

# New Indicators for Visualizing Pattern Formation in Uncatalyzed Bromate Oscillatory Systems

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**Abstract:** Many uncatalyzed bromate oscillators (UBO's) undergo oscillations in electrochemical potential without any observable color change in a closed, stirred (batch) system. We have investigated the effects of adding a wide variety of redox indicators, including diphenylamine derivatives, azo dyestuffs, triphenylmethane derivatives, diimine chelate complexes, and methylene blue to UBO's. We find that in many cases the indicators make the batch oscillations strikingly visible and also allow observation of spatial pattern formation (concentric rings and spirals) in a thin, unstirred layer of solution. In some systems, the indicators act merely to make visible changes in redox potential, while in others they play an active role in the chemistry, and added indicator can lengthen the duration of oscillations or regenerate oscillations or patterns once this behavior has ceased.

## 1. Introduction

Among the numerous oscillatory chemical reactions discovered to date, only a handful have been shown to form moving and/or stationary spatial structures in an undisturbed thin layer of solution. Spontaneous pattern formation has been observed in several bromate oscillators as well as in systems in which iodine appears as an intermediate. Propagating chemical waves and spirals have been found in the Belousov–Zhabotinsky (BZ) reaction ( $\text{BrO}_3^-$ –malonic acid–catalyst),<sup>1</sup> in some uncatalyzed bromate–substrate (UBO) systems,<sup>2</sup> in the bromate–cyclohexanedione (CHD)–ferroin reaction,<sup>3</sup> in the Briggs–Rauscher reaction,<sup>4</sup> and in the  $\text{ClO}_2^-$ – $\text{I}^-$ –malonic acid–starch (CIMA) system.<sup>5</sup>

Waves and spirals can occur either in batch (Petri dish) or in an open reactor configuration.<sup>6</sup> Stationary (Turing) reaction–diffusion patterns are much rarer and have been observed to date only in the CIMA and related reactions<sup>7</sup> and in the methylene blue (MBO) oscillator.<sup>8</sup>

Pattern formation in the above examples can be observed by the following means: (i) If the model system is a BZ-type oscillator, the difference in light absorption between the oxidized and reduced forms of the catalyst can be observed either visually (for ferriin/ferroin and  $\text{Ru}^{\text{III}}\text{bpy}/\text{Ru}^{\text{II}}\text{bpy}$ ), or instrumentally (for  $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$  and  $\text{Mn}^{\text{III}}/\text{Mn}^{\text{II}}$ ). (ii) In some UBO systems with

phenol or aniline derivatives as substrates, intensely colored intermediates form periodically during the reaction, allowing visual observation of the structure.<sup>2</sup> (iii) It is sometimes possible to find an appropriate indicator sensitive to the concentration of an intermediate. In the CIMA<sup>5</sup> and Briggs–Rauscher<sup>4</sup> systems, for example, starch is added to indicate the spatial distribution of iodine.

There are several systems that oscillate under batch conditions and are therefore excellent candidates to show pattern formation in thin layers of solution, but which do not contain colored species that would satisfy conditions i and ii for making any spatial structure visible.

In this paper we investigate the application of several new redox indicators for visualizing batch oscillations and patterns developed in excitable or oscillatory bromate systems in which these phenomena would remain invisible in the absence of indicators. We focus primarily on CHD as a substrate, although we examine a variety of other reagents as well to broaden as much as possible the range of systems for which visual observations are feasible. We also seek to clarify whether the added redox indicators act as true indicators, which function only to make visible the batch oscillations and reaction–diffusion patterns, or whether they play a dual role like the BZ catalysts ferroin or ruthenium(II) bipyridyl by inducing bulk oscillations, excitability, and/or pattern formation, i.e., by significantly affecting the chemistry of the system.

## 2. Experimental Section

**Materials. Stock Solutions.** The following stock solutions were prepared:  $\text{NaBrO}_3$  (Janssen Chimica, 99+%), 1 M, dissolved in distilled water;  $\text{NaBr}$  (Fisher, Certified), 0.2 M, dissolved in distilled water; sulfuric acid (Fisher), 1–10.0 M; 1,4-cyclohexanedione (CHD) (Aldrich, 98%), 0.3 M, dissolved in 1 M  $\text{H}_2\text{SO}_4$  by stirring the solution on a hot plate (40–50 °C) for about 30 min.

**Substrates.** In addition to CHD, described above, pyrogallol (Reanal), gallic acid (Aldrich), hydroxybenzenesulfonic acid (Reanal), and *p*-sulfosalicylic acid (Reanal) were measured by weight for each run and dissolved in a reaction mixture containing no bromate.

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**Indicators.** Stock solutions were prepared, which could be stored and used for several months. For each of the stock solutions, we list the solvent, the standard redox potential ( $E^\circ$ ) and the color of the oxidized and reduced forms: diphenylamine (DPA) (Aldrich), 0.02 M, dissolved in hot 5 M  $\text{H}_2\text{SO}_4$  ( $E^\circ = 0.76$  V, dark blue  $\{\lambda_{\text{max}} = 565$  nm} and colorless); diphenylamine sulfate (Aldrich), 0.02 M, dissolved in hot 5 M  $\text{H}_2\text{SO}_4$  ( $E^\circ$  and colors as for DPA); diphenylamine-4-sulfonic acid sodium salt (Fluka), 0.02 M, dissolved in distilled water ( $E^\circ = 0.85$  V, dark purple and colorless); 2,2'-iminodibenzoic acid (Aldrich), saturated in hot  $\text{H}_2\text{SO}_4$ , filtered on glass wool ( $E^\circ = 0.88$  V, dark blue/black and colorless); chrysoidine hydrochloride (Matheson Coleman & Bell), 0.01 M, dissolved in distilled water ( $E^\circ = 0.7$  V, red and yellow); *p*-ethoxychrysoidine (Reanal), 0.01 M, dissolved in hot 5 M  $\text{H}_2\text{SO}_4$  ( $E^\circ = 1.0$  V, red and yellow); erioglaucine A (Matheson Coleman & Bell), 0.01 M, dissolved in distilled water ( $E^\circ = 1.0$  V, pink and dark blue);  $\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O}$  (Aldrich), 0.01 M, dissolved in distilled water ( $E^\circ = 1.2$  V, orange-red and pale green); ferroin (prepared from 1,10-phenanthroline and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), 0.025 M in water ( $E^\circ = 1.06$  V, blue and orange-red); methylene blue (Fisher) 0.01 M, dissolved in distilled water ( $E^\circ = 0.54$  V, violet and colorless).

**Procedures and Apparatus.** Batch experiments with bromate-CHD-indicator and bromate-aromatic substrate-indicator systems were performed in a thermostated ( $T = 25$  °C) vessel equipped with a Pt vs  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$  electrode pair, and the change in potential of the Pt electrode was monitored with constant stirring with a chart recorder.

For studying wave formation and propagation, a mixture with an oscillatory composition was prepared in a beaker. When the system approached the oscillatory regime, a portion was removed, mixed with indicator and spread in a thin layer in a glass or a plastic Petri dish (10, 7, 6 cm i.d.) or, in some experiments, between a pair of glass plates to prevent contact with air. The thickness of the layer varied between 0.5 and 2.0 mm.

The stability of the oxidized form of each indicator with respect to oxidation by bromate was studied by following the spectrum of an indicator-bromate-acid mixture vs time using a diode-array spectrophotometer.

### 3. Results

As our prototype system we selected the uncatalyzed bromate-CHD oscillator. This system is capable of oscillations in batch for an extended period of time without generating either a precipitate or bubbles. As is the case in most UBO systems, the oscillations in this reaction cannot be seen and are typically observed potentiometrically. Thus, if a two-dimensional structure develops, it cannot be followed by eye. These features make the  $\text{BrO}_3^-$ -CHD system ideal for testing the behavior of our redox indicators in batch and in unstirred layer configurations. The dynamical behavior of the indicator-free  $\text{BrO}_3^-$ -CHD reaction, its skeleton mechanism, and the effects of added ferroin on the system have been described earlier.<sup>10</sup> We begin our present analysis by examining several  $\text{BrO}_3^-$ -CHD-redox indicator mixtures. We then consider systems in which phenol and aniline derivatives react with bromate and the structure formation is made visible by a variety of redox indicators.

**3.1.  $\text{BrO}_3^-$ -CHD-Redox Indicator Systems.** Hundreds of indicators have been used in redox titrimetry,<sup>11</sup> but only a few appear suitable for indicating oscillations and pattern formation in our model system. For the purpose of observing sustained dynamical behavior like oscillations and pattern formation in chemical systems we seek indicators having the following properties: (i) stability, i.e., the oxidized indicator is resistant to destruction by excess oxidant; (ii) good reversibility; (iii) readily visible color difference between the oxidized and

reduced forms; (iv) reasonable solubility in aqueous mixtures; (v) appropriate transition potential, i.e.,  $E^\circ$  should fall within the range of the potential oscillations.

We have identified several members of each major indicator group that satisfy the above criteria. The major groups and representative examples of suitable indicators in each group are: (1) Diphenylamine series, diphenylamine base, diphenylamine sulfate salt, diphenylamine-4-sulfonic acid sodium salt, and 2,2'-iminodibenzoic acid; (2) azo dyestuffs, chrysoidine hydrochloride and *p*-ethoxychrysoidine; (3) triphenylmethane derivatives, erioglaucine A; (4) diimine chelate complexes, ferroin and ruthenium(II) bipyridine; and (5) specific action indicators, methylene blue.

**3.1.1.  $\text{BrO}_3^-$ -CHD-Diphenylamine (DPA) System.** **Batch.** The  $\text{BrO}_3^-$ -CHD batch oscillatory system remains yellow during the course of potential oscillations<sup>10</sup> as a result of bromine, oxidation and/or bromination products of CHD, which are produced during the course of the reaction. Adding a few drops of DPA to the oscillating mixture immediately results in color oscillations between dark blue and yellow. The DPA has little effect on the frequency, but the amplitude of the potential oscillations increases significantly. After 10–15 cycles the blue color gradually fades away and the amplitude of the potential oscillations slowly decreases to its original value. A further addition of DPA makes the color changes visible again.

In one set of experiments with an initial composition of  $[\text{NaBrO}_3] = 0.2$  M,  $[\text{NaBr}] = 0.02$  M,  $[\text{CHD}] = 0.15$  M, and  $[\text{H}_2\text{SO}_4] = 0.3$  M, potential oscillations with increasing amplitude started after an induction period of 52 min (period = 35–40 s). When DPA was introduced during the induction period, the yellow mixture turned blue, but this color gradually faded away (the oxidized form decayed) without any oscillations. When  $5 \times 10^{-5}$  to  $1 \times 10^{-4}$  M DPA was added to a solution that was already oscillating, intense color changes between deep blue and yellow were visible for 8–10 min. When the blue color faded and finally vanished (the potential oscillations continued), the color oscillations could be revived several times by further additions of DPA. Finally, the accumulated oxidation/bromination products of DPA appeared as a precipitate.

In addition to making potential oscillations visible in the  $\text{BrO}_3^-$ -CHD reaction, DPA can restore oscillatory behavior in systems in which oscillations have ceased. This phenomenon, termed consecutive oscillations,<sup>12</sup> was first observed in uncatalyzed bromate oscillators when BZ catalysts were added to the exhausted UBO reaction mixtures.

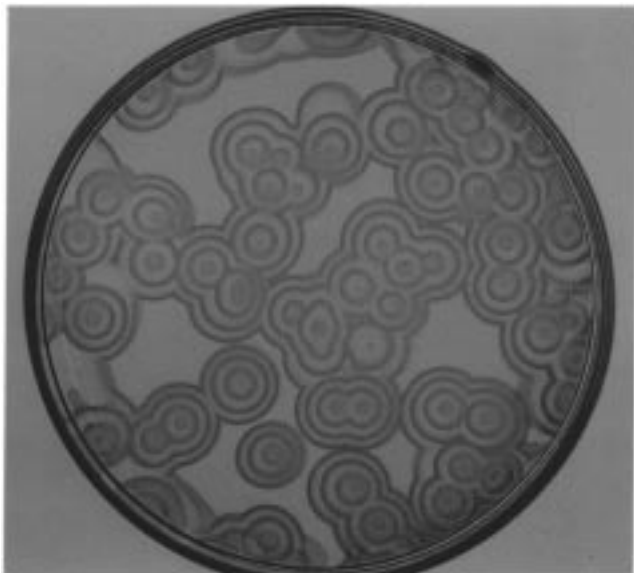
The  $\text{BrO}_3^-$ -CHD-DPA batch oscillator is sensitive to stirring, while the DPA-free system is not. Sufficiently rapid mechanical stirring can even suppress the oscillations in the reaction mixture containing DPA.

**Layer.** If an oscillating  $\text{BrO}_3^-$ -CHD mixture is poured into a Petri dish to form a 0.5–2.0 mm thick layer, no pattern formation is observed. When DPA is introduced, the solution layer becomes dark blue and then turns to yellow, and after a few minutes a striking structure consisting of sharp, regular blue rings emerges in a lemon-yellow environment. Figure 1 shows a fully developed two-dimensional pattern. The evolution of the structure takes much longer than the lifetime of the color oscillations in batch. When the structure starts to fade (after 10–15 min), the solution becomes yellow. If the solution is mixed by swirling the dish, the layer turns blue again, and a new structure develops. This procedure can be repeated 3–5 times until all the DPA is consumed. Adding a few drops of DPA solution to the mixture causes the structure to reappear.

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**Figure 1.** Pattern formation in the  $\text{BrO}_3^-$ -1,4-cyclohexanedione (CHD)-diphenylamine (DPA) system. Initial concentrations (in M):  $\text{NaBrO}_3$ , 0.2; CHD, 0.15;  $\text{H}_2\text{SO}_4$ , 0.3;  $\text{NaBr}$ , 0.02; DPA,  $10^{-4}$ .

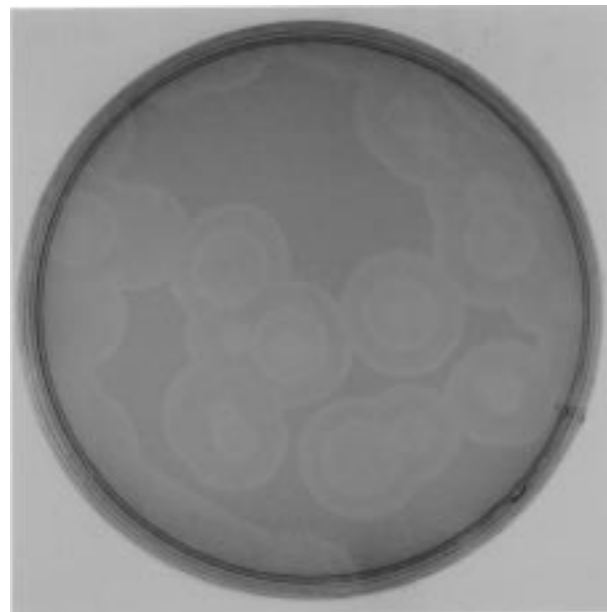
Multiple applications of DPA make it possible to regenerate and maintain the pattern for at least 1 h. By breaking the rings physically, one can produce spirals.

The optimal composition for generating these patterns is  $[\text{BrO}_3^-] = 0.2 \text{ M}$ ,  $[\text{Br}^-] = 0.02 \text{ M}$ ,  $[\text{CHD}] = 0.15 \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.3\text{--}2.0 \text{ M}$ ,  $[\text{DPA}] = 10^{-(4-3)} \times 10^{-4} \text{ M}$  (2–5 drops of stock solution added to a mixture of  $10 \text{ cm}^3$ ). Higher acid concentrations (2.0 M) accelerate the pattern evolution, resulting in short-lived structures with relatively short wavelengths. A sulfuric acid concentration of 0.3 M yields excellent patterns that last for about 30 min with a wavelength of 3–4 mm. Spiral formation is easily produced with this composition.

The  $\text{BrO}_3^-$ -CHD-DPA patterns are quite sensitive to visible light. Illumination can cause the blue rings to break, the speed of propagation to increase, or the structure to vanish, depending upon the intensity. Work on this subject is in progress in our laboratories; preliminary results are reported in ref 13.

**3.1.2.  $\text{BrO}_3^-$ -CHD-Diphenylamine Derivatives.** We also tested several derivatives of DPA in the  $\text{BrO}_3^-$ -CHD system. These species differ from DPA in redox potential, color, stability, and solubility, offering the possibility of differences in the spatial behavior that they produce. In general, except for differences in the color of the patterns produced, the derivatives behaved much like the prototype DPA, although the patterns persisted for a shorter time. The behavior of the diphenylamine sulfate salt of DPA is essentially identical with that of the parent compound. Diphenylamine-4-sulfonic acid sodium salt gives an attractive purple-yellow pattern. The oxidized form of 2,2'-iminodibenzoic acid is nearly black (very dark blue), and the structure is much less well-defined than the patterns observed with other derivatives.

**3.1.3.  $\text{BrO}_3^-$ -CHD-Azo Dye Dye Compounds.** Among the azo dye indicators, chrysoidine hydrochloride and *p*-ethoxychrysoidine proved useful to make visible batch oscillations and pattern formation. There were two major differences between the azo dyes and the DPA derivatives. In batch, the chrysoidines only indicated the oscillations, but they were incapable of reviving oscillation once it had terminated, i.e.,



**Figure 2.** Pattern formation in the  $\text{BrO}_3^-$ -CHD-chrysoidine (Chrys) system. Initial concentrations (in M):  $\text{NaBrO}_3$ , 0.2; CHD, 0.15;  $\text{H}_2\text{SO}_4$ , 0.5;  $\text{NaBr}$ , 0.02; Chrys,  $5 \times 10^{-4}$ .

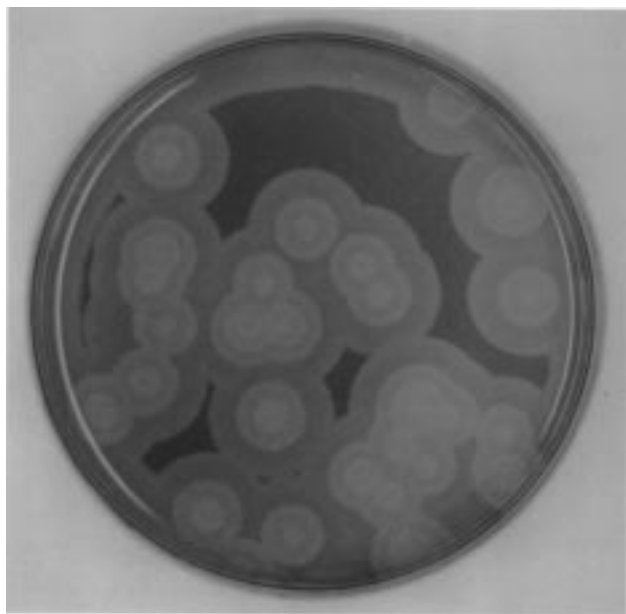
consecutive oscillation was not observed. Because the azo compounds decompose much faster than DPA, the structures persist for much shorter times. Adding chrysoidines to an oscillating  $\text{BrO}_3^-$ -CHD solution in a Petri dish yields pink concentric rings expanding against a reddish background. These structures can be renewed 2–3 times by new additions of the indicator after the color fades. We recommend a composition of  $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$ ,  $[\text{Chrys}] = (5\text{--}8) \times 10^{-4} \text{ M}$  with  $[\text{BrO}_3^-]$ ,  $[\text{CHD}]$ , and  $[\text{Br}^-]$  at the same values as in the DPA system. Figure 2 shows a pattern in one of these systems.

**3.1.4.  $\text{BrO}_3^-$ -CHD-Triphenylmethane Group.** In this group of indicators, erioglaucine at relatively high concentrations ( $1 \times 10^{-3}$  to  $2.5 \times 10^{-3} \text{ M}$ ) yields clearly visible patterns. When the indicator is added to an oscillatory or excitable  $\text{BrO}_3^-$ -CHD mixture, a yellowish-pink oxidized product develops in a few seconds. The solution then gradually turns to dark green. In a Petri dish, yellowish rings develop slowly in this green environment (Figure 3) with a wavelength that depends on the concentration of acid. With  $[\text{H}_2\text{SO}_4] = 0.5 \text{ M}$ ,  $\lambda = 4\text{--}5 \text{ mm}$ . As in the case of DPA, once the structure disappears it can be regenerated 3–4 times by adding more of the indicator.

**3.1.5.  $\text{BrO}_3^-$ -CHD-Diimine Chelate Complexes.** The best known members of this indicator group are the ferroin and Ru(II) bipyridyl complexes. Ferroin is known to act as a catalyst similar to DPA and to indicate many kinds of pattern formation in the  $\text{BrO}_3^-$ -CHD system.<sup>10</sup> The ferroin/ferriin couple possesses the greatest stability and the highest degree of reversibility among the indicators used in this work. A single addition of ferroin suffices to indicate very long lasting (1 h or more) oscillations and structures in the  $\text{BrO}_3^-$ -CHD system. In our experiments, the Ru(bipy) complex gives patterns very similar to those obtained with ferroin, only the colors in the structure are different (orange red–pale green instead of red–blue).

**3.1.6.  $\text{BrO}_3^-$ -CHD-Specific Action Indicators.** Surprisingly, methylene blue, a thiazine-type indicator, is also able to make visible the pattern formation. This compound has an  $E^\circ$  of 0.53 V, the lowest among the indicators we used. Because of this low  $E^\circ$  value, methylene blue is used in redoxometric titrimetry, while the other indicators discussed here are employed in oxidimetry. The spatial pattern in the  $\text{BrO}_3^-$ -CHD-

(13) Kurin-Csörgei, K.; Zhabotinsky, A. M.; Orbán, M.; Epstein, I. R. *J. Phys. Chem. A* **1997**, *101*, 6827.



**Figure 3.** Pattern formation in the  $\text{BrO}_3^-$ -CHD-eriolglucine (Eriogl) system. Initial concentrations (in M):  $\text{NaBrO}_3$ , 0.2; CHD, 0.15;  $\text{H}_2\text{SO}_4$ , 0.5; NaBr, 0.02; Eriogl,  $2 \times 10^{-3}$ .

methylene blue system is rather difficult to see, with pale gray rings developing on a darker gray background.

**3.2. Stability of the Indicators.** The stability of the indicators characterized in terms of the decay rate of their oxidized form, depends upon many factors, including the concentration of acid (the rate of decay decreases as the sulfuric acid concentration increases), the excess of bromate, and the nature of the substituent(s) on the aromatic ring(s) in their chemical structure (sulfonation produces a marked decrease in stability).<sup>14</sup>

To estimate the decay rate, we followed the decrease of light absorbance at 10-min intervals at  $\lambda_{\text{max}}$  in a mixture containing each of our indicators with sulfuric acid and bromate in high excess. We use the half-life ( $t_{1/2}$ ), during which the light absorbance decreases to half its initial value as a qualitative measure of stability. For the diphenylamine series,  $t_{1/2}$  was found to be 70 min for diphenylamine base, 70 min for diphenylamine sulfate salt, 40 min for 2,2'-iminodibenzoic acid, and 20 min for diphenylamine-4-sulfonic acid sodium salt. Thus we have the following sequence of stabilities:  $\text{DPA} \approx (\text{DPA})_2 \cdot \text{H}_2\text{SO}_4 > \text{DPA}-2,2'\text{-DCA} > \text{DPA} \cdot \text{SO}_3\text{Na}$ . This sequence of stabilities is consistent with the observed durations of the visibility of bulk oscillations and spatial patterns in the presence of these indicators.

The measured decay rate of the oxidized form of the indicators alone would suggest a longer lasting visibility of the oscillations and patterns than we observed in the  $\text{BrO}_3^-$ -CHD-indicator systems. The shorter duration of these phenomena in our experiments may arise from several sources, such as formation of bromine, which can oxidize and brominate the indicator, the unknown effects of oxygen, which may influence the behavior of the intensely stirred batch reaction, and reactions between intermediates and the indicators.

**3.3.  $\text{BrO}_3^-$ -Aromatic Substrate-Redox Indicator Systems.** In some UBO's, batch color oscillations (with pyrogallol or gallic acid as substrate<sup>15</sup>) and pattern formation in a thin layer (with pyrogallol, aniline, (2,4-diaminophenyl)phenylamine, or

4-aminobenzenesulfonic acid as substrate<sup>2</sup>) can be seen without adding any indicator or BZ catalyst. In these systems, the periodic formation of highly colored semiquinones is thought to be responsible for the visibility of the phenomena. We investigated several UBO-type systems in which the oscillations and pattern formation would not be visible in the absence of indicators. The indicators we tested were the same compounds used in the  $\text{BrO}_3^-$ -CHD system. The aromatic compounds we employed successfully were pyrogallol, gallic acid, hydroxybenzenesulfonic acid, *p*-sulfosalicylic acid, and 2-bromophenol. Several of these substrates and indicators yielded much sharper and longer lasting color changes than in the systems previously described in refs 2 and 15.

**3.3.1.  $\text{BrO}_3^-$ -Pyrogallol (PG)-Redox Indicator Systems.** Mixtures of bromate and pyrogallol have previously been reported<sup>2,15</sup> to exhibit oscillations in potential and barely visible color changes between light brown and dark brown as well as traveling chemical waves (yellowish brown concentric rings in a somewhat darker brown layer).

Adding indicators such as ferroin, DPA, *p*-ethoxychrysoidine, and eriolglucine to oscillating bromate-pyrogallol solutions yielded dramatic improvements in the visibility of the color changes and in the duration of the oscillations in both the batch and Petri dish configurations. We compared the effects of the indicators at a composition of  $[\text{BrO}_3^-] = 0.087 \text{ M}$ ,  $[\text{PG}] = 0.052 \text{ M}$ , and  $[\text{H}_2\text{SO}_4] = 2.0 \text{ M}$ , which in the absence of indicator gives five oscillations in batch immediately after mixing the components and a short-lived (10 min) pattern in a thin layer.

Three drops of the DPA stock solution generate consecutive oscillations accompanied by blue-yellow color changes and long-lasting structures with sharp boundaries and good visibility. As in the  $\text{BrO}_3^-$ -CHD system, the structures can be revived many times after fading by adding a few more drops of the DPA stock solution. Ferroin produces similar effects, i.e., consecutive oscillations and sustained blue-red spatial structures for nearly 1 h. Because ferroin is so stable, it need not be added more than once to the  $\text{BrO}_3^-$ -PG- $\text{H}_2\text{SO}_4$  system. *p*-Ethoxychrysoidine unexpectedly yields only a very weak color oscillation and no visible structure in a thin layer. The effects of eriolglucine are similar to those of DPA, but significantly more eriolglucine (15–20 drops) is needed to provide good visibility. Figure 4 shows the traveling wave patterns with added DPA.

**3.3.2. Experiments with Other Substrates.** Gallic acid as substrate resulted in qualitatively the same behavior as found with pyrogallol. Two other substrates, sulfosalicylic acid (SSA) and hydroxybenzenesulfonic acid (PSA), merit discussion because these substrates have not been employed previously in UBOs and because their brominated intermediates are quite soluble as a result of the highly hydrophilic sulfo group in the aromatic ring, thereby offering the prospect of longer lasting spatial patterns.

In batch, at a composition of  $[\text{BrO}_3^-] = 0.1 \text{ M}$ ,  $[\text{SSA}] = 0.03 \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 2.0 \text{ M}$ , we observed, after an induction period of 1 h, about 30 oscillations lasting nearly 40 min, with first increasing, and then decreasing, amplitude. Adding 0.01 M NaBr to the original composition resulted in a much shorter ( $\approx 20$  min) induction period and a much longer lasting and more regular oscillatory regime, with more than 100 oscillations persisting for over 2 h. Mixing this prebrominated SSA- $\text{BrO}_3^-$  oscillatory solution with DPA or ferroin yielded easily visible, long-lasting spatial structures.

Hydroxybenzenesulfonic acid proved disappointing as a substrate. With  $[\text{BrO}_3^-] = 0.1 \text{ M}$ ,  $[\text{PSA}] = 0.043 \text{ M}$ ,  $[\text{H}_2\text{SO}_4] = 0.1 \text{ M}$ , 25 oscillations were recorded in batch after a 20-min

(14) Reference 11, p 595.

(15) Körös, E.; Orbán, M. *Nature* **1978**, 273, 371.



**Figure 4.** Pattern formation in the  $\text{BrO}_3^-$ -pyrogallol (PG)-DPA system. Initial concentrations (in M):  $\text{NaBrO}_3$ , 0.0877; PG, 0.052;  $\text{H}_2\text{SO}_4$ , 2.0; DPA  $1.0 \times 10^{-4}$ .

induction period, but a composition modified with  $[\text{NaBr}] = 0.01$  M resulted in precipitation and very poor quality oscillations. DPA, ferroin, and erioglaurine indicated the presence of waves in a layer of the oscillatory mixture, but precipitation occurred both with and without the prebrominated substrate. Similar (poor) results were obtained in a Petri dish when the oscillatory reaction between 2-bromophenol and bromate was tested with indicators.

#### 4. Discussion

Batch oscillators often give rise to two-dimensional pattern formation at compositions falling within or just outside the oscillatory regime, but an unambiguous general relation between batch oscillation and pattern formation has not been established. For example, in the  $\text{H}_2\text{O}_2$ -KSCN- $\text{Cu}^{\text{II}}$ -NaOH,<sup>16</sup> and  $\text{BrO}_3^-$ -phenol<sup>17</sup> oscillators no waves or spirals have been observed to date, either because of the lack of an appropriate detection method or because structure formation does not occur. We have demonstrated here that with carefully chosen indicators, spatial structures can be visualized in many systems in which oscillations could previously only be followed instrumentally and pattern formation could not be observed at all. These examples offer support for the notion that any system that oscillates in batch should be capable of generating spatial structures in an unstirred layer.

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In the BZ oscillators, the catalyst (typically ferroin or cerium(IV)) does not act only as an indicator of the periodic change in the concentrations of the intermediates (i.e., of the change in the redox potential). The catalyst's presence is also essential for the oscillations and/or pattern evolution to occur, because of its active participation in the key steps of autocatalytic  $\text{HBrO}_2$  formation and regeneration of the control intermediate  $\text{Br}^-$ .

The role of some of the indicators added to the UBO systems appears to be different. Depending on the mechanism by which they change color, some compounds serve only to indicate the change in redox potential, while others function also as catalysts such as the redox couples in the BZ system. For example, the chrysooidines and the methylene blue only indicate by color changes the oscillations and pattern formation, but they cannot revive the oscillations and do not induce structure evolution in an exhausted UBO system. On the other hand, diphenylamine and its derivatives, erioglaurine, the diimine chelate group, not only serve as indicators, but act as catalysts as well. These compounds are able to bring about new oscillations after the oscillations have terminated in an indicator-free reaction mixture, and structure evolution in an exhausted UBO systems resumes after addition of these indicators. By analogy with consecutive oscillations,<sup>12</sup> the phenomenon of repetitive structure formation in a solution layer by addition of more indicator may be termed consecutive pattern formation.

The mechanism of the UBO systems is not as well understood as that of the BZ reaction. There should, however, be many similarities, at least in the chemistry of the oxy bromine species. The presence of a one-electron redox couple, the BZ catalyst, is an absolute requirement for a BZ-type oscillator, since the reaction between  $\text{BrO}_2^*$  radical and the reduced form of the catalyst is a crucial step in the mechanism. In a UBO with added indicator, a semiquinone, formed by the interaction between the oxidized and reduced forms of the indicator, may play a role similar to that of a BZ catalyst. DPA, for example, is first oxidized by bromate to diphenylbenzidine (DPB) in an irreversible step. The DPB is then reversibly oxidized to a deeply colored diquinone diimine commonly known as diphenylbenzidine violet (DPBV). A semiquinone-like 1:1 molecular complex between DPB and DPBV can easily be formed and may act like a BZ catalyst. This scheme suggests that UBO systems in the presence of certain indicators (e.g., the diphenylamine series) may be regarded as BZ-type oscillators with regard to both their mechanism and their dynamical behavior.

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