Pattern formation in a ferroin-bromate system

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Stationary mosaic patterns may spontaneously develop in a thin film of solution containing H$_2$SO$_4$, NaBrO$_3$, KBr, ferroin, and 4-cyclohexene-1,2-dicarboxylic acid. The pattern formation is affected by initial reactant concentrations and depends on the generation of elemental bromine. Depending on initial reactant concentrations, a vivid nonsynchronous oxidation transition may also occur. Results of experiments designed to distinguish between physical and chemical mechanisms are presented.

I. INTRODUCTION

Turing$^1$ originally demonstrated and Prigogine and Nicolis$^2$ further developed the notion that macroscopic spatial structures may develop in reaction–diffusion systems containing appropriate nonlinear kinetics. Spatial dissipative structures have since received a great deal of theoretical attention and have been suggested to be the basis of biological self-organization.$^3$

Experimental examples of stationary dissipative structures are few and have only recently appeared. Boiteux and Hess$^4$ report that stationary structures appear in cell free extracts of yeast. Convoluted bands of reduced pyridine nucleotide spontaneously grow into a mixture of previously homogenized oscillatory glycolyzing extracts. Stationary structures have also been observed by Orbán and Körös$^5$ in the uncatalyzed bromate oscillators. In addition to trigger wave behavior similar to that exhibited by the Belousov–Zhabotinsky (BZ) reaction,$^6$ the uncatalyzed reactions may also develop a patterned precipitate which undergoes periodic dissolution and precipitation.

Much of the theoretical activity has concerned dissipative structures in model reaction–diffusion systems. Experimental studies, however, are complicated by the possibility of chemical reaction coupling with a variety of physical processes. Even in dissipative structures arising solely from a reaction–diffusion bifurcation, reaction exothermicity should give rise to temperature inhomogeneity. Calorimetric studies of the homogeneous BZ reaction have demonstrated periodic variation of reaction exothermicity.$^7$ Other oscillatory reactions should behave similarly. Trigger wave behavior in the BZ reaction has been successfully modeled by considering reaction–diffusion only,$^8$ indicating that temperature effects are negligible. However, spatial variation of reaction exothermicity is likely to be much more important in stationary structures than in propagating trigger waves. Temperature effects such as these will enhance the probability of hydrodynamic instability, even when dissipative structures arise primarily from a reaction–diffusion bifurcation.

Experimental studies of spatial behavior in chemical systems typically utilize a thin film of reaction mixture spread over the bottom of a petri dish. The air exposed surface of the solution is another potential source of hydrodynamic instability. Variation of temperature and/or concentration over the surface can lead to convective instabilities driven by surface tension.$^9$ Thus, hydrodynamic instability may be induced by reaction–diffusion dissipative structures even in the absence of temperature effects. Conversely, spatial structures may arise primarily from a chemically driven convective instability. Exchange of matter across the air–reaction mixture interface may also be important in systems exhibiting macroscopic spatial structures. Either volatilization of a reaction component or dissolution of an atmospheric constituent which affects the chemical reaction may play an important role in pattern formation. Other physical factors might also be important to pattern formation in a chemically reacting system.

The task of an experimental investigation of pattern formation in a chemical system is to determine what process is primarily responsible for the structures and to what extent it is coupled with chemical reaction. The subject of this paper is an investigation of stationary spatial structures appearing in a ferroin–bromate system containing 4-cyclohexene-1,2-dicarboxylic acid. In Sec. II, our initial observations of a patterned oxidation transition are presented. The basic features of the ferroin–bromate reaction and its modification in this work are discussed in Sec. III. In Sec. IV, relevant experimental results are presented and in Sec. V, a mechanism consistent with experiment is proposed.

II. INITIAL EXPERIMENTS

During our investigation of trigger wave initiation and propagation in the acidic bromate oxidation of ferroin,$^{10}$ we observed that the bulk transition of the reaction from the reduced to the oxidized state may occur nonsynchronously. A reaction mixture with composition $\alpha$ in Table I was spread over the surface of an optically flat petri dish to a depth of 1.7 mm approximately 1.0 min after mixing. It remained orange until $\sim$33 min when small regions of blue appeared and subsequently grew. Figure 1 shows the patterned oxidation transition at 33.75 min. The entire reaction mixture became uniformly blue at $\sim$34.5 min. The experiment was repeated four times with the time development photographically recorded. Comparison of the photographs revealed that while the overall patterns were different from experiment to experiment, all contained similar convoluted bands of oxidized solution.

The reaction vessel consisted of a circle of plate glass 12.5 cm in diameter surrounded on the sides and bottom by a water jacket. The experiment shown in Fig.
TABLE I. Composition of reactant solutions.

<table>
<thead>
<tr>
<th></th>
<th>α</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaBrO₃ (M)</td>
<td>9.51 × 10⁻²</td>
<td>9.51 × 10⁻²</td>
</tr>
<tr>
<td>KBr (M)</td>
<td>5.74 × 10⁻²</td>
<td>6.05 × 10⁻²</td>
</tr>
<tr>
<td>H₂SO₄ (M)</td>
<td>0.189</td>
<td>0.189</td>
</tr>
<tr>
<td>Ferroin (M)</td>
<td>1.21 × 10⁻³</td>
<td>1.21 × 10⁻³</td>
</tr>
<tr>
<td>C₆H₅(COOH)₂ (M)</td>
<td>8.27 × 10⁻²</td>
<td>8.52 × 10⁻²</td>
</tr>
</tbody>
</table>

When [Br⁻] is below a critical value, the dominant process becomes reduction of BrO₅⁻ by ferroin in the net process

\[ \text{BrO}_5^- + 4 \text{Fe(II)} + 5 \text{H}^+ \rightarrow \text{HOBr} + 4 \text{Fe(III)} + 2 \text{H}_2\text{O}. \]  

(B)

This process involves autocatalytic generation of the reaction intermediate HBrO₂. The switch from process (A) to (B) at the critical [Br⁻] occurs very suddenly with a dramatic color change from orange to blue. We refer to this change as the oxidation transition.

The elemental bromine generated in process (A) reacts destructively with ferroin to form an insoluble substance. We circumvented this problem in our trigger wave studies by the addition of 4-cyclohexene-1,2-dicarboxylic acid, a water soluble unsaturated compound that consumes Br₂ to form the bromohydrin product.¹⁰ Process (A) with excess C₆H₅(COOH)₂ becomes

\[ \text{BrO}_5^- + 2 \text{Br}^- + 3 \text{H}^+ + 3 \text{C}_6\text{H}_5(\text{COOH})_2 \rightarrow 3 \text{C}_6\text{H}_5(\text{OH})(\text{Br})(\text{COOH})_2. \]  

(C)

Patterns did not appear in reaction mixtures prepared with a stoichiometric excess of C₆H₅(COOH)₂ vs Br⁻ according to process (C). In these solutions, the oxidation transition occurred with uniformity throughout. Reaction mixtures containing a large stoichiometric excess of Br⁻ vs C₆H₅(COOH)₂ developed a uniformly distributed brick-red precipitate. The most dramatic patterned oxidation transitions occurred when Br⁻ was in stoichiometric excess to C₆H₅(COOH)₂ by only a

1 was thermostated at 25.0 ± 0.2 °C. A plate glass cover was positioned 2.0 cm above the solution, supported by the sides of the thermostated petri dish, to prevent contamination of the solution by airborne dust. Reactant solutions were repeatedly filtered through 0.8 μm membrane filters to keep them dust free. Solutions occasionally contained some dust and regions of chemical reactivity were prematurely initiated at the heterogeneous centers. These regions could be readily distinguished from the patterned oxidation transition which grew in at latter times.

III. THE CHEMICAL REACTION

The oxidation of ferroin and other weak one-electron reducing agents by acidic bromate has been extensively studied and its essential features are well understood.¹¹ In the system reported here, the reaction remains in the reduced ferroin state as long as [Br⁻] is above a critical value. Initially present bromide is consumed by bromate oxidation in the net process

\[ \text{BrO}_5^- + 5 \text{Br}^- + 6 \text{H}^+ \rightarrow 3 \text{Br}_2 + 3 \text{H}_2\text{O}. \]  

(A)

FIG. 1. The patterned oxidation transition at 33.75 min after mixing. Initial reactant concentrations: [H₂SO₄] = 0.189 M, [NaBrO₃] = 9.51 × 10⁻² M, [KBr] = 5.74 × 10⁻² M, [ferroin] = 1.21 × 10⁻³ M, [C₆H₅(COOH)₂] = 8.27 × 10⁻² M. Temperature: 25.0 ± 0.2 °C. The photograph width represents ~10 cm.
slight amount. No precipitate was visually detectable during experiments with the latter reaction mixture.

IV. OTHER EXPERIMENTS

A. Pattern formation in reduced solution prior to oxidation transition

The initial experiments were concerned with how the patterned oxidation transition was affected by experimental conditions and reactant concentrations. During these experiments, faint hairline patterns were observed at earlier times in reaction mixtures containing an initial concentration of \( \text{C}_5\text{H}_5(\text{COOH})_2 \) lower than that which generated the most distinct patterned oxidation transition. Experiments were carried out with \( [\text{C}_5\text{H}_5(\text{COOH})_2] \) further reduced in an effort to generate more visible early patterns. In a reaction mixture of composition \( \alpha \) except \( [\text{C}_5\text{H}_5(\text{COOH})_2] = 7.58 \times 10^{-3} \text{M} \), very distinct mosaic patterns appeared in the reduced solution. The patterns, shown in Fig. 2, appeared several minutes after the reaction mixture suddenly darkened at 2.5 min. The darkening was characteristic of the stoichiometric point for the bromination of \( \text{C}_5\text{H}_5(\text{COOH})_2 \) according to process (C) in reaction mixtures containing excess \( \text{Br}^- \).

The photograph in Fig. 2 was taken at 6.0 min, the time at which the patterns had developed to maximum clarity and complexity. The major features involve alternating light orange and dark orange-brown bands. The light bands grew from initial hairline bands which appeared at 4.1 min. An important feature not clearly shown in Fig. 2 is very thin colorless lines in the center of the dark bands. The overall features of the mosaic patterns persisted from \(-5.0 \) to \(-7.5 \) min. The patterns were completely stationary; the only changes during this time involved the light bands growing wider and the dark bands narrowing. At 7.5 min the patterns began to fade and by 15.0 min the solution appeared almost homogeneous. At 29.2 min a nonsynchronous oxidation transition occurred, but distinct bands as in Fig. 1 were not observed.

B. Effects of temperature

The pattern formation experiments were conducted in a thermostated petri dish at 25.0 ± 0.2 °C. The air temperature above the reaction mixture was not monitored quantitatively; however, room temperature was usually a few degrees below 25.0 °C. An obvious concern in these experiments was the possibility that convection cells might be established in the layer of solution and in some way be responsible for the pattern formation. Therefore, experiments were conducted in which the air temperature above the reaction mixture was deliberately maintained at a temperature higher than that of the solution.

Two experiments (solution composition \( \alpha \) except \( [\text{Br}^-] = 6.7 \times 10^{-3} \text{M} \) and \( [\text{C}_5\text{H}_5(\text{COOH})_2] = 9.22 \times 10^{-3} \text{M} \)) were carried out with the room temperature at 24.9 °C and the petri dish temperature at 19.9 °C. In all experiments in this section, room temperature and petri dish temperature were repeatedly measured using two thermometers which were interchanged each measurement.

**FIG. 2.** Patterns at 6.0 min after mixing. Initial reactant concentrations are the same as Fig. 1 except \( [\text{C}_5\text{H}_5(\text{COOH})_2] = 7.58 \times 10^{-3} \text{M} \). Temperature: 25.0 ± 0.2 °C. The photograph width represents ~10 cm.
Patterns similar to those in Fig. 2 appeared at ~6.5 min and persisted for 4–6 min. The oxidation transition at ~60 min was not spatially synchronous; however, no patterns as distinct as those in Fig. 1 were observed. A second set of experiments with the room temperature at 22.3 °C and the petri dish temperature at 17.2 °C generated similar results.

Other experiments were done in which the room temperature was elevated and the petri dish temperature was maintained at 25.2 °C. Three experiments using reaction mixtures of composition α in Table I and varying \([C_2H_5(COOH)]_2\) were conducted. To ensure that the temperature of the air in contact with the solution surface was near room temperature, the plate glass cover was not used in these experiments. Room temperature in the first run was 25.7 °C and \([C_2H_5(COOH)]_2 = 7.66 \times 10^{-5} M\). Patterns appeared at ~2.5 min and persisted for ~6.5 min. The patterned oxidation transition was less distinct than that in Fig. 1. In the second run \([C_2H_5(COOH)]_2 = 7.74 \times 10^{-5} M; \text{ room temperature} = 29.0 °C\), patterns appeared at ~2.5 min, persisted for ~9 min, and a distinct patterned oxidation transition was observed. In the third run \([C_2H_5(COOH)]_2 = 7.83 \times 10^{-5} M; \text{ room temperature} = 29.4 °C\), patterns and a patterned oxidation transition similar to those in the second run were observed.

C. Surface effects

Experiments were carried out to investigate possible surface effects involved in the pattern formation. In one series of experiments, the surfactant sodium lauryl sulfate was added to the reaction mixture. Three experiments with increasing concentrations of surfactant were carried out at 25.0 °C (reaction mixture composition α in Table I except \([C_2H_5(COOH)]_2 = 7.58 \times 10^{-5} M; [n-C_{12}H_{25}SO_4Na] = 1.3 \times 10^{-3}, 1.3 \times 10^{-3}, \text{ and } 6.9 \times 10^{-3} M\)). Patterns appeared in all three runs at ~3.0 min and initially developed in a manner similar to experiments without added surfactant. No difference was detected throughout the run with the lowest surfactant concentration. When surfactant concentration was increased tenfold, however, a colloidal substance, observed whenever \(\text{Br}^- \text{ vs } C_2H_5(COOH)_2\) was in stoichiometric excess according to process (C), became more visible. At the highest surfactant concentration, the insoluble substance precipitated from the dark bands in the patterns and remained on the bottom of the petri dish even after the oxidation transition. Similar results were obtained in experiments with the room temperature at 22.8 °C and the petri dish temperature at 17.3 °C.

Other experiments were carried out at 25.0 °C using a reaction mixture with the same composition, but without added surfactant. In these experiments, a region of the solution was sandwiched between the bottom of the petri dish and a 7.7 × 7.7 cm square of plate glass. The plate glass was supported 1.5 mm above the petri dish bottom so that the sandwiched solution was approximately the same thickness as the surrounding solution exposed to air. Typical patterns similar to those in Fig. 2 appeared and developed in the uncovered solution at ~3.0 min. The solution under the plate glass rapidly became bleached, apparently from the reaction between ferroin and \(\text{Br}_2\). Patterns did not develop in the sandwiched reaction mixture.

D. Effect of reaction mixture depth

Experiments were conducted to determine if the pattern formation was affected by the depth of the reaction mixture. Nine experiments were conducted in which only the volume of the reaction mixture spread over the petri dish bottom was varied (composition α except \([C_2H_5(COOH)]_2 = 7.58 \times 10^{-5} M; [n-C_{12}H_{25}SO_4Na] = 1.3 \times 10^{-3} M\)). Addition of sodium lauryl sulfate facilitated spreading the thin films of the reaction mixture. Solution depth was calculated from the reaction mixture volume and area of the petri dish. The calculated depths are only approximate because no attempt was made to correct for the solution adhered to the petri dish sides by capillary action. Therefore, the depths were actually somewhat less than those calculated, particularly for the very thin films of solution. Approximate band spacing was determined by measuring the separation between the centers of adjacent bands in either the initial patterns or in the patterned oxidation transition. At least five measurements were made for each depth using photographs recording the time development of the patterns. The average bandwidths for the various solution depths are given in Table II. No regular patterns were observed with solutions depths of 0.65 mm or less.

E. Effect of bromine on induction period

Qualitative observations showed that when \(\text{Br}^- \text{ vs } C_2H_5(COOH)_2\) was in stoichiometric excess according to process (C), the oxidation transition was significantly delayed. Quantitative experiments were conducted using stirred reaction mixtures with only the initial concentration of \(\text{Br}^-\) varied. A closed reaction vessel was utilized, thermostated at 25.0 ± 0.2 °C, and bromide concentration was monitored with an ion selective electrode. A run began by placing all reagents except \(\text{NaBrO}_3\) into the reaction vessel. Addition of \(\text{NaBrO}_3\) solution by rapid delivery pipet caused a sudden decrease in [\(\text{Br}^-\)]. The induction period was defined as the time between the addition of bromate reagent to the beginning of the oxidation transition, characterized by [\(\text{Br}^-\)] suddenly decreasing. Figure 3 shows the induction period as a function of initial [\(\text{Br}^-\)] for reaction mixtures of composition β in Table I. The vertical dotted line in Fig. 3 corresponds to the [\(\text{Br}^-\)] that is stoichio-

### Table II. Average bandwidth for the various solution depths.

<table>
<thead>
<tr>
<th>Solution depth (mm)</th>
<th>Average band spacing (mm)</th>
</tr>
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<tbody>
<tr>
<td>1.71</td>
<td>2.4</td>
</tr>
<tr>
<td>1.55</td>
<td>2.3</td>
</tr>
<tr>
<td>1.39</td>
<td>2.3</td>
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<tr>
<td>1.22</td>
<td>2.0</td>
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<tr>
<td>1.06</td>
<td>2.0</td>
</tr>
<tr>
<td>0.81</td>
<td>2.1</td>
</tr>
<tr>
<td>0.65</td>
<td>...</td>
</tr>
<tr>
<td>0.49</td>
<td>...</td>
</tr>
<tr>
<td>0.33</td>
<td>...</td>
</tr>
</tbody>
</table>
FIG. 3. Induction period as a function of initial [Br\(^-\)]. Initial reactant concentrations are the same as Fig. 1 except
\[ [\text{C}_2\text{H}_4(\text{COOH})_2] = 8.52 \times 10^{-2} M, \] Temp.: 25.0 \pm 0.2 ^\circ C.
Dotted vertical line corresponds to [Br\(^-\)] stoichiometrically equivalent to \([\text{C}_2\text{H}_4(\text{COOH})_2]\).

FIG. 4. Bromide concentration as a function of time. Initial reactant concentrations are the same as Fig. 1 except
\[ [\text{C}_2\text{H}_4(\text{COOH})_2] = 8.52 \times 10^{-2} M \] and
\[ [\text{KBr}] = 6.01 \times 10^{-2} M. \] Temp.: 25.0 \pm 0.2 ^\circ C.

metrically equivalent to \([\text{C}_2\text{H}_4(\text{COOH})_2]\) according to process (C).

The almost vertical increase in induction period beyond the stoichiometric point in Fig. 3 indicates that the Br\(^-\) product of process (A) dramatically inhibits the onset of autocatalysis in process (B). These results are in general agreement with a study of the cerium (III)-bromate system showing that Br\(^-\) inhibits the onset of process (B) as effectively as does Br\(^-\)\(^3\).

The time of the oxidation transition in the homogeneous system was influenced by the extent that the reaction vessel was closed to the atmosphere. Experiments were conducted to determine the effect of sweeping out volatilized Br\(_2\) above the reaction mixture. One experiment (composition \(\beta\) in Table I and [Br\(^-\)] = 6.05 \times 10^{-2} M) was carried out in an identical manner as those in Fig. 3 and an induction period of 83.1 min was measured. A second experiment was carried out the same as the first except the reaction vessel was modified to accommodate flushing the air space above the reaction mixture with a stream of \(N_2\). An induction period of 48.9 min was measured. The time and quality of the patterned oxidation transitions were also affected by the extent that the petri dish was closed to the atmosphere with the plate glass cover. In both the stirred and the spatially distributed systems with Br\(^-\) in stoichiometric excess, a strong odor of Br\(_2\) was detected whenever the reaction vessel was opened, particularly near the end of the induction period. These observations indicate that the oxidation transition is so strongly inhibited by Br\(_2\) that any loss by volatilization has a significant effect. Evidence that the above observations are not the result of dissolved atmospheric oxygen is presented in Sec. IV.G.

A [Br\(^-\)] vs time chart recorder trace similar to those used in the above experiments and in Fig. 3 is shown in Fig. 4. In this experiment, a stirred reaction mixture exposed to the atmosphere was used (composition \(\beta\) in Table I and [Br\(^-\)] = 6.01 \times 10^{-2} M). An induction period of 35.5 min was measured, somewhat shorter than that corresponding to the closed vessel experiment in Fig. 3. In all experiments with excess Br\(^-\) vs \([\text{C}_2\text{H}_4(\text{COOH})_2]\), a decrease in [Br\(^-\)] similar to that at 4.5 min in Fig. 4 was observed. This decrease corresponds to the stoichiometric point for the bromination of \([\text{C}_2\text{H}_4(\text{COOH})_2]\). An increase in the rate by a factor of 5/2 is expected according to the stoichiometries of processes (A) and (C). The time of the stoichiometric point for a particular reaction mixture was reproducible in both the open and closed vessel experiments; however, the [Br\(^-\)] decrease at the stoichiometric point varied considerably in the open vessel experiments.

F. Reaction of bromine with ferroin

In reaction mixtures prepared with a significant excess of Br\(^-\) vs \([\text{C}_2\text{H}_4(\text{COOH})_2]\), a uniformly distributed brick-red precipitate suddenly appeared upon complete consumption of \([\text{C}_2\text{H}_4(\text{COOH})_2]\). In stirred solution, the appearance of the precipitate always coincided with the stoichiometric point, indicated in the [Br\(^-\)] chart recorder trace. The precipitate at least partially dissolved during the induction period and after completion of the oxidation transition, no trace of precipitate could be detected. Other experiments demonstrated that a brick-red precipitate very similar in appearance is generated by direct reaction of ferroin with bromine water, but no precipitation occurs with ferrin (tris (1,10-phenanthroline) iron (III)) and bromine water. The precipitate in the former solution disappeared following an oxidation transition induced by addition of NaBrO\(_5\) and H\(_2\)SO\(_4\) reagents.

G. Effects of oxygen

The thin film of the reaction mixture in the pattern formation experiments was exposed to the atmosphere; therefore, experiments were conducted to determine if dissolved oxygen affects the reaction. Experiments identical to those described in Sec. IV E were conducted except that oxygen was bubbled into the reaction mixture for 2.0 min immediately before the bromate reagent was added and the reaction vessel sealed. Two experiments were conducted, one with bubbled oxygen and the other without (composition \(\beta\) in Table I and [Br\(^-\)] = 2.87 \times 10^{-3} M). These runs corresponded to limiting Br\(^-\) vs \([\text{C}_2\text{H}_4(\text{COOH})_2]\) (see Fig. 3) and had induction peri-
ods of 7.45 and 7.30 min. Two other experiments with excess Br⁻ vs C₆H₅(COOH)₂ were carried out (composition β in Table I and [Br⁻] = 5.89 x 10⁻⁷ M). Induction periods of 14.61 and 15.13 min were measured for runs with and without O₂, respectively. These four experiments demonstrate that, within experimental error, O₂ has no effect on the duration of the induction period. The results are in agreement with earlier studies on the cerium (III)–bromate system in which no O₂ effects were found. This is in contrast to the Belousov–Zhabotinsky reaction which is strongly affected by O₂.⁶ ⁴(c)

Another test for O₂ effects involved an experiment the same as in Fig. 2 except that it was carried out entirely within a nitrogen purged glove bag. Nitrogen was also bubbled through reactant solutions before they were mixed. No difference in the initial pattern formation or the patterned oxidation transition was detected in this experiment from those experiments exposed to the atmosphere.

V. DISCUSSION

Any explanation proposed to account for the appearance of spatial structures in the ferroin–bromate system must be consistent with the experimental results presented in Secs. II and IV. Some of the experiments were designed to determine if the patterns were due to the establishment of convection cells in the reaction mixture. Other experiments were designed to develop a more complete understanding of the modified ferroin–bromate system in order to determine the extent that chemical reaction is responsible for the pattern formation.

A. Convective cell considerations

Hydrodynamic instabilities are known to occur in thin layers of liquids. Experiments by Bénard over 80 years ago demonstrated that very regular patterns may develop in a thin layer of liquid heated from below.¹⁴ For many years the cells were thought to arise from a buoyancy driven convective instability, an explanation first proposed by Lord Rayleigh.¹⁵ Experiments by Block¹⁶ and theoretical analyses by Pearson⁹ demonstrated that in thin films of liquids exposed to air, convective instabilities are primarily due to surface tension effects.

The experiments in Sec. IV.G were conducted to determine if atmospheric oxygen might be entrained in convection cells and result in spatial concentration inhomogeneities by affecting the rate of reaction. This explanation can be ruled out by the absence of measurable effects on the induction period when reaction mixtures were saturated with oxygen. The pattern formation experiment conducted in a nitrogen atmosphere provides even more convincing evidence that atmospheric oxygen is unimportant.

The experiments in Sec. IV.B were carried out to determine if a simple buoyancy driven convective instability might be responsible for the pattern formation. It is conceivable that material flow in convection cells might cause Br₂ to be volatilized nonuniformly from the solution surface. The experiments demonstrated that pattern formation occurs even when the air temperature above the surface is substantially higher than that of the reaction mixture. Convective instabilities in pure liquids require heating from below; therefore, this explanation can be ruled out if the reaction mixture is regarded as a pure liquid. Convective instabilities may occur in binary liquids for either positive or negative vertical temperature gradients.¹⁷ The ferroin–bromate reaction mixture contains solutes that comprise slightly more than 5% of the mass of the system; however, most are ionic species. The only species that might conceivably form a binary liquid with water is Br₂, but the maximum quantity generated by chemical reaction makes up less than 0.1% of the mass of the system. It seems unlikely that a buoyancy driven convective instability could develop in this system with a stabilizing vertical temperature gradient.

Pearson’s analysis of liquids exposed to air concerned convective instabilities arising from the coupling of surface tension with surface temperature.⁹ The analogous coupling of surface tension with surface concentration in multicomponent systems was also considered. Surface tension–surface concentration instabilities do not require heating from below. Patterns appear in the ferroin–bromate system following the stoichiometric point and generation of Br₂; therefore, an instability of this type seems possible. Addition of sodium lauryl sulfate to reaction mixtures did not disrupt the pattern formation as would be expected in a surface tension instability (Sec. IV.C). However, patterns did not appear in reaction mixture sandwiched between glass plates. This experiment indicates that surface effects play a fundamental role in the pattern formation. These effects might include volatilization of Br₂ and/or a possible surface tension–surface concentration convective instability. The importance of Br₂ volatilization was demonstrated by the oxidation transition being significantly delayed in the sandwiched solution.

Evidence that a convective instability plays a role in the pattern formation is given in Table II. The lack of banding in reaction mixtures with depths of 0.65 mm and less was unequivocal. Nonsynchronous oxidation transitions were observed in even the thinnest films, but no discernible banding was detected below the critical depth. This depth was actually somewhat less than 0.65 mm (Sec. IV.D), suggesting that the convective instability is primarily a surface phenomenon. This conclusion is supported by the surprisingly small dependence of band spacing on solution depth.

B. Chemical reaction considerations

The initial experiments varying C₆H₅(COOH)₂ vs Br⁻ established that the pattern formation depends on the chemical generation of Br₂. Other experiments demonstrated that Br₂ dramatically affects the chemical reaction (Fig. 3). We now consider the effects of Br₂ on the chemical reaction and the role it plays in both the initial pattern formation and the patterned oxidation transition.

A recent report suggests that Br₂ may act as a control intermediate in a BZ type system containing oxalic
acid in place of malonic acid. In this system, Br₂ was physically removed with an inert carrier gas, and an analysis showed periodic evolution of Br₂. More surprising is a study showing that the acidic bromate oxidation of ferroin may become oscillatory when Br₂ is physically removed at an appropriate rate. Only an intermediate partial removal generates oscillatory behavior; an increase or decrease in removal rate causes the oscillations to cease.

Homogeneous bromate reactions in which Br₂ is physically removed are obviously relevant to chemical mechanism considerations for the modified ferroin-bromate system. Simple stoichiometry shows that for an experiment in Fig. 3 with initial [Br⁺] = 6.01 × 10⁻⁷ M, about 3.3 × 10⁻⁷ M Br⁻ remains following the stoichiometric point according to process (C). This remaining Br⁻ can generate a maximum [Br₂] of 1.98 × 10⁻⁴ M by process (A), assuming complete reaction. An induction period of 40.7 min was measured for initial [Br⁺] = 6.01 × 10⁻⁷ M. Assuming the points in Fig. 3 that occur before the stoichiometric point can be extrapolated to higher [Br⁺], the induction period for the same initial [Br⁺] in a reaction mixture containing excess C₆H₅(OOH), would be about 12.0 min. The similarly extrapolated induction period at the stoichiometric point is ~11.5 min; therefore, an additional 3.3 × 10⁻⁷ M Br⁻ with excess C₆H₅(OOH)₂ should increase the induction period by about 0.5 min. In contrast, an increase of ~29.2 min results from the generation of 1.98 × 10⁻⁴ M Br₂ when C₆H₅(OOH)₂ is stoichiometrically limiting. These semiquantitative considerations demonstrate the powerful influence of Br₂ on the system.

We conclude that in systems with significant accumulation of Br₂, the autocatalytic generation of HBrO₃ in process (B) is controlled by HBrO in a manner similar to control by bromide. Before the stoichiometric point in the modified ferroin-bromate system, HBrO₃ is maintained at a low concentration by Reaction (A2), preventing the onset of autocatalysis, according to the FKN mechanism. Therefore, the reaction proceeds in process (C) at a rate limited by Reaction (A1). Process (C) is simply process (A) plus the reaction of Br₂ with C₆H₅(OOH), to form the bromohydrin product, or Reactions (A1)+(A2)+3 (A3)+3 (C1). [Direct reaction of HBrO with C₆H₅(OOH) generates an identical stoichiometry.] We have the reactions

\[
\begin{align*}
\text{BrO}_3^- + \text{Br}^- + 2 \text{H}^+ & \rightarrow \text{HBrO}_3 + \text{HBr}, \\
\text{Br}^- + \text{HBrO}_3 + \text{H}^+ & \rightarrow 2 \text{HBrO}, \\
\text{Br}^- + \text{HBrO} + \text{H}^+ & \rightarrow \text{Br}_2 + \text{H}_2\text{O}, \\
\text{Br}_2 + \text{C}_6\text{H}_5\text{(COOH)}_2 + \text{H}_2\text{O} - \text{H}^+ + \text{Br}^- + \text{C}_6\text{H}_5\text{(OH)}(\text{Br})(\text{COOH})_2.
\end{align*}
\]

However, when Br⁻ is depleted and Br₂ has accumulated following the stoichiometric point, the resulting increased [HBrO₃] may significantly alter the kinetic behavior as the reverse of Reaction (A1) becomes important. Indeed, computer modeling of the BZ reaction in a continuously stirred tank reactor (CSTR) showed that Reaction (A1) occurs to a significant extent during times when [HBrO₃] is high.

In a reaction mixture containing excess C₆H₅(COOH)₂ to prevent accumulation of Br₂, the onset of process (B) occurs when Br⁻ becomes sufficiently consumed that Reaction (A2) can no longer suppress autocatalysis. At the critical bromide concentration, [Br⁻] = (kₐ₁/kₐ₂)(kₐ₃/kₐ₄) [BrO₃⁻], the oxidation transition occurs with a burst of HBrO₃ autocatalysis and concurrent oxidation of ferroin. We have the reactions

\[
\begin{align*}
\text{BrO}_3^- + \text{HBrO}_3 + \text{H}^+ & \rightarrow 2 \text{Br}_2 + \text{H}_2\text{O}, \\
\text{Br}_2 + \text{Fe(II)} + \text{H}^+ & \rightarrow \text{HBrO}_3 + \text{Fe(III)}, \\
2 \text{HBrO}_3 & \rightarrow \text{BrO}_3^- + \text{HOBr} + \text{H}^+.
\end{align*}
\]

In a system containing stoichiometrically limiting C₆H₅(COOH)₂, the buildup of Br₂ inhibits the onset of process (B) because the corresponding increase in [HBrO₃] makes Reaction (A1) more favorable. Thus, HBrO₃ is maintained at concentrations lower than that necessary to initiate process (B) because it is consumed by reaction with HBrO by reaction with Br⁻ in Reactions (A1) and (A2). The effectiveness of HBrO₃ as an inhibitor of process (B) is underscored when the stoichiometry of Reaction (A1)+(A2) is considered. This process is stoichiometrically equivalent to the biomolecular termination of HBrO₃ (Reaction (B3)); however, it is autocatalytic in HBrO₃.

\[
\text{HOBr} + 2 \text{HBrO}_3 \rightarrow \text{H}^+ + \text{BrO}_3^- + 2 \text{HOBr}. 
\]

Inhibition of process (B) by HBrO₃ becomes important only at low bromide concentrations, or when [Br⁻] < \((k_{r_A1} k_{r_A3} [Br_2])/((k_{r_A2} k_{r_A4} [H^+]^2))/\). Typical concentrations of Br₂ give Br⁻ concentrations near [Br⁻]. Thus, the oxidation transition is delayed when Br₂ accumulates because just when bromide is consumed to its critical concentration, the elevated [HBrO₃] becomes an effective inhibitor of process (B).

This chemical mechanism satisfactorily accounts for the patterned oxidation transition, assuming that a non-uniform spatial distribution of Br₂ is established by the initial pattern formation. The oxidation transition is delayed in Br₂ rich regions because the onset of HBrO₃ autocatalysis is inhibited by the elevated [HBrO₃]. That the initial patterns serve as a template for the patterned oxidation transition is easily verified on examination of photographs recording the time development of the system. The light bands in the initial patterns are apparently rich in Br₂ because they form bands of reduced solution during the oxidation transition.

The same mechanism may also account for oscillatory kinetics in bromate reactions when accumulated Br₂ is physically removed. In a system with an appropriate [HBrO₃], the balance between HBrO₃ autocatalysis and termination by HBrO₃ autocatalysis may force the reaction to proceed by small periodic bursts. Process (B) "turns on", causing an increase in [HBrO₃], and is quickly "turned off" by process (A1)+(A2). The short burst of process (B) generates ferrilin which is subsequently reduced by reaction with the organic substrate.

The initial pattern formation appears to be a chemic-
ally driven convective instability; however, a mechanism for chemical feedback similar to that for the patterned oxidation transition does not seem applicable. Experiments monitoring bromide as a function of time demonstrate that during the initial pattern formation the [Br\textsuperscript{+}] is too high for the reverse of Reaction (A1) to be significant. The chemical reaction appears to be necessary, however, because all attempts to reproduce the pattern formation with bromine water and various colloidal suspensions failed. Noyes\textsuperscript{21} has recently suggested that ferroin may be oxidized by HOBr, initiating a radical reaction sequence which ultimately results in the generation of Br\textsuperscript{2}, when an oxidizable organic species is available. It is conceivable that radical reaction is enhanced in Br\textsuperscript{2} rich regions containing an elevated [HOBr]. However, it is not evident how such reaction might enhance the onset of a convective instability.

It is possible that the role of chemical reaction in the initial pattern formation is simply to provide a continuous source of Br\textsuperscript{2}. Volatilization of Br\textsuperscript{2} from the solution surface coupled with its low surface tension and nonpolar character may give rise to a surface tension–surface concentration convective instability. The ferroin–bromine colloidal suspension may also play a role in the instability. It is apparent from qualitative observations that the colloidal substance is concentrated in the dark bands during the pattern formation (Fig. 2). It has recently been demonstrated that chemically driven convective instabilities not associated with adverse temperature gradients are possible.\textsuperscript{22} However, the convection relies on a buoyancy mechanism and therefore does not seem applicable to the ferroin–bromate pattern formation. A surface tension–surface concentration convective instability enhanced by Br\textsuperscript{2} volatilization and possibly chemical feedback seems to be a more plausible explanation.

VI. CONCLUSION

The modified ferroin–bromate reaction in a thin film of solution reproducibly exhibits stationary spatial structures. These structures represent a unique example of spatial self–organization in a chemical system. The patterns are not the result of a purely physical process such as the development of buoyancy driven convection cells from an adverse temperature gradient, but rather arise from a chemically driven convective instability. This instability depends on the chemical generation of Br\textsuperscript{2} and appears to be primarily a surface phenomenon. A spatially nonuniform distribution of Br\textsuperscript{2} results which later serves as a template for a patterned oxidation transition.

Other examples of pattern formation in chemically reactive systems may also rely on hydrodynamic instability. The patterns in Fig. 2 are strikingly similar in appearance to the dissipative structures in glycolyzing cell free extracts of yeast.\textsuperscript{4} Zhabotinsky\textsuperscript{23} reported pattern formation that appears to be equivalent to the patterned oxidation transition in Fig. 1. These patterns appeared in a BZ system containing acetylacetone in place of malonic acid during the bulk oscillation from the reduced to oxidized state.

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\textsuperscript{12}We acknowledge the suggestion by A. T. Winfree concerning the possibility of convection cells giving rise to the pattern formation.
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