

Complex Dynamical Behavior from Coupling between a Catalyzed Belousov–Zhabotinskii-Like Reaction and Its Uncatalyzed Oscillatory Component in a Flow Reactor

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We have investigated the relationship between the ferroin-catalyzed gallic acid/bromate oscillatory reaction with its uncatalyzed oscillatory component in the light of experimental findings and mechanistic understanding. Low stirring and high temperature increase the oscillation frequency and decrease the amplitude in this catalyzed system, which has been explained in terms of stirring and mixing effects. The uncatalyzed component is reported to exhibit bistability at 20 °C (room temperature) in a new concentration region and oscillations and bistability at very low flow rate in the presence of an additional feed of bromide ions.

Introduction

Investigation of coupled chemical oscillators has become a subject of prime interest in recent years. The chlorite–bromate–iodide system,¹ a fascinating example of the coupled chemical oscillator, involves coupling between the parent system and its three oscillatory components linked through a common species viz. I^- and was investigated in the past by Epstein et al. The ferroin-catalyzed Belousov–Zhabotinskii reaction using gallic acid (GA) as the organic substrate² has an uncatalyzed³ gallic acid/bromate component, which itself exhibits bistability and oscillations in a continuous flow stirred tank reactor (CSTR). Because of the coupling of the parent system with its uncatalyzed component, the ferroin-catalyzed GA oscillator exhibits a wide range of amplitudes and periods including complex oscillations under various experimental conditions. Oscillation periods as low as 7 s or less have been obtained in our laboratory experiments under various conditions of stirring and temperature. It also demonstrates unusually large stirring and temperature effects. The present work is an effort to build up a relation between this catalyzed oscillator with its uncatalyzed component in the light of experimental findings and mechanistic understanding.

Catalyzed System

We have investigated the ferroin-catalyzed GA system² at different stirring rates and temperatures. The experiments were carried out in a thermostated cylindrical CSTR (volume, 21.4 mL) of standard design described elsewhere.⁴ The Pt electrode potentials were recorded on a $x-t$ chart recorder with reference to a $Hg-Hg_2SO_4-Na_2SO_4$ electrode in nonpremixed mode of mixing of the chemicals.

The traces of oscillation potentials at three different temperatures (viz. 25, 30, and 35 °C) are shown in Figures 1, 2, and 3 respectively at different stirring rates. For the experiment carried out at 25 °C, we obtained simple periodic oscillations (Figure 1a) at high stirring (S , 2500 rpm), complex oscillations

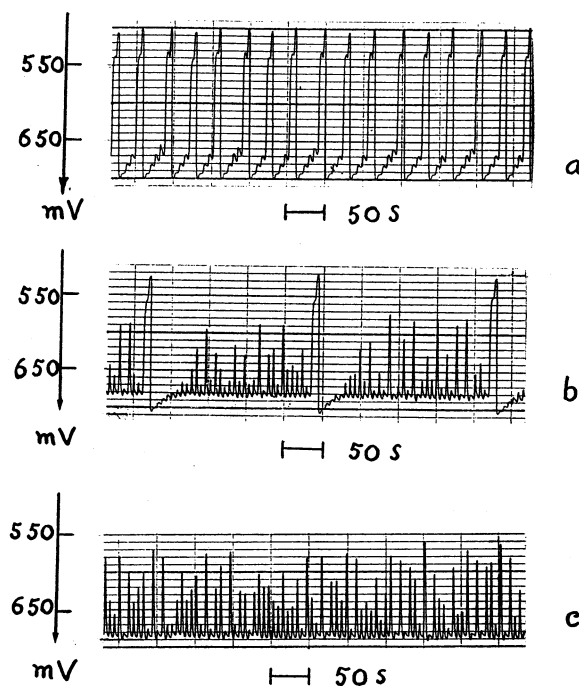


Figure 1. Traces of oscillation potentials at 25 °C for different stirring rates: (a) 2500, (b) 1500, and (c) 1000 rpm. The composition inside the CSTR: $[NaBrO_3]_0$, 0.25 M; $[GA]_0$, 0.03525 M; $[Ferroin]_0$, 0.00037 M; $[H_2SO_4]_0$, 1M. Residence time, 38.9 min.; subscript “o”, for the concentration inside the reactor before any reaction could occur.

(Figure 1b) comprising of many small amplitude oscillations of varying amplitudes between two large amplitude oscillations at intermediate stirring (S , 1500 rpm), and aperiodic oscillations (Figure 1c) at low stirring (S , 1000 rpm). At 30 and 35 °C, the oscillations become aperiodic at all stirring rates in the range, $S = 2500-1000$ rpm; the low stirring induces an additional decrease in the amplitude of the aperiodic oscillations. The traces of aperiodic oscillations at 30 °C are shown in Figure 2a–c at three different stirring rates, $S = 2500$, 1500, and 1000 rpm, respectively. Figure 3a,b are the traces of aperiodic oscillations

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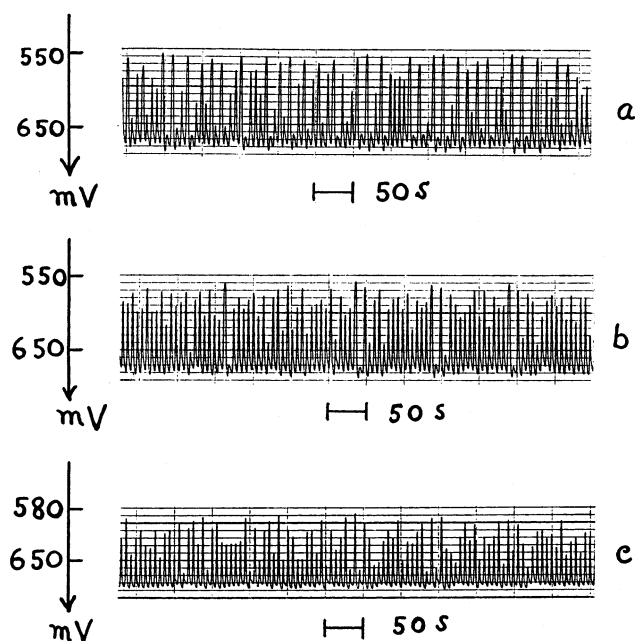


Figure 2. Traces of oscillation potentials at 30 °C with different stirring rates: (a) 2500, (b) 1500, and (c) 1000 rpm. The composition and other parameters are the same as in Figure 1.

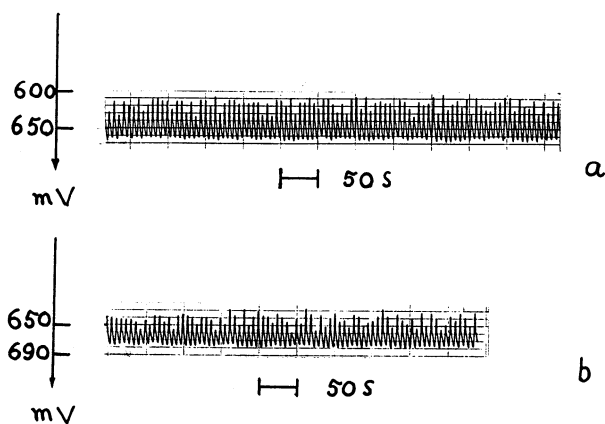


Figure 3. Traces of oscillation potentials at 35 °C with different stirring rates: (a) 2500 and (b) 1500 rpm. The composition and other parameters are the same as in Figure 1.

at two different stirring rates, $S = 2500$ and 1500 rpm, respectively, for the experiment carried out at 35 °C.

The potential traces in Figure 1 for this catalyzed system clearly suggest that the reciprocal of stirring rate acts as a control parameter in the route from normal to complex to aperiodic oscillations from Figure 1 part a to part c. Although the complex oscillations in this catalyzed system were reported in the past⁵ at a high flowrate ($1.3 \times 10^{-3} \text{ s}^{-1}$), the low flow rate ($4.2 \times 10^{-4} \text{ s}^{-1}$) complex oscillations appear to be most interesting. For all of the potential traces of oscillations in Figures 1–3, the high potential state corresponds to an extension of the thermodynamic branch appropriate to the flow and stirring condition of the system. The low potential state of the oscillations corresponds to an attempt to transit to low potential flow branch, which is being consistently opposed by the switching on of the autocatalytic production of HBrO_2 via steps K_3 , K_4 , and the stoichiometric reaction D_1 in the following section. Eventually, the oscillatory state transits to the low potential flow branch at a still higher stirring rate. On the decrease of the stirring rate by small steps, this low potential flow branch may transit back to high potential oscillatory branch

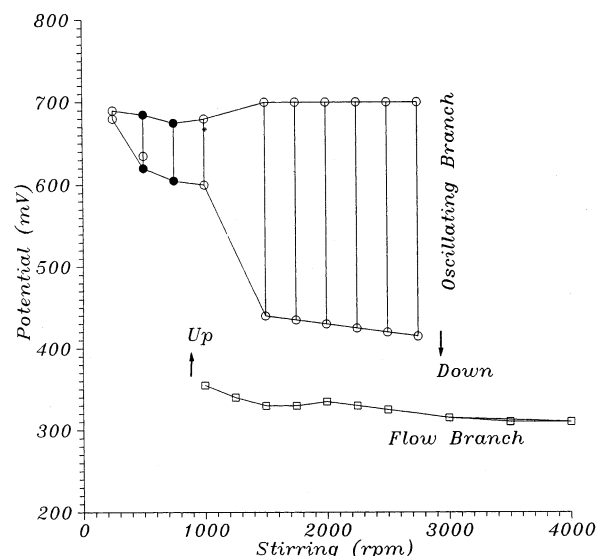


Figure 4. Hysteresis between an oscillating branch and a flow branch in catalyzed GA system in terms of potential as a function of stirring rate at 25 °C. The vertical lines with circles at the ends indicate oscillation amplitudes at different stirring rates: open circles, when stirring increased and closed, when decreased after an up transition from the flow branch to the oscillatory branch. The composition inside the CSTR: $[\text{NaBrO}_3]_0$, 0.2 M; $[\text{GA}]_0$, 0.0345 M; $[\text{Ferrioin}]_0$, 0.00037 M; $[\text{H}_2\text{SO}_4]_0$, 1 M. Residence time, 31.9 min.

as shown in Figures 1–3. This hysteresis behavior between an oscillatory state and a flow branch in the catalyzed GA system⁴ is shown in Figure 4. Figure 4 demonstrates that high stirring in the catalyzed system destabilizes the thermodynamic branch, which is the same^{6–8} as that observed in the minimal bromate oscillator (MBO). This bifurcation of the oscillatory state from the thermodynamic branch with stirring rate as the bifurcation parameter seems to be a supercritical Hopf bifurcation, because the oscillation amplitude, which is very small at low stirring, increases gradually with increase of stirring.

Uncatalyzed Component System

A few years ago Liu et al.⁵ investigated the uncatalyzed GA system in a CSTR to obtain bistability and oscillations (both simple and complex) at high flow rates of the feed chemicals at an elevated temperature, 40 °C. A high temperature of the reactor was required apparently to avoid the solubility limitation of GA as much as possible. They reported bistability in the flowrate range 12–4 mL/min and oscillations in the flowrate range 6–1.7 mL/min with the help of two phase diagrams: (a) residence time – $[\text{BrO}_3^-]_0$ phase plane at a constant GA concentration and (b) residence time – $[\text{GA}]_0$ phase plane at a constant BrO_3^- concentration.

They reported⁵ that the uncatalyzed GA system exhibits only one steady state at 20 °C (room temperature). The following experiment demonstrates that this uncatalyzed oscillator indeed exhibits bistability at 20 °C in a different region of concentration space, which was obtained using feed tubings of unequal diameters.

In this experiment, the chemicals from two reservoirs, one containing KBrO_3 in 1.5 M H_2SO_4 and the other GA in 1.5 M H_2SO_4 , were fed into the CSTR⁹ in nonpremixed mode of mixing. The tubing from the reservoir feeding GA had a much larger diameter than that of the tubing from the reservoir feeding KBrO_3 . This arrangement minimizes the difficulties arising out of the solubility limitation of GA. The result of this bistability experiment is presented in Figure 5. The down transition of

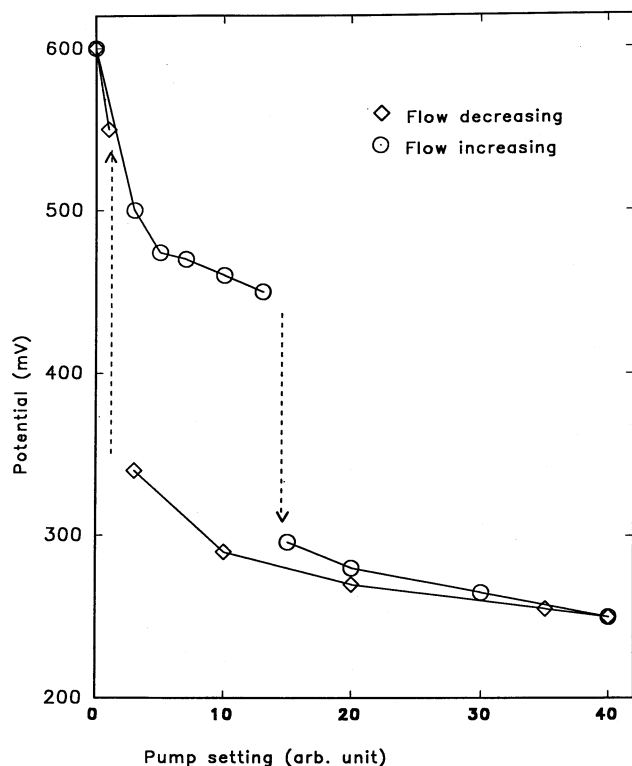
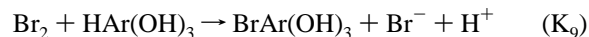
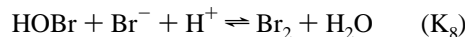
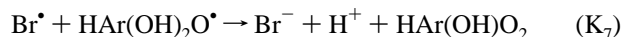
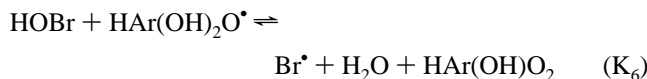
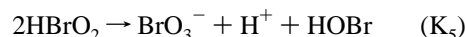
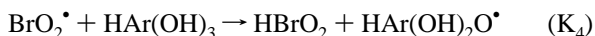
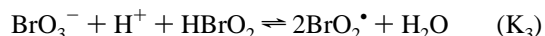
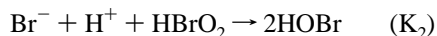
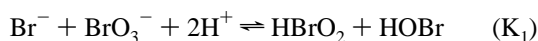
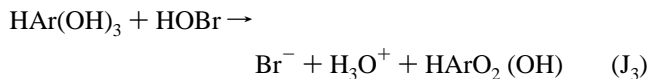
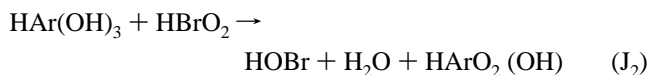
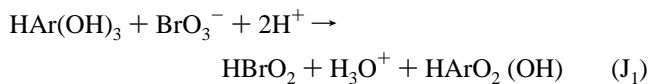


Figure 5. Hysteresis diagram in terms of potential as a function of pump setting in the uncatalyzed GA system: $[\text{KBrO}_3]_0$, 0.0396 M; $[\text{GA}]_0$, 0.0026 M; $[\text{H}_2\text{SO}_4]_0$, 1.5 M; S, 1150 rpm; temperature 20 °C (KBrO_3 contains 0.06% Br^- as impurity).

this bistability hysteresis was obtained at a very high flow rate (3.4 mL/min) similar to the experiments of Liu et al.⁵ and the up transition, from the flow branch to the thermodynamic branch at a very low flowrate, 0.73 mL/min.

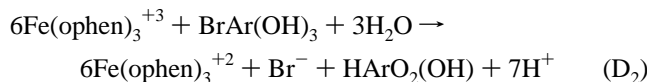
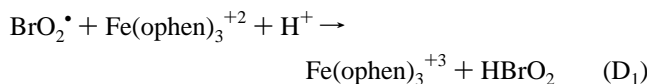
Discussion

Jwo et al.¹⁰ proposed the mechanistic steps of the uncatalyzed BrO_3^- –GA oscillating system by appropriate modifications of the Orban–Körös–Noyes (OKN) mechanism.^{11,12} The steps for the Br^- ion controlled mechanism are given below:



where $\text{HAr}(\text{OH})_3$ represents gallic acid.

Complex and aperiodic oscillations in ferroin catalyzed GA system are common. This is presumably due to the coupling of the uncatalyzed component oscillator^{5,10} steps (J_1 – J_3 , K_1 – K_9) with the catalyst $\text{Fe}(\text{phen})_3^{+2}$ through the stoichiometric reactions D_1 and D_2 given below:



The stoichiometric reaction D_1 joins the uncatalyzed step (K_4) to enhance the autocatalytic production of HBrO_2 . The stoichiometric reaction D_2 combines with the uncatalyzed steps J_3 , K_7 , and K_9 to accelerate the regeneration of Br^- to switch the system from low bromide concentration state (process B)^{13,14} to high bromide concentration state (process A).

It is worthwhile to point out that the small amplitude oscillations between two large oscillations (e.g., in Figure 1b) take place with distinct changes in the color of the solution inside the CSTR. Therefore, these small oscillations are related to the chemical dynamics of the catalyzed system and, hence, deterministic in nature.

The difficulty to obtain bistability and oscillations in the uncatalyzed³ GA system is related to the fact that GA itself is not a good candidate to maintain the critical Br^- generation feedback loop via steps J_3 , K_7 , and K_9 particularly at low flow rates, when very little of Br^- ion present as impurity in BrO_3^- enters the CSTR. Thus, oscillations cannot begin until a sufficient concentration of the Br^- -regenerating species accumulates. This often occurs in a batch reactor, but in a flow reactor, this species is apparently washed out too fast to accumulate. It is suggested that the present uncatalyzed component system, in the low flow rate region, may be similar to the MBO^{15–17} and that the additional Br^- in the feedstream is critical because that is where the Br^- feedback comes from. Figure 6 demonstrates a bistability⁴ between a high potential oscillatory state and a low potential flow branch as a function of pump setting using an additional feed of Br^- ions to the uncatalyzed system. The down and up transition of this bistability hysteresis were obtained at pump settings 12 (flow rate, 7 mL/min) and 1 (flow rate, 0.5 mL/min), respectively. Therefore, the use of an additional feed of Br^- ions appears to have identical role like that of the use of ferroin catalyst in the uncatalyzed GA system.³

The effectiveness of mixing is a central problem in chemical reactor engineering. The mixing process takes place in two

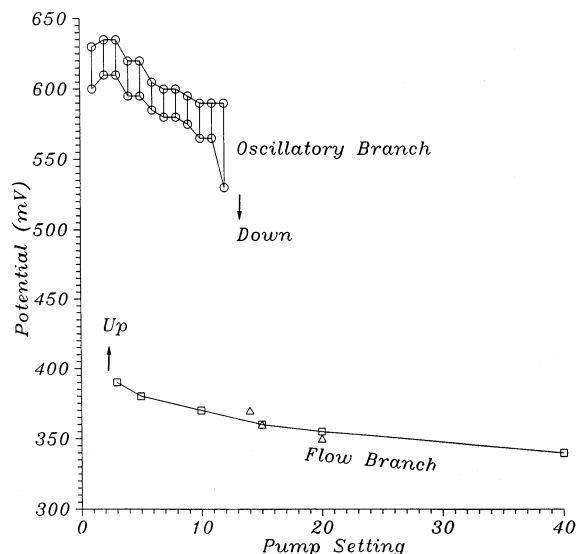


Figure 6. Hysteresis diagram in terms of potential as a function of pump setting in the uncatalyzed GA system: the composition of the reactor, $[\text{NaBrO}_3]_0$, 0.2 M; $[\text{NaBr}]_0$, 0.68×10^{-4} M; $[\text{GA}]_0$, 0.0235 M; $[\text{H}_2\text{SO}_4]_0$, 1 M; S, 1500 rpm; temperature, 25 °C (NaBrO_3 contains 0.05% Br^- as impurity).

levels, macromixing and micromixing. Macromixing is the formation of macroscopic heterogeneities and their breakdown into tiny segregated liquid packets, which have not yet mixed on the molecular level. Macromixing is rapid with good stirring. The decay of this segregation by molecular diffusion is called micromixing, which has a characteristic time of the order of 1 s. A strong stirring effect is observed if the chemical relaxation time is faster than that of micromixing. Both macro-^{18–22} and micromixing^{8,25} models have been used to model stirring and mixing effects in BZ-CSTR experiments.

Gyorgyi et al.^{20–22} suggested that the existence of spatial inhomogeneities in BZ-CSTR experiments may lead to the formation of partially independent oscillators in different parts of the reactor. Coupling between these areas may result in complicated periodic and aperiodic behavior in the bulk of the reactor as we have illustrated in Figures 1–3 for the catalyzed GA system. We assume a small volume (less than 1% of the reactor volume) in the end of the inlet tubes such that it has a composition different from either the pure feedstock or the bulk reaction mixture in the main reactor. There is a weak diffusive connection between the inlet ports and the bulk, which allows us to suppose that all reactants are available in the tips of the inlets. Thus, oscillations may occur slightly inside the inlet port, even though the feedstock itself, does not contain all reactants under nonpremixed mode. The oscillatory area inside an inlet port is treated as a small CSTR, from which the reaction intermediates are continuously washed into the CSTR. If oscillations occur inside the inlet, they may perturb the main reactor in a way which may lead to aperiodic behavior. This approach has features similar to the mixing models introduced by Kumpinski et al.¹⁸ and Bar-Eli et al.¹⁹ to investigate stirring effects in nonlinear chemical processes. Both of these studies addressed the effect of dead spaces on the operation of a CSTR; that is, they are models for macromixing. The aperiodic behavior in the fexroin catalyzed GA system is apparently much more

complex (vide Figures 1–3) than that observed in classical CSTR BZ experiments. This is obviously due to an additional coupling between the component uncatalyzed oscillations with the parent catalyzed oscillations via the stoichiometric reactions D_1 and D_2 .

Epstein and others^{23,24} introduced the theory that imperfect mixing increases the net rate of nonlinear second-order reaction kinetics compared to that one would expect on the basis of average reactant concentrations. At low stirring, the level of imperfect mixing is enhanced leading to the consumption of more Br^- ions from the bulk. Gyorgyi et al.⁸ modelled the stirring effect in the MBO^{15–17} using the “segregated feed” model of micromixing introduced by Villermaux.²⁵ They showed that more Br^- ions are held up in the segregated volumes because of slow mixing at low stirring rate and thus are not available in the well-mixed bulk. As a result, the effective Br^- ion concentration in the bulk of the reactor is decreased⁸ at low stirring rate. The above two theories suggest that the duration of the slow process $\text{A}^{13,14}$ in a complete oscillation cycle should decrease at low stirring to make the oscillation period shorter and also the oscillation amplitude smaller.

At high temperature, a significant amount of GA should oxidize to semiquinone, $\text{HArO}_2(\text{OH})$, before the reactions J_3 , K_7 , and K_9 and the stoichiometric reaction D_2 could occur, to regenerate Br^- ions. Consequently, the level of Br^- concentration in the bulk is decreased further at elevated temperatures for all of the time to make the oscillation periods shorter and also the amplitudes smaller as demonstrated in Figures 1–3.

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References and Notes

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