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Controlled Excitations of the Belousov−Zhabotinsky Reaction: Experimental Procedures

Catalina Peralta, Claudia Frank, Alex Zaharakis, Carolyn Cammalleri, Matthew Testa, Stephen Chaterpaul, Christian Hilaire, Daniel Lang, Daniel Ravinovitch, Sabrina G. Sobel, and Harold M. Hastings*

Department of Chemistry and Department of Physics and Astronomy, Hofstra University,
Hempstead, New York 11549-1510

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The purpose of this research was to explore the unstirred, ferroin-catalyzed Belousov−Zhabotinsky (BZ) reaction as an experimental model for the response of excitable media to small perturbations (slightly larger than the threshold for excitations). Following Showalter et al. (Showalter, K.; Noyes, R. M.; Turner, H. *J. Am. Chem. Soc.* **1979**, *101*, 7463−69), we used a positively biased silver electrode to release silver ions into a BZ reaction mixture, removing bromide ions and causing an excitation if sufficient bromide was removed. We found (1) a scaling region in which the delay before activation increased linearly as the size of the perturbation decreased, qualitatively consistent with but not fully explained by the Oregonator of Field et al. (Field, R. J.; Kőrõs, E.; Noyes, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 8649−64); (2) evidence for a 10 s oligomerization time scale; and (3) that activations were always delayed until after the end of a pulse of current, with the delay essentially constant for sufficiently long pulses, an effect not seen in simple ODE models but consistent with the anomalously large current apparently required for activation (Showalter, K.; Noyes, R. M. *J. Am. Chem. Soc.* **1976**, *98*, 3730−31) and explainable by bromide transport. Overall, the BZ system appeared to be well-suited as an experimental prototype, despite its complexity.

Introduction

An excitable medium is a system in which sufficiently large stimuli generate waves of activation but smaller stimuli die out as the system returns to equilibrium, as illustrated in Figure 1. The unstirred ferroin-catalyzed Belousov−Zhabotinsky (BZ) reaction is the prototype spatially distributed excitable chemical system.[2−8] The BZ reaction, in the excitable, non-oscillatory regime (cf. ref 8), is typically stimulated by using a silver wire with[9−12] or without[13] a pulse of positive current to remove the inhibitory species Br^- through the formation and subsequent oligomerization of AgBr.[11,12] The purpose of this paper is to explore the silver wire perturbed BZ reaction as an experimental model for the response of excitable media to perturbations.

BZ Kinetics. The fundamental behavior of the excitable BZ reaction is given by the Field−Köros−Noyes (FKN) model[5] and incorporated in the Oregonator,[6] a system of three differential equations that captures essentially all of the qualitative behavior of the BZ reaction. Oregonator kinetics is expressed in terms of the concentrations of three chemical species: $x = [HBrO_2]$, a fast activator or auto-catalytic species, $y = [Br^-]$, an inhibitor to auto-catalysis, and $z = [Fe(phen)_3^{3+}]$, which regenerates Br^- on a slow time scale

$$dx/dt = k_3[BrO_3^-][H^+]^2y - k_2[H^+]xy + k_5[BrO_3^-][H^+]x - 2k_4x^2$$

$$dy/dt = -k_3[BrO_3^-][H^+]^2y - k_2[H^+]xy + (f/2)k_c[MA]_0z$$

$$dz/dt = 2k_5[BrO_3^-][H^+]x - k_c[MA]_0z \qquad (1)$$

Here, $[MA]_0$ denotes the initial concentration of malonic acid ($CH_2(COOH)_2$), and k_2, k_3, k_4, and k_5 are rate constants from the FKN mechanism. The rate constant k_c and stoichiometric factor f are expendable quantities related to the FKN Process C

$$2Fe(phen)_3^{3+} + MA + BrMA \rightarrow fBr^- + 2Fe(phen)_3^{2+} + \text{other products} \qquad (2)$$

where BrMA denotes bromomalonic acid. The stoichiometric factor f serves as a bifurcation parameter, with a blue/oxidized steady state (high $[Fe(phen)_3^{3+}]$ and $[HBrO_2]$, low $[Br^-]$) for low f (less than ∼0.5), a red/reduced steady state (low $[Fe(phen)_3^{3+}]$ and $[HBrO_2]$, high $[Br^-]$) for high f (greater than ∼2.414), and oscillatory dynamics (blue/red) for intermediate values of f ($\sim 0.5 < f$ less than ∼2.414).[8] The red/reduced state observed in experimental BZ systems with added Br^- shortly after mixing can be explained by Br^- release during bromination of MA to form BrMA.[14]

For $f > 2.414$ (the excitable, non-oscillatory regime), Process C liberates sufficient Br^- to prevent auto-catalysis of $HBrO_2$. The Oregonator can be stimulated by reducing initial $[Br^-]$; reduction below a critical level allows relatively rapid auto-catalytic production of $HBrO_2$, oxidizing ferroin to ferriin (red to blue), generating a blue/oxidized wave of activation. Process C subsequently reduces ferriin to ferroin, regenerates Br^-, and halts auto-catalysis, allowing the reaction mixture to return to steady state.

Preliminary Work. We first sought to quantify the effects of small stimulations by briefly immersing a thin oxidized silver wire (diameter 49 μm) into a BZ reaction mixture. We modified Shakashiri's[13] recipe by reducing the final $[BrO_3^-]$ to 0.125 M to meet the Showalter−Noyes[9] criterion $[BrO_3^-][H_2SO_4] < 0.045\ M^2$ for excitable, non-oscillatory behavior. All reagents were used as received. Nanopure water was used for all experiments. Ferroin was prepared from ferrous sulfate (Cenco) and 1,10-phenanthroline (Aldrich, 99%).

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* Corresponding author. E-mail: Harold.Hastings@Hofstra.edu.

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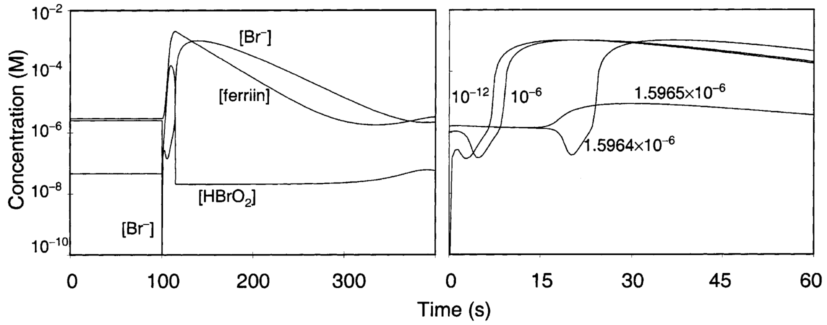

Figure 1. Computer simulation of the response of the BZ reaction to stimulation by reduction in $[Br^-]$. The Oregonator model was integrated numerically with an adaptive quadratic Runge−Kutta algorithm using WinPP.[15] Parameters: $f = 2.6$, in the excitable, non-oscillatory range; other Oregonator parameters were assigned standard values.[8] Initial concentrations corresponded to current−pulse experiments described as follows: $[BrO_3^-] = 0.1$ M, $[H^+] = 0.31$ M, corresponding to $[H_2SO_4] = 0.3$ M, and [malonic acid] = 0.0413 M. $[HBrO_2]$, $[Br^-]$, and [ferriin] are set equal to equilibrium values of 4.64914×10^{-8}, 2.51985×10^{-6}, and 2.93130×10^{-6} M, respectively. Left: reducing $[Br^-]$ to 10^{-12} M at $t = 100$ s generates an activation (see text) with [ferriin] reaching 10^{-3} M 9.4 s later. Right: smaller reductions in $[Br^-]$ produce delayed activations, with a reduction to 10^{-6} M causing an activation ([ferriin] = 10^{-3} M) after 13.1 s, a reduction to 1.5964×10^{-6} M causing an activation after 43.2 s, and a reduction to 1.5965×10^{-6} M failing to cause an activation.

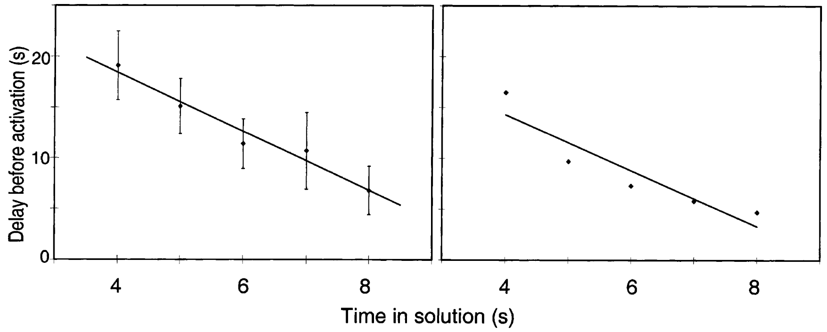

Figure 2. Left: silver wire perturbation of BZ reaction, no current pulse. A 49 μm diameter oxidized silver wire was inserted into an excitable, non-oscillatory BZ reagent mixture for the time indicated. The delay from removal of the wire to target formation was measured with nine replicates for each time in solution. Data shown as mean ±2 standard deviations (σ). Right: simulation with Oregonator model together with bromide removal. This model reproduces the right scaling range but displays markedly nonlinear behavior.

Water (1.50 mL), sulfuric acid (6.0 M, 0.60 mL), malonic acid (0.20 M, 2.50 mL), potassium bromide (0.20 M, 1.00 mL), and ferroin (0.0121 M, 0.50 mL) were combined in an 89 mm diameter glass Petri dish and then stirred thoroughly. Potassium bromate (0.25 M, 6.00 mL) was then added to the solution and mixed until homogeneous. The resulting 12.1 mL of reagent mixture filled the dish to a depth of 2.1 mm. After an induction period lasting approximately 3 min during which disorganized waves flashed through the solution, the solution was allowed to sit for an additional 7 min to allow the solution to settle in the red phase in the absence of perturbations. The behavior during the induction period has been widely noted[8] and may reflect the effects of imperfect mixing, as described in ref 16 for the oscillatory BZ reaction.

Simulation. The Oregonator model, modified to incorporate removal of Br^- in response to a silver wire stimulus, was integrated numerically with WinPP.[15] Parameters and initial concentrations were set as in Figure 1, except that $[BrO_3^-] = 0.125$ M to match experiment, and $[HBrO_2]$, $[Br^-]$, and [ferriin] are set equal to equilibrium values of 5.81138×10^{-8}, 3.14981×10^{-6}, and 4.58015×10^{-6} M, respectively. We defined an activation to occur when $z = 0.001$ M, approximately 1/3 of its maximum value of 0.0032 M in simulations.

Preliminary Results. We found that no activations were generated if the wire was inserted for short times (≤3 s in our experimental preparation) and activations 7−19 s after removal of the wire (15−23 s after insertion of the wire) for stimulations lasting 4−8 s (Figure 2a), with approximately linear scaling

$$\text{delay before activation} = -2.9 \times (\text{time in solution}) + 30 \text{ s}, R^2 = 0.96 \quad (3)$$

We found that the scaling region could be reproduced by incorporating removal of Br^- in the second Oregonator equation while a simulated silver wire was immersed

$$-k_r H(t_0 - t)\min(t, t_0)y \quad (4)$$

yielding the modified Oregonator equation

$$dy/dt = -k_3[BrO_3^-][H^+]^2y - k_2[H^+]xy + (f/2)k_c[MA]_0z - k_rH(t_0 - t)\min(t, t_0)y \quad (5)$$

Here, H denotes the Heaviside function $H(v) = 1$ for $v \geq 0$, $H(v) = 0$ for $v < 0$, t_0 is the duration of the stimulus, and k_r is a fitted rate constant. We found a scaling range similar to experiment for stimulations lasting 4−8 s

$$\text{delay before activation} = -2.8t_0 + 25.3, R^2 = 0.86 \quad (6)$$

for $k_r = 0.06$ s^{-1}, but markedly nonlinear scaling (Figure 2b).

Materials and Methods

Experimental. Current Pulse Stimulation. To establish a more precise relationship between the size of the perturbation and the time delay before activation and to avoid disturbing the reaction mixture, we followed the protocol of Showalter et al.,[10] who used a positively biased silver electrode (with respect to a platinum reference electrode) to release Ag^+ ions, causing activations in the BZ reaction.

Preparation of the Excitable BZ Reaction Mixture. The BZ reaction mixture was prepared as stated previously, except for further reducing final [BrO_3^-] to 0.10 M through the use of a 0.20 M stock solution of $KBrO_3^-$.

Pulse Generation and Control. We developed a circuit using a zener diode and a LM 353 operational amplifier to control the release of Ag^+ from a silver electrode by biasing that electrode to either +0.788 V (on) or −1.965 V (off) with respect to a platinum electrode, as in ref 9, irrespective of the amount of current drawn. The switch that controlled the state of the electrode was also connected to an electronic timing circuit to facilitate accurate timing of short pulses. In a second implementation, we used an analogue input/output board (Measurement Computing USB-3101) to deliver similar pulses and to measure currents.

Experimental Protocol. An unoxidized thread of silver wool (49 μm diameter, 99.9%) with a negative bias of −1.965 V was immersed into the BZ reagent mixture to its full depth of 2.1 mm. A pulse of +0.788 V was then applied by the circuit through the silver wire to stimulate the formation of a target. The delay between the end of each current pulse and the subsequent target formation was timed with an electronic stopwatch. This experiment was conducted for pulse durations of 0.1−15 s. Five trials were done for each pulse duration, in three separate series with the order randomized within each series: (a) 1−11 s in 1 s steps; (b) 12−15 s in 1 s steps; and (c) 0.1, 0.3, and 0.6 s. After each trial, the wire was cleaned with concentrated nitric acid and then washed with water. For all trial runs, the room temperature was maintained at 69−70 °F (∼21 °C). We also sought to understand how a current pulse was responsible for preventing activations during the pulse by repeating a few silver wire stimulations with no current pulse.

Simulation. We used a 1-D partial differential equation (PDE) version of the Oregonator model, with modifications to incorporate addition of Ag^+, formation of AgBr, oligomerization, and consequent removal of Br^-. Parameters and initial values are as in Figure 1, with initial [$HBrO_2$], [Br^-], and [ferriin] at equilibrium values. Also, the diffusion constant was set at $D = 2000\ \mu m\ s^{-1}$,[17] the spatial step was at $\Delta x = 50\ \mu m$ (corresponding to 1.25 s of diffusion), and the stimulus was applied at one end of a 2 mm long segment with no-flux boundary conditions. Again, WinPP was used for integration. We defined an activation to occur when [ferriin] reached 0.001 M at a distance of 250 μm from the wire, corresponding with photographs taken when activations were first consistently observed.

Results

Experimental. As in the no-current case, we found a delay from the end of a pulse before target formation depending approximately linearly upon the duration of the current pulse for pulse durations ≤11 s but remained relatively constant for longer pulses (Figure 3). The standard deviation σ was very small for pulse durations between 1 and 11 s (rms σ: 0.12 s) but larger for pulse durations <1 s (rms standard deviation σ: 0.29 s) and for pulse durations ≥12 s (rms σ: 0.22 s). Some deviation from linearity was apparent for pulse durations ≤11 s, with the deviation largest for current pulses of 6 s. Targets formed 9.51 ± 0.08 s (mean ± σ) after the end of a 6 s pulse. Although delays fell below the regression line for very short pulses (duration <1 s), 95% confidence intervals included the regression line.

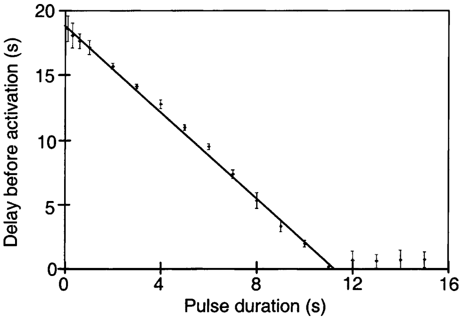

Figure 3. Silver wire perturbation of BZ reaction, current pulse. A 49 μm diameter wire was inserted into an excitable, non-oscillatory BZ reagent mixture, and positive current pulses of durations 0.1−15 s were applied (see text). The delay after the end of a pulse until target activation is shown as mean ±2σ. For pulses of duration ≤11 s: delay before activation = −1.69 × pulse duration + 19.0 s, $R^2 = 0.99$. Although extrapolation predicts a maximum delay of 11.24 s, activations never occurred during current pulses of 12−15 s. Instead, we found a relatively constant delay of 0.73 ± 0.20 s.

Although an 11 s pulse generated targets with a delay of 0.24 ± 0.07 s, that is, 11.24 s after the start of the pulse, targets never occurred during pulses of 12−15 s. Instead, target formation was always delayed until after the pulse ended, by an average of 0.73 ± 0.20 s.

Simulation. We found that PDE simulations reproduced the observed range of delays; however, the observed linear behavior was never reproduced without current-driven Br^- inflow. Current-driven Br^- inflow either delayed activations and reproduced the observed linear behavior or prevented activations altogether. PDE behavior was thus similar to ODE behavior. We observed wave velocities of ∼170 $\mu m\ s^{-1}$, somewhat larger than the limiting velocity of $2(\beta D)^{1/2} = 110\ \mu m\ s^{-1}$ predicted[8] from the observed $\beta = 1.47\ s^{-1}$ in simulations.

We found that a 0.1 s current pulse at 0.1 mA in our 1-D PDE model with a 10 s oligomerization time scale (rate constant = 0.1) generated an activation after a delay of 12 s. This delay agrees reasonably with the 18 s delay observed experimentally, especially considering that the presence of ferroin, the red/reduced form of the catalyst, may delay the observability of a small (0.5 mm) region of ferriin, the blue/oxidized form of the catalyst.

At 0.1 s, the 0.1 mA pulse releases 1.0×10^{-10} mol of Ag^+, yielding [Ag^+] = 0.0031 M in a 50 μm region surrounding a 50 μm diameter silver wire (making the outside radius, 75 μm, somewhat larger than the critical radius for propagation[17,18]) immersed in a 2.1 mm deep solution, as in the experiment. The resulting [Ag^+] was ∼50× the activation threshold ($6.3-6.4 \times 10^{-5}$ M) found in a similar simulation. The analogous PDE system, with diffusion-limited oligomerization (∼$10^{10}\ s^{-1}$),[19] was too stiff for WinPP.[15] However, reducing the oligomerization time scale from 10 to 0.01 s reduced the threshold to $1.6-1.7 \times 10^{-6}$ M. Finally, [BrO_3^-] = 0.1 M limits [Ag^+] to ∼10^{-3} M because $AgBrO_3$ is poorly soluble,[20] with K_{sp} reported in the range of 5 to 14 × $10^{-5}\ M^2$.[20−25]

Discussion

The excitable, non-oscillatory BZ reaction can be stimulated to generate an activation through the use of thin silver wire to introduce Ag^+ ions into the reaction medium. Ag^+ ions are readily released from the oxide coating of a thin oxidized wire. Alternatively, Ag^+ ions may be released by applying a positive potential (typically 0.8 V) with respect to a platinum reference electrode. In both cases, Ag^+ combines with Br^-, forming AgBr ion pairs. Subsequent oligomerization of AgBr then reduces the available Br^- below the threshold required to generate activation. The Oregonator model for the excitable, non-oscillatory BZ reaction can be stimulated in computer simulations by $[Br^-]$ from the equilibrium value below an activation threshold, directly by setting initial conditions or indirectly by modeling the release of Ag^+, formation of AgBr, and consequent removal of Br^- from participating in the reaction. One can also include oligomerization of AgBr, diffusion, and active (current-driven) transport of ions when a potential is applied.

Showalter et al. had observed that an anomalously large current pulse was required to generate an activation, a factor of 10^4 larger than the current apparently required to remove bromide ions near the wire.[9] They also observed an “anomalous localization phenomena in which incipient trigger waves did not start propagating until considerably after the pulse [of current] had been delivered”.[10]

Later, workers[11,12] argued that formation of AgBr by itself does not effectively remove Br^- from participating in the BZ reaction. Instead, they found that oligomerization of AgBr to intermediate clusters, $(AgBr)_4$, and eventually to larger, essentially nonreactive clusters, $(AgBr)_6$, which they studied outside of the BZ reaction, was required to prevent Br^- from participating in the reaction. Formation of $(AgBr)_4$ is relatively fast; thus, formation of $(AgBr)_6$, which takes place at a rate of about 10% per second when $[Ag^+] \approx [Br^-]$, is the rate-limiting step. However, other research[19] suggested that oligomerization of silver halides is a diffusion-limited process with a rate constant of $\sim 10^{10}$ s^{-1}. The last two statements appear in contradiction since a diffusion-limited process with concentrations $\sim 10^{-6}$ M should proceed on a sub-millisecond time scale.

We found that small stimuli, reducing $[Br^-]$ somewhat below the activation threshold, generated delayed activations; that is, activation occurred later than it would have occurred following almost complete removal of $[Br^-]$. Silver wire stimulation without current pulse, silver wire stimulation with a current pulse, and stimulation of ODE and PDE Oregonator simulations yielded comparable ranges of delays, although the maximum delay observed in experimental systems, 20 s, was less than half the maximum delay observed in simulations. However, such long delays required stimuli very close to the activation threshold, perhaps difficult to achieve in experimental systems.

We found a scaling range of an approximately linear stimulus−delay behavior in both no current and current−pulse experimental systems. However, most simulations displayed logarithmic scaling, with delay before activation t scaling as $-\ln(|s - s_a|)$, where s is the size of the stimulus and s_a is the activation threshold. It is easy to see how such a logarithmic scaling might arise. Consider, for simplicity, a one-variable model, $dx/dt = g(x)$, with activations generated when x exceeds a positive threshold x_a (i.e., let x denote the reduction in $[Br^-]$ below steady state and x_a denote the minimum reduction in $[Br^-]$ required to generate an activation). Let $y = x - x_a$, yielding a one-variable system

$$dy/dt = f(y) \tag{7}$$

with an activation threshold at $y = 0$. Assuming first-order kinetics near the threshold, the evolution of y from its initial value y_0 is given by

$$y = y_0\, e^{kt} \tag{8}$$

Consider the time t until y reaches a value y_1, en route to an activation. Then,

$$y_1 = y_0\, e^{kt} \tag{9}$$

Solving for t yields

$$\begin{aligned} I &= (1/I)(\ln(y_1) - (\ln(y_0)) \\ &= -(1/k)\ln(y_0) + (1/k)\ln(y_1) \end{aligned} \tag{10}$$

a logarithmic dependence upon the size of the stimulus y_0, as seen in virtually all simulations that did not incorporate bromide inflow. We shall explore possible explanations after briefly discussing the time scale of oligomerization.

Our observations on thresholds and time scales are more consistent with a 10 s time scale for oligomerization of AgBr than for the much faster time scale implied by a diffusion-limited oligomerization process. In particular, diffusion of Ag^+ over the course of a 10 s oligomerization time scale increased the threshold current from 1/2000 of the current in a 0.1 s, 0.1 mA pulse to 1/50 of this current, explaining the anomalously large current described in ref 10. In addition, the formation of poorly soluble $AgBrO_3$ would limit $[Ag^+]$ over a 10 s scale, further increasing the activation threshold. However, we expect less effects over the 10^{-6} s time scale of diffusion-limited oligomerization. In addition, most results on oligomerization assume $[Ag^+] \approx [Br^-]$, but oligomerization may be affected by the large excess of Ag^+ ($[Ag^+] \gg [Br^-]$) in the silver wire stimulated BZ reaction.

The BZ reaction, especially with Ag^+ stimulation, admits many feedback control structures. The question of control has been extensively discussed,[23,26−28] and additional references are in ref 24. As additional evidence for complex control, we observed a wave velocity in simulations of ~ 170 $\mu m\ s^{-1}$, 50% higher than that predicted from the formula $2(\beta D)^{1/2} = 110$ $\mu m\ s^{-1}$, possible evidence that the presence and diffusion of Ag^+ enhances propagation.

Finally, current-driven bromide inflow may retard the BZ reaction, even stopping propagation in simulations at sufficiently high levels. Since even a short current pulse makes $[Ag^+] \gg [Br^-]$ near a silver electrode, cf. ref 10, current-driven bromide inflow may be an important factor in dynamics of the current−pulse system.

For all of these reasons, we will leave a detailed theoretical study until a subsequent paper and simply conclude by observing that no current experiments did not strictly exclude logarithmic stimulus−delay behavior and that a more detailed model is needed to fully understand the experimental results. In conclusion, the silver wire stimulated BZ reaction displays interesting, complex behavior as an experimental model for the response of excitable media to perturbations, with dynamics driven by a variety of processes involved in Br^- removal.

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