Stationary and Moving Structures in Uncatalyzed Oscillatory Chemical Reactions[1]

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Abstract: Trigger waves, mosaic, and transient striped patterns have been observed in a variety of aromatics, bromate, and sulfuric acid unstirred systems. The aromatics investigated so far include 1,2,3-trihydroxybenzenes, aniline, 2,4-diaminodiphenylamine, 4-aminobenzenesulfonic acid, and phenol.

Introduction

In oscillatory chemical systems the concentration in time of several intermediates shows nonmonotonic behavior. Temporal bulk oscillations are established when the solution is well stirred; concentration inhomogeneities in space may develop in unstirred systems resulting in a variety of structures.

Zaikin and Zhabotinsky[2] and Winfree[3] have been the first who experienced the development of chemical waves in a system composed of bromate, malonic acid, bromomalonic acid, sulfuric acid, and ferroin when spread in a thin layer. Field and Noyes[4,5] explained the appearance of this waves in terms of the FKN mechanism[6] by showing that the propagation of chemical waves is the result of reactions responsible for temporal oscillation coupled with diffusion. Chemical waves are observable when tris(dipyridine)ruthenium(II),[7,8] -cerium(III),[9] or -manganese(II)[10] is used instead of ferroin. Field and Noyes[6] measured the velocity of trigger-wave propagation and established a relationship between velocity and the chemical composition of the system. Showalter and Noyes[11] reported a deliberate generation of trigger waves by placing a small crystal of silver nitrate or inserting a polarized silver wire into the reaction mixture. Reusser and Field[12] modeled numerically the propagation mechanism and authors reported on the transition from phase waves to trigger waves.

Zhabotinsky and Zaikin[13] observed the existence of "small-cell structure" in two-dimensional systems. In the 1,4-pentanedione, bromate, ferroin, and sulfuric acid system these authors experienced that the transition of catalyst from reduced to oxidized state was accompanied by the appearance and gradual disappearance of spatially organized nonuniformities. Spontaneous pattern formation in acidic bromate oxidation of ferroin was observed by Showalter.[14] In malonic acid, bromate, ferroin, and sulfuric acid system with the composition suggested by Winfree[3] mosaic structure can also appear. When this solution is just before termination in producing chemical waves (about 100 min after starting the reaction) a mosaic pattern existing for a couple of minutes replaces the wave structure.

Many aromatic compounds react with acid bromate in an oscillatory manner even in the absence of a catalyst, and the conditions for temporal oscillation have been described in some recent papers.[15,16] We observed also the occurrence of different types of spatial inhomogeneities in unstirred aromatics-bromate-acid reacting systems. These include both propagating chemical waves and different stationary structures. Here we report on a series of experiments directed to gather information on these phenomena.

Experimental Section

All reagents were of analytical grade (Merck and Reanal) with the exception of 2,4-diaminodiphenylamine (Eastman-Kodak), and have been used without further purification.

The stock solutions were as follows: 10 M sulfuric acid, 0.5 M sodium bromate, 1 M 1,2,3-trihydroxybenzene (THB), 0.1 M aniline (in 0.1 M sulfuric acid), 0.05 M 4-aminobenzenesulfonic acid, 0.05 M 2,4-diaminodiphenylamine (in 0.5 M sulfuric acid), 0.1 M phenol. All stock solutions were thoroughly filtered.

The experiments were performed at a temperature of 24-25 °C by mixing the reagents and layering in a Petri dish of 95-mm diameter.

The optimal concentrations and other characteristics of the different spatial oscillatory systems are given in Table I.

The photographs were taken using a 13 DIN black and white Orwo film. The chemical waves in the THB-acid bromate system were poorly visible on the photographs; the black and white enlargement was printed from a 17 DIN Orwo color diapositive.

Results

In the aromatics-acid bromate systems under strict experimental conditions three types of spatial structures were observable in a thin unstirred layer: trigger waves, mosaic structures, and transient striped structures.

Trigger waves evolve, e.g., with 1,2,3-trihydroxybenzene, aniline, 2,4-diaminodiphenylamine, and 4-aminobenzenesulfonic acid, respectively, as aromatics. The waves propagate with a velocity of about a few millimeters per minute. In most cases the optimal chemical composition for the formation of waves (for two-dimensional excitability) differs from that proper for temporal oscillation in a stirred solution. However, there are systems where temporal oscillation and the development of spatial structure occur at the same chemical composition. This is the reason why sometimes during wave propagation bulk oscillation (periodic color change) can also be viewed.

Chemical waves realized with uncatalyzed bromate oscillators start to propagate from many pacemaker centers, and the number of waves from a single center is less than in the Belousov-Zhabotinsky (BZ) systems. The "lifetime" of the whole phenomenon is also much shorter. The development of waves is not disturbed by gas evolution; however, with many systems precipitate formation can be experienced. Besides concentric circles spiral structures also appeared with 2,4-diaminodiphenylamine substrate.

The catalysts used in Belousov-Zhabotinsky reaction either promote the development of the chemical waves or are ineffective throughout. If the system is still capable of consecutive oscillation[17] (i.e., adding a BZ catalyst to the uncatalyzed reacting system after termination of oscillation, the catalyst can reinitiate the oscillation with much enhanced amplitude) the presence of a catalyst makes the contours of the chemical waves more clear and pronounced than they exhibit themselves in the absence of the catalyst.

The addition of a crystal of silver nitrate generates trigger

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Table I. Optimum Concentrations, Color Changes during the Course of the Reaction, Thickness of the Layer, and Other Remarks on Some Chemical Systems Exhibiting Traveling and Stationary Structures

substrate	optimum concn	color change during the reaction	thickness of the layer and other characteristics of the spatial structure
aniline	2.2 M H_2SO_4 0.055 M $NaBrO_3$ 0.022 M aniline	blue, 6-7 min; yellow wave, yellow solution, 10-12 min; cell-structure, precipitation	<0.07 cm: waves ~0.10 cm: waves + structure ~0.15 cm: structure
1,2,3-trihydroxybenzene	2.0 M H_2SO_4 0.087 M $NaBrO_3$ 0.052 M THB	red-brown, 5 min; abrupt change to yellow through transient structure, darkening, yellow circles in golden-brown solution, clear solution	~0.06 cm: waves wave velocity: 5-6 mm/min
2,4-diaminodiphenylamine	2.2 M H_2SO_4 0.11 M $NaBrO_3$ 0.011 M diamine 0.0005 M Mn(II)	wine red, 1-2 min; spots, 3-4 min; circles in pink solution, 10 min; mosaic structure, precipitation	<0.07 cm: waves ~0.1 cm: waves + structure >0.1 cm: structure wave velocity: 2-3 mm/min
4-aminobenzenesulfonic acid	1.7 M H_2SO_4 0.08 M $NaBrO_3$ 0.026 M substrate	blue, 1 min; grayish-blue, 3 min; abrupt change to yellow through transient structure, darkening, 4 min; yellow circles in grayish-yellow solution, clear solution	0.14 cm, waves, wave velocity: 8-10 mm/min
phenol	2.0 M H_2SO_4 0.05 M $NaBrO_3$ 0.026 M phenol	yellow, 6-8 min; mosaic structure, precipitation	0.10 cm mosaic structure

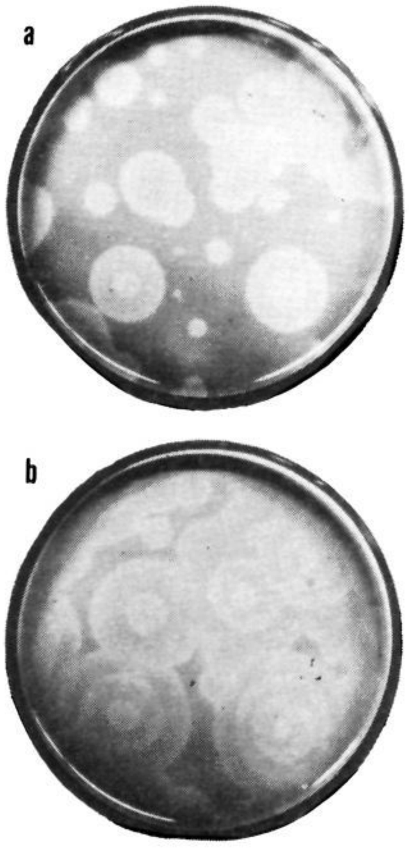

Figure 1. The development of chemical waves in 1,2,3-trihydroxybenzene-acid bromate system. For experimental conditions see Table I.

waves; these waves, however, propagate slower than those starting spontaneously.

In Figure 1 the evolution of chemical waves in the 1,2,3-trihydroxybenzene-acid bromate system is shown in two photographs.

In Figures 2 and 3 photographs of traveling waves are visible for two different aromatics: aniline and 2,4-diaminodiphenylamine.

It is worth noting that in the systems investigated also one-dimensional periodicities (similar to that reported first by Busse[18]) appear. In a glass tube 30 cm long and 1 mm in diameter leading centers formed at the ends and at different sites, and narrow bands moved along the tube with a velocity of a few millimeters per minute.

Stationary structures (mosaic and transient striped) are the other types of inhomogeneity manifesting themselves in the uncatalyzed bromate oscillatory systems. With some aromatics (including phenol, 2-bromophenol, and aniline and 2,4-diaminodiphenylamine in a layer thickness of more than 1 mm) mosaic structures with sharp boundaries arise some minutes after spreading the mixture in a Petri dish. After the structure is disrupted by stirring it emerges again after a few minutes. The boundaries become more and more diffuse in time and finally either the solution turns homogeneous or a precipitate separates. In the bulk the color changes from dark to light monotonically.

Two photographs shown in Figure 4 demonstrate the development of a mosaic structure in the aniline-acid bromate

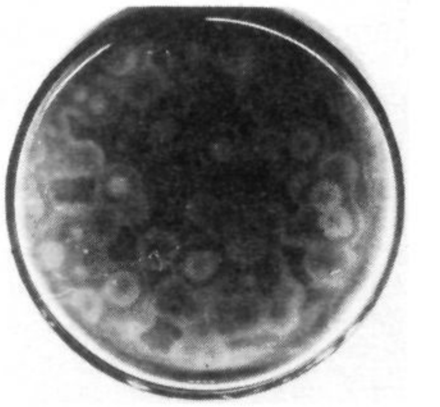

Figure 2. Chemical waves with 2,4-diaminodiphenylamine. For chemical composition see Table I. Thickness of the layer: 0.07 cm.

Figure 3. Chemical waves with aniline. For experimental conditions see Table I. Thickness of the layer: 0.07 cm.

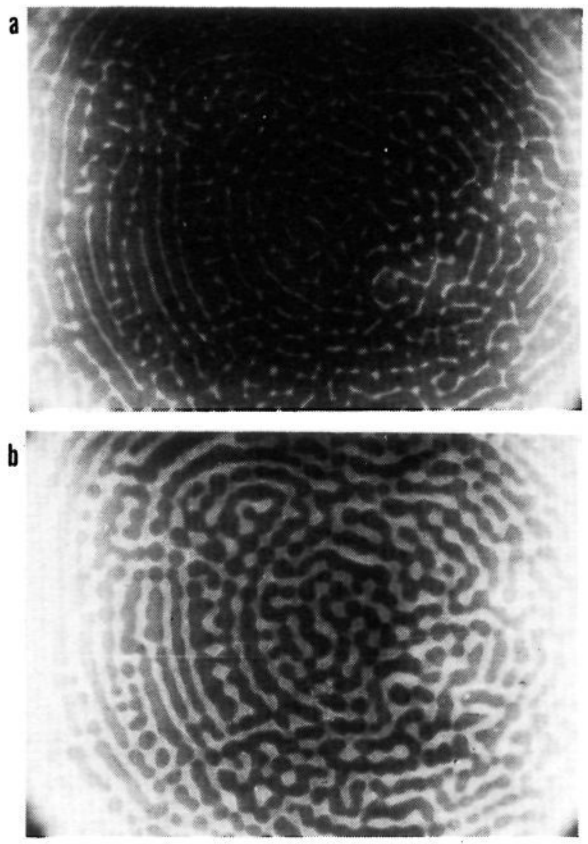

Figure 4. The development of mosaic pattern in aniline-acid bromate system. For chemical composition see Table I. Thickness of the layer: 0.15 cm.

system. The pictures were taken in 9-min intervals. A rather similar pattern formation was observed by Boiteux and Hess in glycolyzing yeast extract.[19]

Trigger waves and mosaic structures can be effectuated with the same aromatics by changing the experimental conditions: the composition of the reaction mixture and the thickness of the layer.

Within a narrow concentration range and at a definite layer thickness trigger waves and mosaic pattern occur simultaneously. This is shown in Figure 5.

Sometimes also striped structures appear and this happens in a certain phase of the events. When, e.g., 4-aminobenzenesulfonic acid is mixed with acid bromate and spread in a Petri dish after a few minutes the grayish-brown solution changes to yellow. Actually a phase wave moves across the solution and along the transition zone a striped structure appears which disappears in a few seconds. This transient structure is shown in Figure 6.

Discussion

The mechanism of trigger-waves propagation can be interpreted analogously as described by Field and Noyes[5] for the Belousov-Zhabotinsky spatial system. In the uncatalyzed bromate oscillators the development of waves is due to the oxidative bromination of aromatics coupled with diffusion.

For explaining the temporal oscillation in the uncatalyzed systems a skeleton mechanism has been proposed recently[20] which resembles that suggested for the metal ion catalyzed bromate oscillators. Here the role of the catalyst is taken over by the aromatics to reduce $BrO_2\cdot$ radical (see reaction K4). The formation of a variety of organic radicals, further quinones, quinone imines, and semiquinones is responsible for the color change during both temporal and spatial oscillations.

When the reagents (aromatics, bromate, and sulfuric acid) are mixed, the solution immediately changes to a dark color (brown, blue, or red—depending on the nature of the aromatics). The intensive color is mainly due to a semiquinone formed in quinone-hydroquinone type interaction. This dark color gradually becomes lighter. At a certain phase of the color change light pacemaker centers appear from which chemical waves start to propagate into a region of darker color. In the dark region the bromide concentration is above $[Br^-]_{critical}$, and here bromate reacts with bromide and the stoichiometry of the reaction is generated by the sequence of (K1) and (K2):

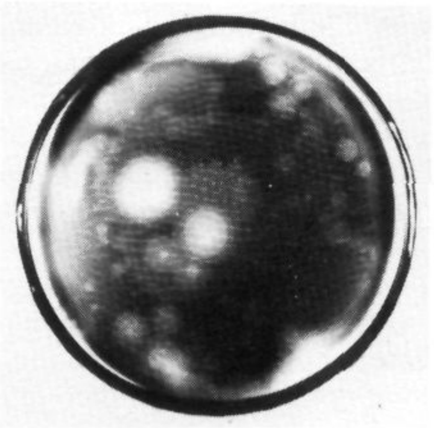

Figure 5. Simultaneous occurrence of chemical waves and mosaic pattern in aniline-acid bromate system. For chemical composition see Table I. Thickness of the layer: 0.10 cm.

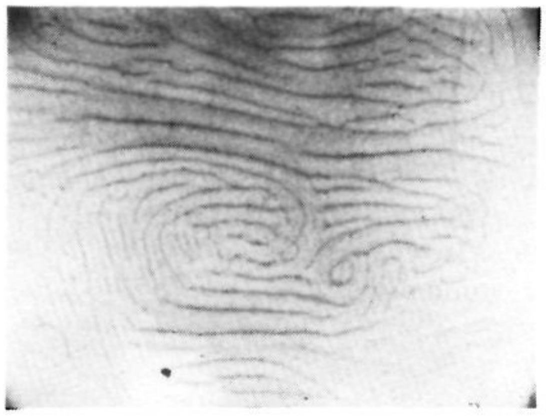

Figure 6. Transient striped structure with 4-aminobenzenesulfonic acid. For experimental conditions see Table I.

$$\mathrm{BrO_3^- + Br^- + 2H^+ \rightleftharpoons HBrO_2 + HOBr} \qquad \text{(K1)}$$

$$\mathrm{HBrO_2 + Br^- + H^+ \rightarrow 2HOBr} \qquad \text{(K2)}$$

$$\mathrm{BrO_3^- + 2Br^- + 3H^+ \rightarrow 3HOBr} \qquad \text{(A)}$$

At the front of the moving band the concentration of bromide ion drops below $[Br^-]_{critical}$. The autocatalytic formation of $HBrO_2$ is switched on, and this is realized by the following sequence of reactions:

$$\mathrm{BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2^{\cdot} + H_2O} \qquad \text{(K3)}$$

$$\mathrm{BrO_2^{\cdot} + HAr(OH)_2}{}^{23} \rightarrow \mathrm{HBrO_2 + HAr(OH)O^{\cdot}} \qquad \text{(K4)}$$

$$\mathrm{2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+} \qquad \text{(K5)}$$

$$\mathrm{BrO_3^- + 4HAr(OH)_2 + H^+ \rightarrow HOBr + 4HAr(OH)O^{\cdot} + 2H_2O} \qquad \text{(B)}$$

At the boundary of the reducing and the oxidizing zone a sharp concentration gradient exists: the bromide concentration is at its minimum and the $HBrO_2$ concentration is at its maximum. Species formed in reaction B undergo further reaction and regenerate bromide ion, the control intermediate in reaction C:

$$\mathrm{HOBr + HAr(OH)O^{\cdot} \rightarrow Br^{\cdot} + HArO_2 + H_2O} \qquad \text{(K6)}$$

$$\mathrm{Br^{\cdot} + HAr(OH)O^{\cdot} \rightarrow Br^- + HArO_2 + H^+} \qquad \text{(K7)}$$

$$\mathrm{HOBr + 2HAr(OH)O^{\cdot} \rightarrow Br^- + 2HArO_2 + H^+ + H_2O} \qquad \text{(C)}$$

By the accumulation of bromide ions process A is switched on again; a new wave can start to propagate from the pacemaker center.

The emergence of mosaic and transient patterns realizable with the uncatalyzed oscillatory chemical reactions awaits exact interpretation. Zhabotinsky and Zaikin[13] suggested that the "small-cell structure" in the Belousov-Zhabotinsky reaction arises from a diffusive instability caused by the inequalities among the diffusion coefficients of several reactants. Wintree[21] is of the opinion that oxygen transport in convective Benard cells is the cause. Our observation unambiguously supports the importance of that kind of hydrodynamic flow in the onset of macroscopic order from a homogeneous solution layer excitable to oscillation. What we actually see as a pattern is the intermediates and/or products of the reaction which exhibit macroscopic order by a slight convective motion. The oxygen mixed by this motion into the liquid layer probably plays a role also in developing the structures. In closed system, i.e., sealing the surface of the layer from an imposed parameter gradient of a convective sort, neither transient nor mosaic structures emerged. When the glass plate was removed from the top of the Petri dish, the pattern appeared. The bringing on and suppressing the structure is possible several times until the reaction proceeds to a certain extent. In light of the above interpretation the dependency of occurrence of mosaic structure on the thickness of the liquid layer can also be understood. Since the development of the mosaic patterns is accompanied in most of the cases by precipitate formation, the theory of periodic precipitation outlined by Flicker and Ross[22] may offer a further contribution to the explanation of these complex phenomena.

The results presented in this paper strongly suggest that chemical waves and/or stationary patterns can be brought about in every chemical reacting system exhibiting temporal oscillation.

Investigations are in progress in order to reveal more about these peculiar phenomena.

References and Notes

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(23) $HAr(OH)_2$ stands for the aromatics in general.

Photoelectron Spectra of the Cyclophanes

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Abstract: The He(Iα) photoelectron spectra of the complete set of cyclophanes have been recorded. It is shown that the band pattern of all these spectra can be rationalized in terms of a simple molecular orbital model which takes "through-space" and "through-bond" interactions between the π orbitals of the upper and lower benzene moieties into account. The "through-space" interaction parameter $\tau(D)$ depends linearly on the mean interdeck distance D, within the range $240\ \text{pm} < D < 340\ \text{pm}$. Severe symmetry restrictions are imposed on the "through-bond" interactions. As a result the lowest ionization energies of the cyclophanes decrease little with increasing number of bridging groups. Correlation of the first four bands of the photoelectron spectra of the cyclophanes supports the previously derived assignment of the spectrum of [2.2](1,4)cyclophane (=paracyclophane): first maximum $^2B_{2g}$, $^2B_{3g}$, $^2B_{3u}$; second maximum $^2B_{2u}$. It is shown that this assignment is supported by the electronic absorption spectra of the paracyclophane radical cation and of the benzene dimer radical cation, the photoelectron spectra of 4,5,7,8-tetramethyl[2.2](1,4)cyclophane, [3.3]paracyclophane, and the Birch reduction product of [2.2.2.2](1,2,4,5)-cyclophane, and the ESR spectra of 4,5,7,8- and 4,5,15,16-tetramethyl[2.2]paracyclophane radical cations.

I. Introduction

The recently reported preparations of [2.2.2.2.2]-(1,2,3,4,5)cyclophane[2a] and of [2.2.2.2.2.2](1,2,3,4,5,6)-cyclophane (="superphane")[2b] terminate the series of cyclophanes shown below, so that all of them are now available for the investigation of their chemical and physical properties. For simplicity the cyclophanes have been labeled **N**(x, y, . . .), where **N** is the number of bridging ethano groups and x, y, . . . are their position, if necessary. The syntheses of the cyclophanes investigated in this work are described in the following references: [2.2](1,4)cyclophane = **2**(1,4);[3] [2.2.2](1,2,3)-cyclophane = **3**(1,2,3);[4] [2.2.2](1,2,4)cyclophane = **3**(1,2,4);[5] [2.2.2](1,3,5)cyclophane = **3**(1,3,5);[6] [2.2.2.2](1,2,3,4)cyclophane = **4**(1,2,3,4);[7a] [2.2.2.2](1,2,3,5)cyclophane = **4**(1,2,3,5);[7b] [2.2.2.2](1,2,4,5)cyclophane = **4**(1,2,4,5);[8] [2.2.2.2.2](1,2,3,4,5)cyclophane = **5**;[2a] [2.2.2.2.2.2]-(1,2,3,4,5,6)cyclophane = **6**.[2b]

In Figures 1 and 2 are presented the He(Iα) photoelectron spectra of the cyclophanes (1), with the exception of **2**(1,2) = 1,2;5,6-dibenzocyclooctane and **2**(1,3) = [2.2]metacyclophane, both of which have "open" exo structures, i.e., at variance with

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