drop of perturbant from a conventional Pasteur pipet to the reaction medium. The average drop size of the pipet was estimated (by weighing 2 × 50 drops of water) to be 31 μL.

Results and Discussion

Under our experimental conditions, the oscillating BZR evolves toward an excitable steady state with a sudden stop of oscillations.[11] When the oscillating state is sufficiently near the transition to the quiescent excitable state, we found that the addition of $AgNO_3$ or HOBr has two effects. (1) A nearly instantaneous appearance of a new Ce^{IV} spike is observed when the Br$^-$ concentration is driven below the critical[4,5] Br$^-$ concentration, C_{Br}^{crit}. This is the excitability property already found in the oscillating[10] and nonoscillating[11] state. (2) When the Br$^-$ concentration after perturbation is still slightly above C_{Br}^{crit}, the time required to return to the oscillating state increases the closer this state gets to the border of the excitable steady state. This divides the oscillatory cycle into two regions, i.e., into one where the Br$^-$ concentration after perturbation is lower than C_{Br}^{crit} and into another where the Br$^-$ concentration is higher than C_{Br}^{crit}. Depending upon in which of the two domains of the cycle the perturbation is applied, we either observe excitation or a temporary or complete inhibition of the oscillations (depending upon how near the oscillating system is the border of the excitable steady state). A similar behavior, i.e., increase of relaxation time found in a continuous-flow, stirred tank reactor, has been denoted as "critical slowing down".[21-23]

Figure 1 shows the inhibition effect when the oscillating BZR is perturbed by HOBr. The figure also shows that, due to its excitability property, single Ce^{IV} spikes may be induced by adding the same amount of HOBr somewhat later to the quiescent HOBr-inhibited BZR. Quite analogous is the situation using $AgNO_3$ as perturbant. Figure 2 qualitatively shows the increasing inhibition effect of $AgNO_3$ as the system gets closer to the transition to the quiescent excitable steady state. This somewhat surprising result indicates that, under our experimental conditions, Ag^+ ions may also directly inhibit the BZR or induce reactions doing so.

Although both HOBr and $AgNO_3$ remove Br$^-$ ions, it seems that their inhibition effect is subject to different but analogous mechanisms. When HOBr is added, it removes Br$^-$ ions rapidly and produces bromine

$$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O \tag{1}$$

which subsequently reacts with malonic acid to form Br$^-$ ions and bromomalonic acid (BrMA)

$$Br_2 + MA \rightarrow BrMA + H^+ + Br^- \tag{2}$$
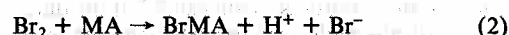
Thus, the removed and produced Br$^-$ ions balance. When the perturbation by HOBr is now applied sufficiently near the transition to the quiescent excitable domain such that the Br$^-$ concentration is not forced below C_{Br}^{crit}, the additional BrMA-producing and Br$^-$-liberating step (2) may "push" the BZ system across the border into the excitable nonoscillating regime as indicated in Figure 1.

It seems more tricky to explain the similar behavior of $AgNO_3$. In contrast to HOBr, $AgNO_3$ *irreversibly* removes Br$^-$ ions, limited only by the solubility product of AgBr

$$Ag^+ + Br^- \rightarrow AgBr \tag{3A}$$

$$[Ag^+][Br^-] = 7.7 \times 10^{-13} \tag{3B}$$

A possible explanation may be that in the presence of solid AgBr the added silver ion "buffers" the bromide concentration. If a small amount of silver ion is added so that a precipitate of AgBr is formed such that moles of precipitate is approximately equal to the moles of free Ag^+, the concentration of Br$^-$ will be insensitive to formation or consumption of small amounts of this ion. If that concentration is a little above the critical value, the simultaneous presence of Ag^+ and AgBr will keep the system in an excitable nonoscillatory state as is observed. Interestingly, a similar observation and interpretation has recently been reported by Körös and co-workers using Hg^{II} or Tl^{III} ions as perturbants.[24,25] These

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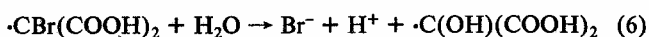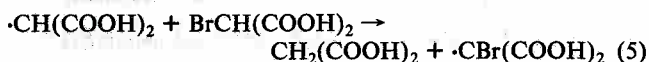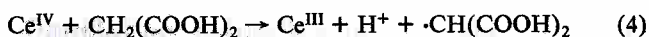
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metal ions are well-known as highly stable water-soluble bromo complexes. Körös et al.[24] observe an increase in period lengths when perturbant is added and explain[25] the increase of period length by a buffer effect of the bromo complexes of the metal ion formed.

However, experimental evidence now also exists[26,27] which shows that Ce^{IV} ions form bromo complexes, $CeBr^{3+}$, as proposed in the context of the BZR by Jwo and Noyes[28]. Another explanation of the Ag^+-induced inhibition effect may be based on the potentially different chemical behavior of $CeBr^{3+}$ and Br^- uncomplexed Ce^{IV} ions, which in H_2SO_4 are known to be present as sulfato complexes.[27] While Ce^{IV} via radical reaction steps liberates Br^- ions from BrMA[28]

$$Ce^{IV} + CH_2(COOH)_2 \rightarrow Ce^{III} + H^+ + \cdot CH(COOH)_2 \quad (4)$$

$$\cdot CH(COOH)_2 + BrCH(COOH)_2 \rightarrow \\ CH_2(COOH)_2 + \cdot CBr(COOH)_2 \quad (5)$$

$$\cdot CBr(COOH)_2 + H_2O \rightarrow Br^- + H^+ + \cdot C(OH)(COOH)_2 \quad (6)$$

the $CeBr^{3+}$ complex is assumed[26] to react with malonyl radicals and produce Ce^{III} ions and BrMA

$$CeBr^{3+} + \cdot CH(COOH)_2 \rightarrow BrMA + Ce^{III} \quad (7)$$
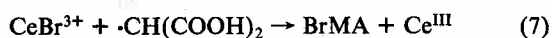
If we assume that a considerable amount of the total Ce^{IV} concentration is present as $CeBr^{3+}$ ions, the addition of Ag^+ ions (not driving the Br^- concentration below C_{Br}^{crit}) increases, due to the formation of AgBr, the amount of Br^- uncomplexed Ce^{IV}. According to the reaction sequence (4)–(6), Br^- uncomplexed Ce^{IV} ions liberate Br^- ions and finally "push" the oscillating system across the border into the quiescent excitable domain. Thus, the inhibition of the oscillations by $AgNO_3$ may, as in the case of HOBr, be qualitatively explained by an indirect liberation of Br^- ions. The same arguments have also been used to explain observed positive phase shifts at the platinum electrode in the $AgNO_3$-perturbed oscillating BZR far from transition to the excitable steady state.[10]

Another effect of silver ions is the acceleration of the nucleophilic attack of water on bromo or other halogeno organic compounds.[29] Since BrMA is the bromo organic species which is present in greatest concentrations,[30,31] we tested, according to eq 8, the influence of hydroxymalonic acid on the oscillating BZR.

$$CHBr(COOH)_2 + Ag^+ + H_2O \rightarrow \\ CH(OH)(COOH)_2 + AgBr + H^+ \quad (8)$$
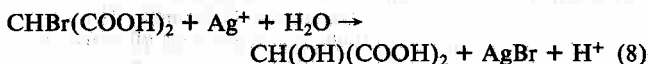
However, we observe that the effect of added hydroxymalonic acid is opposite to that expected if hydroxymalonic acid generated by eq 8 plays the dominant role in the inhibition of the oscillations. Instead of inhibition, we observe that addition of hydroxymalonic acid causes a significant *decrease* in period lengths (Figure 3A). With this decrease of period length, the inhibition of Ag^+ ions appears even more dramatic (Figures 3, B, and C).

From a topological point of view, it seems interesting that the inhibition by $AgNO_3$ in Figure 2 or Figure 3B is similar to ap-
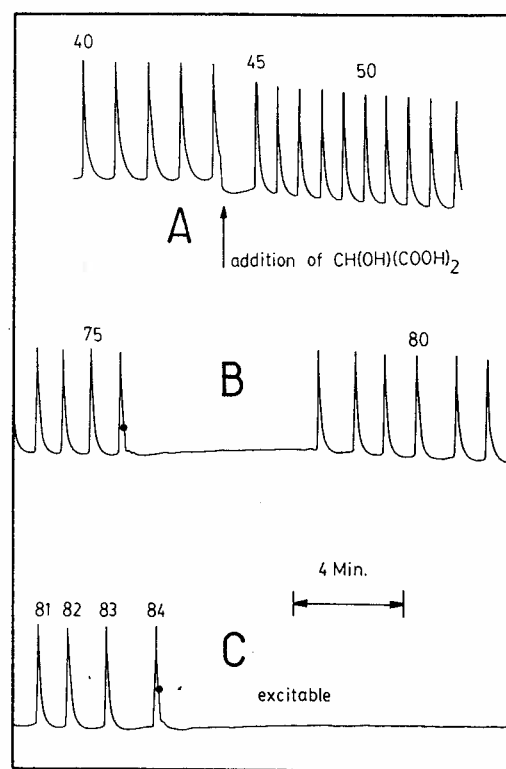

Figure 3. (A) Effect of the addition of hydroxymalonic acid. After addition, the concentration of unreacted hydroxymalonic acid was 2.5×10^{-2} M. (B and C) Dots indicate addition of one single drop of a 0.25 M $AgNO_3$ solution. Increasing value of the ordinate shows an increasing Ce^{IV}/Ce^{III} concentration ratio. Numbers indicate how many oscillations have taken place.

parent "phase singularities" of some biological oscillators, as for example for the heartbeat (see ref 32, p 271). Winfree demonstrated that certain "phase singularities" are expected to occur in perturbed oscillators using a suitable amount of perturbant such that the system's response lies between *type 1* and *type 0* phase resetting curves.[33] Because of the many analogies which exist between the BZR and other oscillating systems, he predicts that such phase singularities should also be observed in the BZR.[34] Although the analogy to the heartbeat inhibition[32] is indeed striking, we note, however, that our observed "phase singularity" does not occur at the transition between *type 0* and *type 1* resetting but at the transition between the oscillatory and excitable steady states. The question remains if this "singular behavior" near the transition between oscillating and excitable domains can also be extended to other classes of excitable oscillators. If so, this would offer an alternative condition when "phase singularities" in biological or other excitable oscillators are expected to occur.

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