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Phase Response Relationships of the Closed Bromide-Perturbed Belousov–Zhabotinsky Reaction. Evidence of Bromide Control of the Free Oscillating State without Use of a Bromide-Detecting Device

Peter Ruoff†

Department of Chemistry, University of Oslo, Blindern, Oslo 3, Norway *(Received: October 19, 1983)*

The use of bromide-selective electrodes in the oscillating Belousov–Zhabotinsky reaction (BZR) is still somewhat controversial. In this paper further evidence of bromide control in the oscillating BZR without any use of a bromide-detecting device is given. It is shown that the addition of silver ions, bromide ions, or hypobromous acid to the oscillating BZR results in phase shifts at the platinum electrode which behave as predicted by models simulating the Field–Körös–Noyes mechanism. Additional complexities due to higher initial Ce(IV) concentrations are reported and discussed.

Introduction

In its now classical form, the Belousov–Zhabotinsky reaction (BZR) is the metal-ion-catalyzed bromination of an organic material in aqueous acidic media. Under suitable conditions it may result in many repeated nearly unchanged concentration oscillations of the catalyst and other intermediates. Oscillations were first reported by Belousov[1] using citric acid as the organic substrate and the study was initiated by Zhabotinsky,[2] showing that different organic substrates may be used. The basic mechanism of the oscillations is now well established, notably by the work of Field, Körös, and Noyes[3] (FKN mechanism). In this mechanism, Br^- ions play the role of a control intermediate.[4] On the basis of the FKN mechanism several mathematical models[5–10] have been developed which qualitatively or semiquantitatively simulate most of the observed phenomena. However, in a series of papers, Noszticzius and co-workers question the importance of Br^- ions in the oscillating BZR. The argument is based mainly on the experimental fact that Br^--selective electrodes are also sensitive to hypobromous acid[11,12] and other compounds[13] which may contribute considerably to the electrode's potential.

Like many oscillating systems BZ oscillations are structurally stable and exhibit a limit cycle, i.e., periodicities in concentration are stable to perturbations in amplitude and frequency but not in phase.[14] In this paper we report an investigation on the phase shifts observed at a platinum electrode when the Br^- concentration of an oscillating BZR is perturbed by solutions of KBr, $AgNO_3$, or HOBr. It will be shown that the phase shifts observed at the platinum electrode behave exactly as predicted by models which simulate the FKN mechanism. This constitutes evidence of Br^- control without the use of a Br^--detecting device. Finally, we report and discuss additional complexities due to an increased initial Ce(IV) concentration when $AgNO_3$ is used as the perturbant.

Experimental Section

All experiments were performed in a closed stirred thermostat-regulated glass container at 25 °C. The stirring rate was kept constant at ca. 500 rpm with a magnetic stirrer. The oscillations were followed with a platinum electrode against a double junction

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† Permanent address: Rogaland Regional College, P.O. Box 2540 Ullandhaug, N-4001 Stavanger, Norway.

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Ag/AgCl reference electrode (Metrohm, sleeve type) with a saturated KCl solution as the inner electrolyte, and 1 M H_2SO_4 as the outer electrolyte. All chemicals were of analytical grade and used without further purification. As organic substrate malonic acid (MA) was used. The reaction volume was 150 cm^3 and oscillators were started by rapidly mixing the reagents in the following order: 1 M H_2SO_4–MA–$(NH_4)_2Ce(NO_3)_6$–$KBrO_3$. The initial compositions were $C_{MA} = 0.28$ M, $C_{Ce(IV)} = 5.0 \times 10^{-4}$ or 2.1×10^{-3} M, and $C_{KBrO_3} = 0.1$ M.

When the experiments were run under anaerobic conditions, nitrogen was first bubbled vigorously for 20 min into the sulfuric acid. Then the reagents were added and bubbling of nitrogen continued. So that the dry nitrogen gas would not carry off solvent, the gas was passed through two washing bottles filled with water before going into the reaction vessel.

After the induction period, the oscillator ran several free cycles. Then perturbation experiments were performed by adding a single drop of perturbant from a conventional Pasteur pipet to the reaction medium. After perturbation the system was allowed to resettle until limit cycle oscillations again appeared. Under our experimental conditions, the BZR evolves toward an excitable steady state. Near the border between the excitable and oscillating regime the oscillations may become irregular with a considerable increase of period length.[5] Therefore, in the experiments only the first 30–35 oscillations were used. Thus, several runs had to be performed until a complete phase response curve was obtained. Because of the slight increase in period lengths the experimentally determined phase shifts (see below) are expressed in fractions of the period length P_0 of the preceding unperturbed cycle.

As perturbants, aqueous solutions of KBr, HOBr, and $AgNO_3$ 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 was again 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 perturbation experiments were started. During the experiments the HOBr solution was stored at 0 °C. The HOBr solution was analyzed by potentiometric titration in 1 M H_2SO_4 by using a 0.01 M KBr solution as titrant and a Br^--selective electrode (Philips, IS 550) for determination of the end point. The yield of HOBr formed was 82% of the theoretical value.

The average drop size of the Pasteur pipet was estimated (by weighing 2 × 50 drops of water) to be 31 μL.

Simulation Models and Method of Calculation

Calculations were performed on a CDC CYBER digital computer using the program package DARE P with a version of Gear's algorithm.[15] In the models treated numerically, phase response curves were calculated by the following procedure. The model oscillator was first allowed to converge to the limit cycle by running several cycles freely. Thereafter one period of the limit cycle was recorded for all variable intermediates. Then for various positions in the cycle, instantaneous perturbations were applied ("phase of stimulation") and the phase shift was calculated. Because of the relationship between the redox potential of the platinum electrode and the logarithm of the Ce(IV)/Ce(III) concentration ratio, calculations of phase shifts (see next section) were performed for only the Ce(IV) variable.

The simplest model treated numerically was the Oregonator developed by Field and Noyes.[4] It consists of the following five irreversible reaction steps:

$$A + Y \rightarrow X + P \qquad (O1)$$

$$X + Y \rightarrow 2P \qquad (O2)$$

$$A + X \rightarrow 2X + Z \qquad (O3)$$

$$2X \rightarrow A + P \qquad (O4)$$

$$Z \rightarrow fY \qquad (O5)$$

where X = $HBrO_2$, Y = Br^-, Z = 2Ce(IV), A = BrO_3^-, and P = HOBr. The concentrations of A and P are constant. As in the original work,[5] the resulting differential equations were first written in dimensionless form. Original rate constants were used, only corrected for the experimental values of BrO_3^- and H^+ ions. The parameters k_{O5} and f were fixed at 1.0. We also considered a model which explicitly includes HOBr as an intermediate:

$$BrO_3^- + Br^- + 2H^+ \rightleftarrows HBrO_2 + HOBr \qquad (R1)$$

$$k_{R1} = 2.1\ M^{-3}\ s^{-1} \qquad k_{-R1} = 1 \times 10^4\ M^{-1}\ s^{-1}$$

$$HBrO_2 + Br^- + H^+ \rightleftarrows 2HOBr \qquad (R2)$$

$$k_{R2} = 2 \times 10^9\ M^{-2}\ s^{-1} \qquad k_{-R2} = 5 \times 10^{-5}\ M^{-1}\ s^{-1}$$

$$BrO_3^- + HBrO_2 + H^+ \rightleftarrows 2BrO_2\cdot + H_2O \qquad (R3)$$

$$k_{R3} = 1 \times 10^4\ M^{-2}\ s^{-1} \qquad k_{-R3} = 2 \times 10^7\ M^{-1}\ s^{-1}$$

$$Ce^{3+} + BrO_2\cdot + H^+ \rightleftarrows Ce^{4+} + HBrO_2 \qquad (R4)$$

$$k_{R4} = 6.5 \times 10^5\ M^{-1}\ s^{-1} \qquad k_{-R4} = 2.4 \times 10^7\ M^{-1}\ s^{-1}$$

$$2HBrO_2 \rightleftarrows HOBr + BrO_3^- + H^+ \qquad (R5)$$

$$k_{R5} = 4 \times 10^7\ M^{-1}\ s^{-1} \qquad k_{-R5} = 2 \times 10^{-10}\ M^{-2}\ s^{-1}$$

$$Ce^{4+} + BrMA \rightarrow gBr^- + Ce^{3+} + \text{product} \qquad (R6)$$

$$k^*_{R6} = k_{R6}C_{BrMA} = 1.0\ s^{-1} \qquad g = 0.9$$

$$HOBr + Br^- + H^+ \rightleftarrows Br_2 + H_2O \qquad (R7)$$

$$k_{R7} = 8 \times 10^9\ M^{-2}\ s^{-1} \qquad k_{-R7} = 2.0\ M^{-1}\ s^{-1}$$

$$Br_2 + MA_{enol} \rightarrow BrMA + Br^- + \text{product} \qquad (R8)$$

$$k^*_{R8} = k_{R8}C_{MA_{enol}} = 1.0\ s^{-1}$$

This model is similar to a mechanism previously used by Showalter et al.,[9] extended by the inclusion of bromine hydrolysis (R7) and the bromination of MA_{enol} (enol form of malonic acid) (R8), as treated for irreversible reaction steps by Ganapathisubramanian et al.[10] Concentrations of BrO_3^-, H^+, H_2O, BrMA (bromomalonic acid), and MA_{enol} are treated as constants. As in the Oregonator, k_{R6} and g are variable parameters. Their values are still somewhat uncertain.

In all model calculations, the phase shifts are first expressed in the time scale of the respective models, i.e., in the Oregonator we are using the dimensionless τ scale,[4] while in the reaction scheme R1–R8 the time is given in seconds. However, in order to compare the theoretical results with experiments, we have, as in the case of the experimentally determined phase shifts, also expressed the calculated phase shifts in fractions of the unperturbed period length P_0 of the model.

Theoretical Predictions and Comparison with Experiments

The Initial Phase Shift of the Ce(IV) Spike. The essential feature of the FKN mechanism is that Br^- ions act as a control intermediate.[3,4] Above a certain critical bromide concentration, $C_{Br^-}^{crit}$, Br^- is removed by reactions with bromate and other intermediates until $C_{Br^-}^{crit}$ is reached. The sum of these reactions is denoted as process A. Then an autocatalytic process sets in which drives the Br^- concentration far above $C_{Br^-}^{crit}$ so that a new cycle can start.

According to the FKN mechanism, the addition of Br^- ions during process A should lengthen the period since more Br^- ions have to be removed in order to reach $C_{Br^-}^{crit}$. On the other hand, removing Br^- ions (but not forcing the Br^- concentration below $C_{Br^-}^{crit}$) should lead to a shortened period. More specifically, the addition of Br^- ions should lead to a *delay* in the appearance of the Ce(IV) spike (compared with the unperturbed oscillations) while *irreversible removal* of Br^- ions should lead to a corresponding *advance*. In the following it will be shown that this initial phase shift of the experimental Ce(IV) spike (in the paper simply

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[15] Wait, J. V.; Clarke, D. DARE P Users Manual, Version 4, Report 299, University of Arizona, 1976.

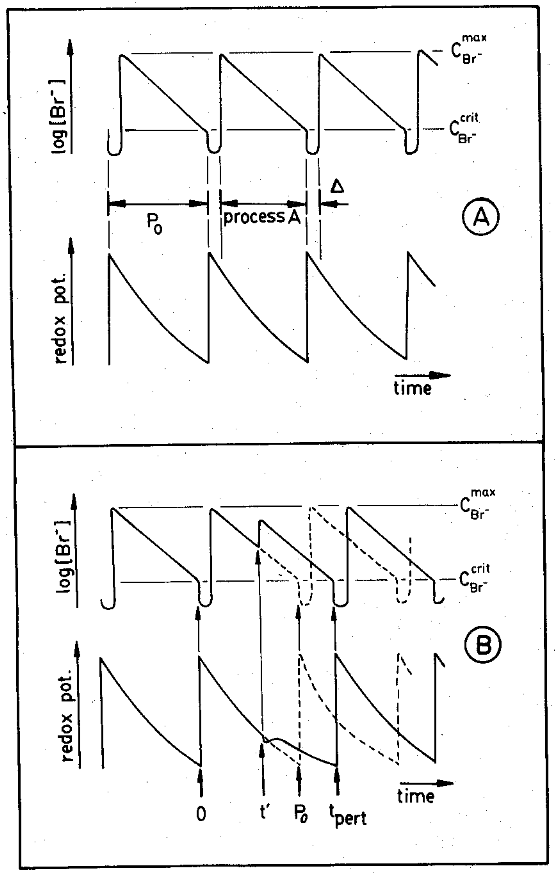

Figure 1. (A) Partition of the unperturbed period P_0 in Δ and the slow Br^- removing process A. (B) The initial phase shift $\Delta\phi$ at the platinum electrode is defined as the time difference between the appearance of the perturbed Ce(IV) maximum (at $t = t_{pert}$) and the unperturbed Ce(IV) top (at $t = P_0$). Addition of Br^- ions at $t = t'$ ("phase of stimulation") causes a delay in the Ce(IV) spike (positive phase shifts), while an irreversible removal of Br^- ions causes an advance in the appearance of the Ce(IV) top (negative phase shifts).

denoted as the "phase shift") behave exactly as predicted by the FKN mechanism.

Addition of Br^- Ions. A simple model of the FKN mechanism may be constructed by using for process A the following irreversible reaction

$$A + Y \rightarrow \text{product} \qquad (S1)$$

$$k_{S1} = 2.1 \text{ M}^{-1} \text{ s}^{-1}$$

where $A = BrO_3^-$ and $Y = Br^-$, while "product" is here an uninteresting reaction product. The autocatalytic process is regarded as an indifferent reaction which lasts a certain time Δ and finally drives the Br^- concentration to C_{Br}^{max} (Figure 1A). The rate equation for Y during process A is simply

$$d(\ln [Y]) = -k^*_{S1}\, dt \qquad k^*_{S1} = k_{S1}C_A = \text{constant} \qquad (1)$$

We will now consider an instantaneous addition of Br^- ions, ΔC_{Br}, at $t = t'$ (the "phase of stimulation"). The new Br^- concentration at $t = t'$ is $C'_{Br} + \Delta C_{Br}$. Integrating eq 1 from $C'_{Br} + \Delta C_{Br}$ to C_{Br}^{crit}

$$\int_{C'_{Br}+\Delta C_{Br}}^{C_{Br}^{crit}} d(\ln [Y]) = -k^*_{S1}\int_{t'}^{t_{pert}} dt \qquad (2)$$

and from C'_{Br} to C_{Br}^{crit}

$$\int_{C'_{Br}}^{C_{Br}^{crit}} d(\ln [Y]) = -k^*_{S1}\int_{t'}^{P_0} dt \qquad (3)$$

we get an explicit expression of the phase shift $\Delta\phi$ which is given by (Figure 1B)

$$\Delta\phi = (t_{pert} - t') - (P_0 - t') = t_{pert} - P_0 \qquad (4)$$

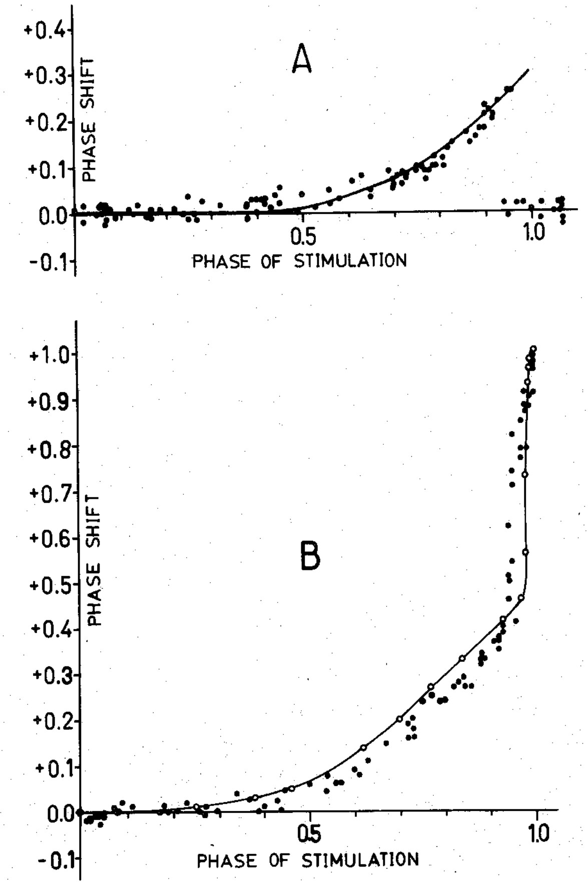

Figure 2. Experimental and calculated phase response curves (phase shift vs. the phase of stimulation) using Br^- ions as perturbant. (A) The perturbation strength in the experiment is 2.1×10^{-5} M of unreacted added KBr. The solid line represents eq 5a and 5b with $\Delta C_{Br} = 6.0 \times 10^{-6}$ M, $\Delta = 15$ s, $P_0 = 40$ s, $k_{S1} = 2.1$ M^{-1} s^{-1}, and $C_{Br}^{max} = 10^{-4}$ M. (B) The perturbation strength in the experiment is 2.1×10^{-1} M of unreacted added KBr. The solid line represents the calculation using the Oregonator (curve 1 in Figure 3A). In both (A) and (B) the initial Ce(IV) concentration was 2.1×10^{-3} M and the reaction medium was in contact with air.

From Figure 1B we see at once that $\Delta\phi \geq 0$, as expected. Inserting eq 2 and 3 in eq 4 we obtain the retarded phase shift, $\Delta\phi_{ret}$:

$$\Delta\phi_{ret} = (1/k^*_{S1}) \ln \left(\frac{C'_{Br} + \Delta C_{Br}}{C'_{Br}}\right) \qquad (5a)$$

Integrating the unperturbed system from $t = \Delta$ to $t = t'$, we obtain the following expression for C'_{Br}:

$$C'_{Br} = C_{Br}^{max} \exp(-k^*_{S1}(t' - \Delta)) \qquad (5b)$$

Despite the simplicity of the model it is surprising how good the agreement with the experiment actually is. Figure 2A shows the experimental data for a low concentration of added Br^-. The solid line on Figure 2A represents eq 5a and 5b. The jump back to the zero line occurs at 0.94 in the experiment and not at 1.0 as in the model.

An improved model but still a skeleton is the Oregonator model (O1–O5). In Figure 3A we see the calculated phase shifts for three different concentrations of added Br^- ions. Although the Oregonator gives a better description of the jump to the zero line, the behavior of low perturbant concentrations is essentially that of our simple model. Using a high added Br^- concentration in the model (curve 1 in Figure 3A), we observe a characteristic top at the end of the cycle. This is actually found in the experiment and Figure 2B shows the good semiquantitative agreement.

Irreversible Removal of Br^- Ions. The FKN mechanism predicts an advance in the appearance of the Ce(IV) spike ($\Delta\phi$ < 0) when Br^- ions are irreversibly removed from the reaction medium. With our simple model (S1, Figure 1), similar calcu-

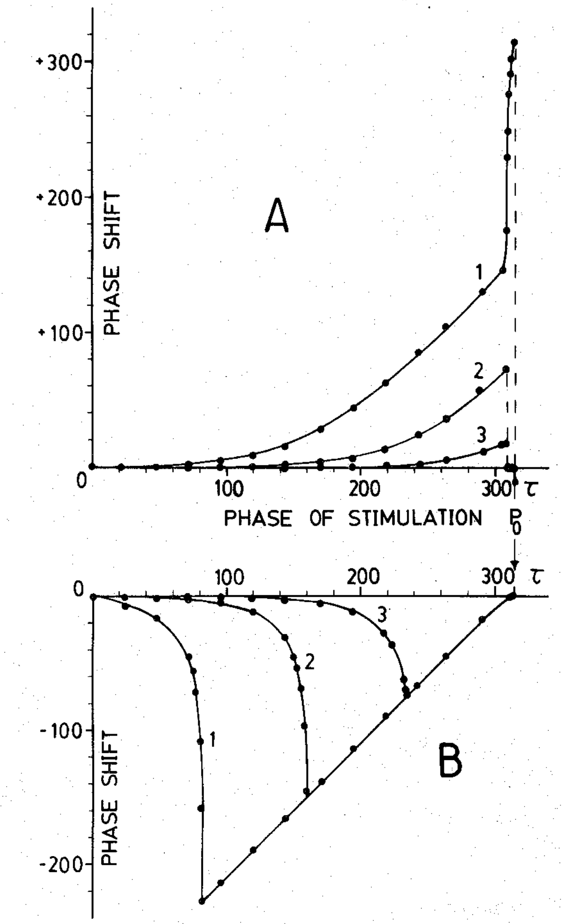

Figure 3. Calculated phase shifts using the Oregonator (P_0 = 314.4 ≙ 21.7 s). (A) Addition of Br^- ions (M of added unreacted Br^- ions): curve 1, 5 × 10^{-5}; curve 2, 5 × 10^{-6}; curve 3, 5 × 10^{-7}. (B) Irreversible removal of Br^- ions (M of instantaneously removed Br^- ions): curve 1, 5 × 10^{-4}; curve 2, 5 × 10^{-5}; curve 3, 5 × 10^{-6}.

lations, as performed in the previous section, lead to the following expressions for the advanced phase shifts, $\Delta\phi_{adv}$:

$$\Delta\phi_{adv} = (1/k^*_{S1}) \ln\left(\frac{C'_{Br} - \Delta C_{Br}}{C'_{Br}}\right) \quad \text{if } C'_{Br} - \Delta C_{Br} > C_{Br}^{crit} \quad (6a)$$

$$\Delta\phi = -(P_0 - t') \quad \text{if } C'_{Br} - \Delta C_{Br} \leq C_{Br}^{crit} \quad (6b)$$

Interesting is the linear relationship in eq 6b. It states that when the Br^- concentration is forced below C_{Br}^{crit} a Ce(IV) spike is immediately induced. This is the excitability property of the BZR recently found experimentally in nonoscillatory states.[16,17] We therefore call eq 6b the "excitable branch".[18]

Figure 3B shows the calculated phase shifts from the Oregonator when Br^- ions are instantaneously removed, for example by the addition of $AgNO_3$. In the calculations of Figure 3B, the solubility product of AgBr[19] was not considered, i.e., we used the approximation that in situations when the Br^- concentration was lower than the amount of Br^- ions removed, the resulting Br^- concentration was made equal to zero. However, we also performed calculations with the inclusion of the solubility product of AgBr[19] using the model R1–R8. The results are shown in Figure 4. The experimental data using different $AgNO_3$ solutions as perturbants are presented in Figure 5. We note that, in the model calculations, the excitable branch (solid lines in Figure 5, A and B) lies parallel beneath the experimental curve (dashed line). The reason for this is probably due to the neglect of various intermediate reaction steps in the models which cause an additional delay in the appearance of the Ce(IV) spike. Nevertheless, for low perturbant concentrations (Figure 5, A and B) we obtain a semiquantitative agreement between computations and experiments. Figure 2 together with Figure 5 clearly shows that the free oscillating state is controlled by Br^- ions.

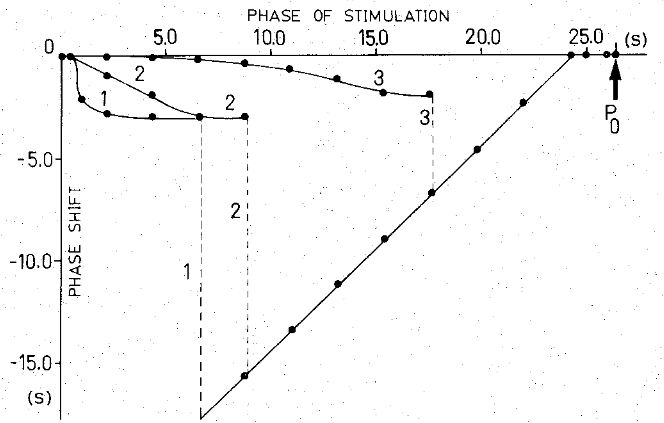

Figure 4. Calculated phase shifts using the model R1–R8 (P_0 = 26.4 s) where $AgNO_3$ irreversibly and instantaneously removes Br^- ions. Note the buffer effect of the solubility product of AgBr just before the sudden jump to the excitable branch. The perturbation strengths (M of added unreacted Ag^+ ions) are as follows: curve 1, 3.3 × 10^{-4}; curve 2, 3.3 × 10^{-5}; curve 3, 3.3 × 10^{-6}.

TABLE I: Average Experimental Period Length in the Dependence on Initial Ce(IV) Concentration

$C_{Ce(IV)}$, M	P_0,[a] s
2.1 × 10^{-3}	45–47
5.0 × 10^{-4}	28–30

[a] Anaerobic condition; however, no significant difference between anaerobic and aerobic conditions was observed.

Addition of HOBr. We found it interesting to use hypobromous acid as an additional check of the bromide control. By R7, HOBr reacts rapidly with Br^- ions and forms bromine which subsequently reacts with malonic acid to produce Br^- ions and bromomalonic acid (R8). Thus the removed and produced Br^- ions balance and we therefore expect either a zero phase shift or, due to the delay inherent in the reaction sequence R7–R8, a slight delay in the appearance of the Ce(IV) pulse. Only in the case when the HOBr concentration is so high that the Br^- concentration is forced below C_{Br}^{crit} should we immediately induce a Ce(IV) spike, i.e., observe the excitable branch. This predicted behavior is indeed found by calculations using the FKN model R1–R8 (Figure 6). Characteristic is the continuation of the excitable branch into the domain of positive phase shifts at the end of the cycle. This is due to the delay of R7–R8 mentioned above. Figure 7 shows the experimental results using two different initial Ce(IV) concentrations. It is interesting to note that, at higher initial Ce(IV) concentrations (Figure 7B), the jump to the excitable branch occurs much later in the cycle than when the lower initial Ce(IV) concentration is used (Figure 7A). This effect is not unexpected, since Ce(IV) itself initiates radical reactions which finally liberate Br^- ions[20]

$$\text{Ce(IV)} + CH_2(COOH)_2 \rightarrow \text{Ce(III)} + H^+ + \cdot CH(COOH)_2 \quad (A1)$$

$$\cdot CH(COOH)_2 + BrCH(COOH)_2 \rightarrow CH_2(COOH)_2 + \cdot CBr(COOH)_2 \quad (A2)$$

$$\cdot CBr(COOH)_2 + H_2O \rightarrow Br^- + H^+ + \cdot C(OH)(COOH)_2 \quad (A3)$$

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[16] (a) Ruoff, P. *Chem. Phys. Lett.* **1982**, *90*, 76. (b) *Ibid.* **1982**, *92*, 239. (c) *Naturwissenschaften* **1983**, *70*, 306.

[17] Ruoff, P. *Chem. Phys. Lett.* **1983**, *96*, 374.

[18] In this context, it is interesting to note that certain biological oscillators also have such an excitable branch. Thus, the record of phase response curves of these oscillators immediately leads us to the existence of their excitable kinetics.

[19] "Handbook of Chemistry and Physics"; CRC Press: Cleveland, 1980, 60th ed, p B-220.

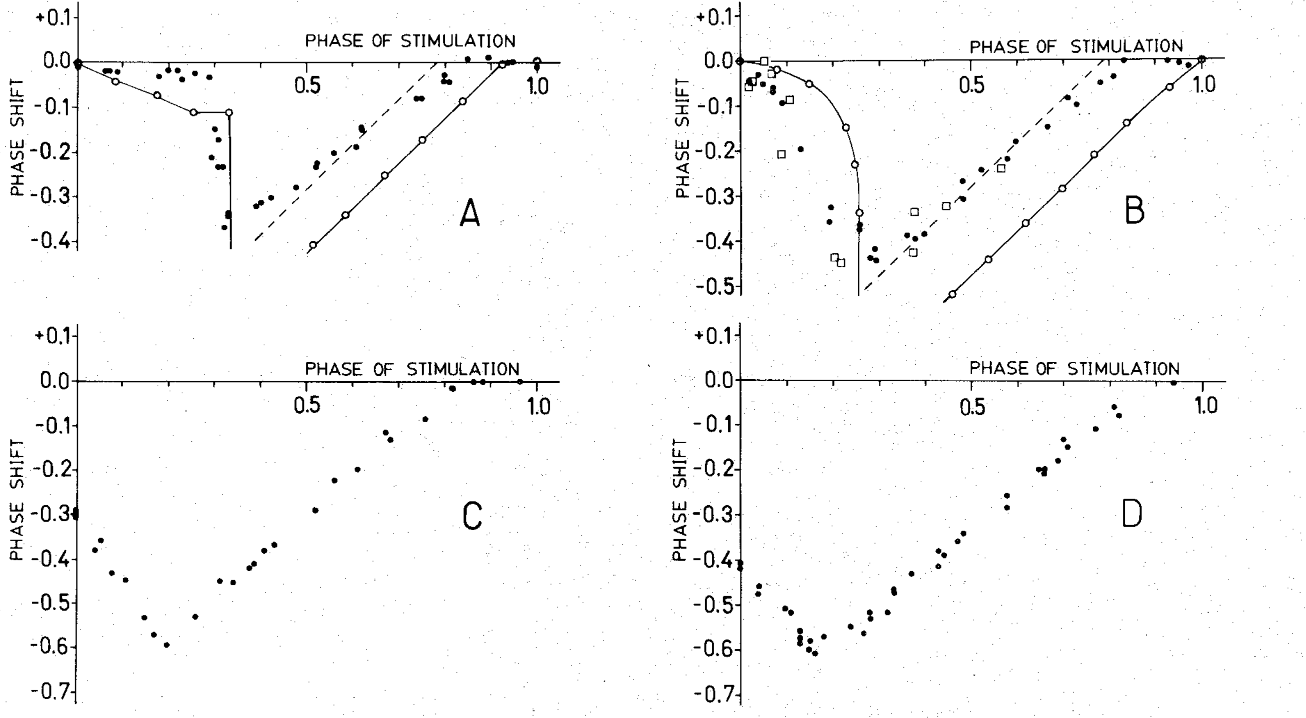

Figure 5. Experimental phase response curves using different concentrations of $AgNO_3$ as perturbant (M of added unreacted $AgNO_3$): (A) 1.0×10^{-5}, solid line; curve 2 of Figure 4. (B) 2.0×10^{-5}, solid line; curve 1 of Figure 3B. (C) 5.0×10^{-5}. (D) 2.0×10^{-4}. In the excitable branch, the experiments show a greater, nearly constant delay in the appearance of the Ce(IV) spike (dashed line) than found by computation. The experiments were performed under a nitrogen atmosphere, but the same results were obtained when the reaction medium is in contact with air (open squares in B). The initial Ce(IV) concentration was 5.0×10^{-4} M.

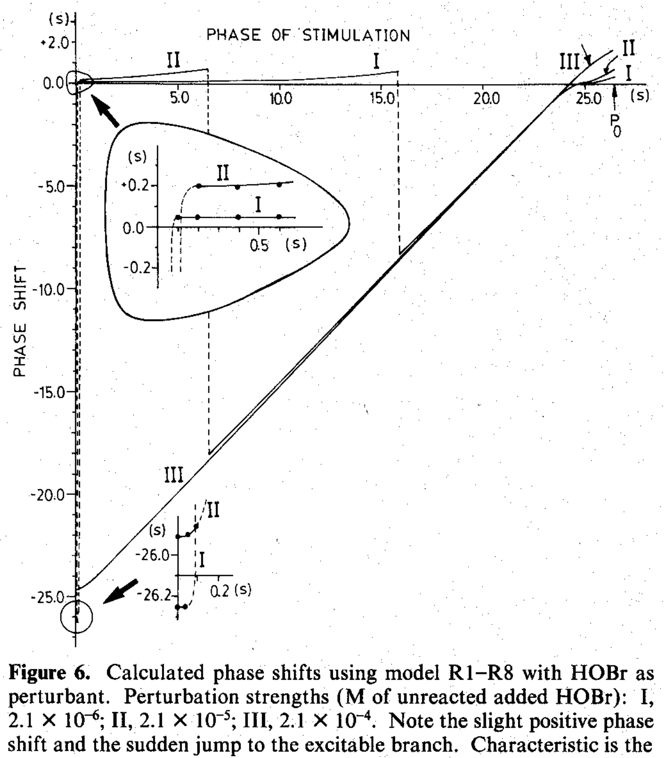

Figure 6. Calculated phase shifts using model R1–R8 with HOBr as perturbant. Perturbation strengths (M of unreacted added HOBr): I, 2.1×10^{-6}; II, 2.1×10^{-5}; III, 2.1×10^{-4}. Note the slight positive phase shift and the sudden jump to the excitable branch. Characteristic is the continuation of the excitable branch into the domain of positive phase shifts. Inserts show details found in the model at the beginning of the cycle.

and so causes an increased Br^- concentration at the beginning of process A (increased $C_{Br}{}^{max}$) when the Ce(IV) concentration is high. As a result, we observe an increase in the period P_0 (Table I), while the same amount of perturbant has to be applied much later in the cycle in order to reach $C_{Br}{}^{crit}$. Apart from this effect, the experimental results in Figure 7 are in semiquantitative agreement with calculations. In the experiment we also observe the characteristic continuation of the excitable branch into the domain of positive phase shifts. This effect is even more pronounced in the experiment than in theory. A related delay at the

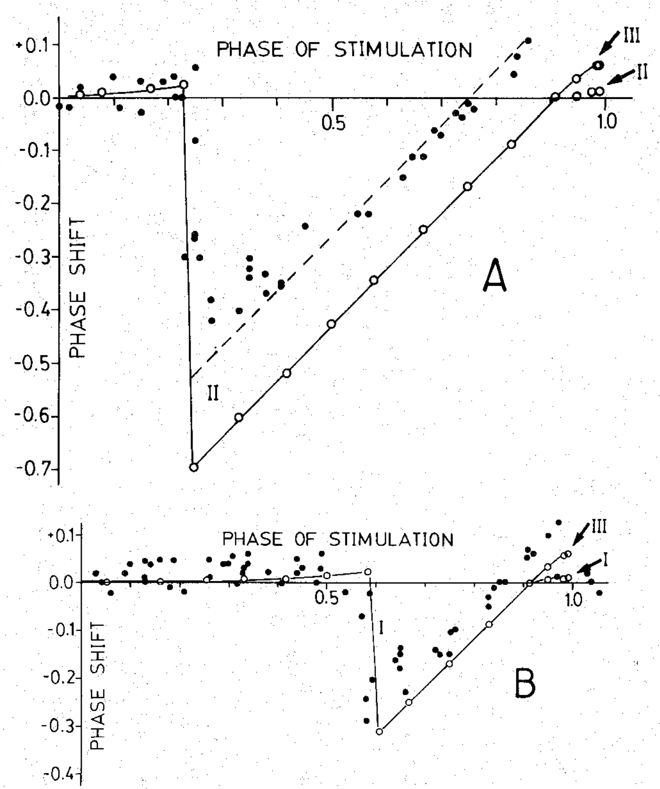

Figure 7. Experimental phase shifts using HOBr as perturbant. The perturbation strength is 8.5×10^{-5} M of added unreacted HOBr. Initial Ce(IV) concentration is (A) 5.0×10^{-4} and (B) 2.1×10^{-3} M. Solid lines represent calculations from Figure 6. As in the case of added $AgNO_3$, we observe that the calculated excitable branch lies under the experimental data.

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(20) Jwo, J.-J.; Noyes, R. M. *J. Am. Chem. Soc.* **1975**, *97*, 5422.

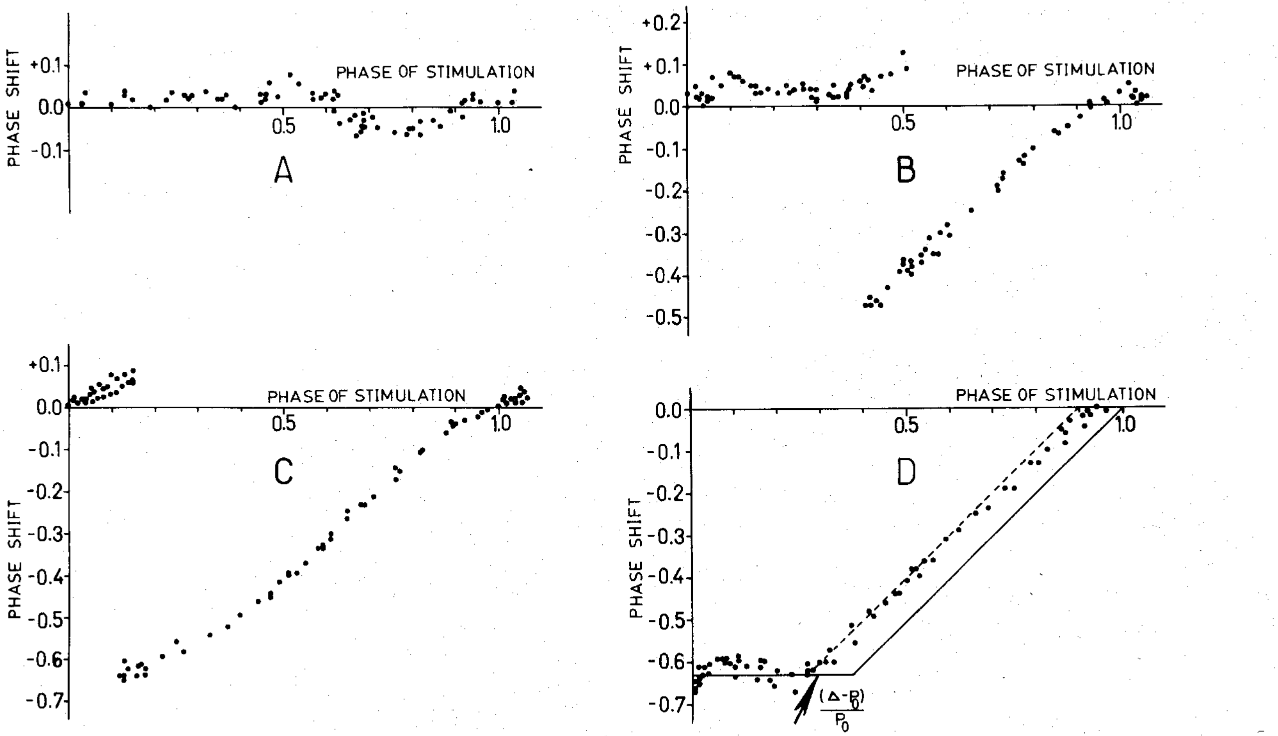

Figure 8. Experimental phase shifts using $AgNO_3$ as perturbant and an initial Ce(IV) concentration of 2.1×10^{-3} M. Perturbation strengths (M of added unreacted $AgNO_3$): (A) 2.1×10^{-6}, (B) 2.1×10^{-5}, (C) 1.1×10^{-4}, and (D) 2.1×10^{-4}. Note the nearly constant positive (A–C) and negative phase shifts (D), and the local maximum (B–D) at the beginning of the cycle.

platinum electrode has recently been observed by Ganapathisubramanian and Noyes,[21] when HOBr is added continuously to an oscillating BZR. Figure 5 and Figure 7 summarize the different and similar behaviors of the BZR when HOBr and $AgNO_3$ are added as Br^- removing reagents. Together with the data in Figure 2, there should be no doubt about the role of Br^- ions in this BZ system.

Additional Complexities. As already found in the case of HOBr, an increased initial Ce(IV) concentration may influence the point where the jump to the excitable branch occurs. Using an increased initial Ce(IV) concentration and $AgNO_3$ as perturbant (the reaction medium either in contact with air or under a nitrogen atmosphere), we found that the addition of $AgNO_3$ does not lead to an advance at the beginning of the cycle as in Figure 5, but to a (nearly constant) delay in the phase shift (Figure 8A–C). By adding a very high concentration of $AgNO_3$ (Figure 8D) we observe a nearly constant negative phase shift prior to the normal excitable branch. The experiments in Figure 8A–C indicate that the addition of Ag^+ ions cannot now be related to the removal of free Br^- ions. A similar situation when $AgNO_3$ is slowly added into an excitable BZR[16b,c] has recently been reported. There we found period lengths which were considerably longer than those observed in the normal unperturbed oscillating BZR with the same initial composition of the reagents. Attempts to simulate this effect[16b,22] failed. Interestingly, a related observation has also been reported by Körös and co-workers[23,24] using Hg(II) or Tl(III) ions as perturbants. These metal ions are well-known as forming highly stable water-soluble bromo complexes. Körös et al.[23] observe an increase in period lengths when perturbant is added and explain[24] the increase of period length by a buffer effect of the bromo complexes of the metal ion formed. However, in the case of Ag^+, bromo complexes, although they may exist,[25] seem very unlikely to be formed under our experimental conditions. An alternative explanation seems to be the following. Experimental evidence[26,27] now exists that Ce(IV) ions form bromo complexes, $CeBr^{3+}$, as suggested by Jwo and Noyes.[20] Although such complexes may also buffer the Br^- concentration to a certain extent, we doubt whether buffer theory in the traditional sense can solely explain the slightly positive phase shifts, i.e., account for the rather paradoxical behavior that the addition of a Br^- removing reagent temporarily increases the Br^- production. More probably, the reason for the positive phase shifts may lie in the different chemical behaviors between $CeBr^{3+}$ and the Br^--uncomplexed Ce(IV) ions which are present as sulfato complexes.[27] While $CeBr^{3+}$ is assumed to react with malonyl radicals[26] and form BrMA and Ce^{3+}

$$CeBr^{3+} + \cdot CH(COOH)_2 \rightarrow BrCH(COOH)_2 + Ce^{3+} \qquad (A4)$$

the Br^--uncomplexed Ce(IV) ions induce radical reactions A1–A3 which finally liberate Br^- ions.[20] If a high initial Ce(IV) concentration is used, it appears reasonable to assume that a considerable amount of the total Ce(IV) concentration is present as $CeBr^{3+}$ ions. When $AgNO_3$ is now added, it may either react with free Br^- ions or directly with $CeBr^{3+}$. In both cases, however, the amount of Br^--uncomplexed Ce(IV) will increase (A5–A7), which

$$CeBr^{3+} \rightleftarrows Ce(IV) + Br^- \qquad (A5)$$

$$Ag^+ + Br^- \rightarrow AgBr \qquad (A6)$$

$$CeBr^{3+} + Ag^+ \rightarrow Ce(IV) + AgBr \qquad (A7)$$

due to the sequence A1–A3 frees more Br^- ions, thus leading finally to a delay in the appearance of the Ce(IV) spike. FKN[3] nicely illustrates the delay due to A1–A3 by perturbing an oscillating BZR with Ce(IV) ions (see Figure 8 of ref 3 and our Figure 1). Reactions A7 and A1–A3 may also provide an ex-

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planation why an increased period length is observed when Ag^+ ions are slowly added to a nonoscillating excitable BZR using an increased (2.1×10^{-3} M) initial Ce(IV) concentration.[16b,c]

In addition, Ag^+ ions may also accelerate the conversion of bromo organic compounds (as, for example, $\cdot CBr(COOH)_2$) to the corresponding hydroxy organic intermediates (A8). Reactions

$$\cdot CBr(COOH)_2 + Ag^+ \rightarrow \cdot C(OH)(COOH)_2 + AgBr + H^+ \qquad (A8)$$

such as the A8 may be of importance in further Br^- releasing (radical) reaction steps as indicated in the work of Edelson et al.[8]

The nearly constant negative phase shift using high concentrations of $AgNO_3$ added is also remarkable (Figure 8D). Topologically, this may be explained by interpreting Δ as an absolute refractory period.[16b,c] When the system is perturbed inside Δ, a refractory period implies that the system has to wait the time ($\Delta - t'$) until the next Ce(IV) spike can be induced (in order to oscillate with the period length Δ). Thus, according to eq 4, the phase shift is

$$\Delta\phi = (\Delta - t') - (P_0 - t') = (\Delta - P_0) \qquad t' < \Delta \qquad (7a)$$

$$\Delta\phi = (t' - P_0) \qquad t' \geq \Delta \qquad (7b)$$

Using an approximate value of P_0 of 40 s and a Δ value of 15 s, we obtain the solid line in Figure 8D. However, as mentioned above, the real system's response is always subject to a certain delay due to an intermediate not in the model-realized reaction steps. To account for this, we may add a suitable small positive constant to eq 7b. This is indicated by the dashed line in Figure 8D. The mechanistic explanation of the (nearly) constant phase shifts in Figure 8 appears also to be due to the formation of $CeBr^{3+}$. The effect of $CeBr^{3+}$ may be considered as a type of Br^- buffering, since when Ag^+ ions are added, the sum of reactions A7 and A1–A3 balance the Br^- removal of $AgNO_3$. The experimental data of Figure 8 support this. At the beginning of the cycle, we have a high Ce(IV) concentration while the Br^- concentration increases. Therefore, also $CeBr^{3+}$ becomes high and should cause, due to reactions A7 and A1–A3, an increase of the (positive or negative) phase shift when Ag^+ ions are added. However, as both the Ce(IV) and the Br^- concentration decrease slightly later in the cycle, the $CeBr^{3+}$ amount also should be lowered and more negative phase shifts should be the result when Ag^+ ions are added. Therefore a local maximum of the phase shifts at the beginning of the cycle should be observed. At a "phase of stimulation" of about 0.1 such a maximum is indeed found (Figure 8B–D). This again demonstrates the important role Br^- ions play in this system.

Concluding Remarks

Although our experimental and calculated data are still in semiquantitative agreement, our results clearly demonstrate the Br^- control of the free oscillating MA BZR. Even seemingly contradicting results due to a higher initial Ce(IV) concentration confirm the basic FKN mechanism and provide an explanation of the increased period lengths observed when $AgNO_3$ is added at low rates of flow into an excitable BZR with same initial concentrations of reagents. The goal of further work is to construct a mechanism which accounts more quantitatively for these effects.

Certainly, phase shift experiments may also be applied to other related chemical oscillators. Although similar methods are well-established in the investigation of biochemical or biological rhythms, purely chemical oscillating systems seem especially well-suited to this form of investigation, since here most of the state variables are generally known, provided a realistic chemical mechanism exists.

Note Added in Proof. While this paper was in press, the author became aware of two papers using similar methods for studying the BZR[28] and the Briggs–Rauscher oscillator.[29]

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Registry No. Br^-, 24959-67-9; HOBr, 13517-11-8; Ag, 7440-22-4; Ce, 7440-45-1; BrO_3^-, 15541-45-4; $CH_2(COOH)_2$, 141-82-2.