J. Phys. Chem. A **2003,** *107,* 4452−4456

Reaction−Diffusion Patterns of the Chlorite−Tetrathionate System in a Conical Geometry

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Received: October 11, 2002; In Final Form: March 12, 2003

We experimentally study the spatiotemporal reaction−diffusion patterns exhibited by the chlorite−tetrathionate reaction in a conical piece of gel. Since the nonequilibrium states of this reaction−diffusion system depend on the thickness of the gel, one can observe simultaneously such phenomena as spatial bistability, excitability waves, and a monostable state coexisting at different height over the cone. This new geometry allows for the exploration of gel size effects on pattern selection down to smaller dimensions than in previous experiments.

1. Introduction

Spatial and spatiotemporal reaction−diffusion patterns in chemical systems far from thermodynamic equilibrium have been extensively studied and are a major research field in nonlinear science.[1−3] The underlying reaction kinetics is usually extremely complex, and many reactions exhibiting bistability or oscillations in open homogeneous systems are commonly used to produce a wide variety of patterns such as Turing patterns, excitability waves, phase waves, front patterns, etc. Among these, the chlorite−tetrathionate (C−T) reaction, an acid autoactivated reaction, was initially used to study the propagation velocity and morphological instabilities of the activation front in quasi-two- and three-dimensional closed systems.[4−8] Studies of this reaction in open reactors were only recently published by our group.[9,10] In the well-mixed conditions of a continuous stirred tank reactor (CSTR), the reaction only exhibits monostability or bistability between two steady states separated by a pH difference that can be as large as 8 units. In the range of concentrations explored, the dynamics of the reaction can be appropriately described by a single overall rate equation, initially proposed by Nagypál and Epstein.[11] This is consistent with the abscence of oscillatory dynamics in homogeneous open reactor. However, this reaction was recently performed in an open spatial reactor consisting of thin films of gel diffusively fed from one side (called one-side-fed reactor or OSFR), and it exhibited unexpected spatiotemporal dynamics.[9,10] Indeed, beside the now classic phenomenon of spatial bistability, new spatiotemporal instabilities (excitatory and oscillatory) were shown to develop due to "long-range activation", i.e., the fact that a driving activatory species diffuses much faster than other species. This introduces appropriate time scale differences in the exchange rates between the chemicals entering or escaping the spatial reactor. Detailed numerical and experimental evidences for this new source of instability are reported in refs 9 and 10. The experimental studies were performed in an annular shaped OSFR. This reactor consists of a thin flat ring of inert gel set in a CSTR. The outer rim of the ring is in contact with the contents of the CSTR while all other faces are pressed against impermeable walls. The CSTR is continuously fed with fresh reactants, which allows for sustaining nonequilibrium conditions. Reactants and products are exchanged at the solution−gel interface.

The stoichiometry and kinetics of the C−T reaction can be approximated by the following overall balance equation as was proposed by Nagypál and Epstein:[11]

$$7ClO_2^{\,-} + 2S_4O_6^{\,2-} + 6H_2O \rightarrow 7Cl^- + 8SO_4^{\,2-} + 12H^+ \quad (1)$$

with a reaction rate $v = k[ClO_2^-][S_4O_6^{2-}][H^+]^2$.[6,7,11] Due to the quadratic autocatalysis in $[H^+]$ this reaction exhibits "clock" reaction dynamics.[11] The typical behavior of clock reactions is as follows. In batch, they exhibit a more or less long induction period followed by a fast switch to equilibrium. In CSTR, at high flow rate, the residence time is small so the extent of reaction in the tank is small and the concentrations in the tank are close to those in the input premixed flow. The content of the CSTR is in a state belonging to the so-called "flow branch" (branch F). At low flow—or large residence time—the extent of reaction is large; the reaction is almost completed. It is in a state belonging to the so-called "thermodynamic branch" (branch T). In standard reactions, these two branches connect smoothly at intermediate flow values, but in the case of reactions with destabilizing processes such as autocatalysis or substrate inhibition, both branches can be simultaneously stable over a finite range of flow rates. Note that the input flow can be replaced by other control parameters such as the concentration of an input species in the feed flow. However, by extension, we continue to call "flow state" the state with a small extent of reaction and "thermodynamic state" the state with a large extent of reaction.

We consider now the situation in an OSFR when the content of the CSTR is kept in a flow state. As the reactants diffuse inside the gel from the CSTR interface, they react together. Thus, the extent of the reaction at a given point in the gel depends on the distance *r* to this boundary. Close to the interface, the extent of reaction is small and the system remains in the flow state, forming a boundary layer. Far from the CSTR, the extent of reaction is high and the reaction is almost completed (T state). The fast switch that would be observed in a batch reactor leads now to the formation of a steep front between the boundary layer in the F state and a T state at larger distances. We call the resulting global chemical state in the gel an "FT" state. When the thickness *l* of the gel is small, the boundary layer can extend to the whole system, which is then altogether in a flow state. By extension, we call F such a state of the gel. In the same way that, for intermediate values of the flow rate, the CSTR

10.1021/jp027193s CCC: $25.00

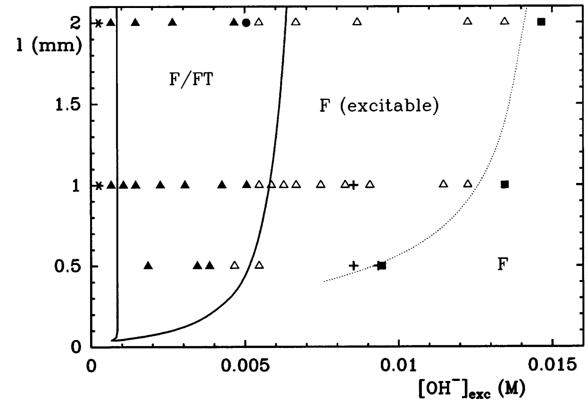

Figure 1. Out of equilibrium phase diagram in the plane ($[OH^-]_{exc}$, l) for the C−T reaction in annular OSFR: ■, monostable (nonexcitable F state); △, monostable (excitable F state); ▲, bistable (stationary F or FT state); ●, bistable (with front oscillations in the FT state); $*$, CSTR switches to the thermodynamic state. Computed results: full line, limits of the bistability domain; $+$, points for which the F state has been checked to be excitable. The dotted line is merely a guide for the eyes showing the limit of the excitability domain. Experimental conditions: residence time of the reactor, $\tau = 600$ s; $T = 25$ °C; $[NaClO_2]_0 = 1.9 \times 10^{-2}$ M; $[K_2S_4O_6]_0 = 0.5 \times 10^{-2}$ M.

can present two stable states, the F and FT states of the gel can be both stable for intermediate values of l for the same state of the CSTR. This is what is called "spatial bistability".[12,13] If the content of the CSTR is in a T state, then the gel also is in the T state. This is a third stable state of the gel−CSTR system.

The nonequilibrium phase diagram of the reaction−diffusion behavior of the chlorite−tetrathionate reaction is partly recalled in Figure 1.[10] In these previous experiments, a ring-shaped OSFR was flowed with four solutions, a sodium chlorite solution, a potassium tetrathionate solution, a perchloric acid solution, and a sodium hydroxide solution. For the sake of clarity, α, the control parameter previously used, was recalculated in terms of $[OH^-]_{exc}$, which represents the concentration excess of base to acid in the input flow. $[OH^-]_{exc} = [NaOH]_0 - [HClO_4]_0$, where $[NaOH]_0$ and $[HClO_4]_0$ are the feed concentrations of sodium hydroxide and perchloric acid, respectively. l, is the depth of the gel. Beside the stationary F state of the gel, the diagram shows a large region of spatial bistability. Furthermore, two instabilities of the "long-range activation" type are observed: an excitatory instability of the F state as well as an oscillatory instability of the front in the FT state. This is due to the fact that the autocatalytic species H^+ has a higher diffusion coefficient than other species involved in the reaction.[10] For small sizes—typically when the size of the gel becomes comparable to a few times the size of the boundary layer—the chemical state in the gel is expected to become very sensitive to the size of the gel, and bistability should eventually vanish at very small sizes. This feature is clearly observed in numerical simulations both on simplified and more extensive models of the reaction.[10] However, in previous experiments it was not possible to explore such small dimensions.

Here we report the use of a conical geometry to further investigate the spatiotemporal patterns of the C−T reaction. This has two main advantages. (1) It enables experimental observation of sizes in the range of 1.5−0.05 mm, while in previous experiment the smallest ring that could be processed was 0.5 mm deep. (2) As the bifurcation parameter l is unfolded over the height of the cone, the construction of the phase diagram needs few experiments.

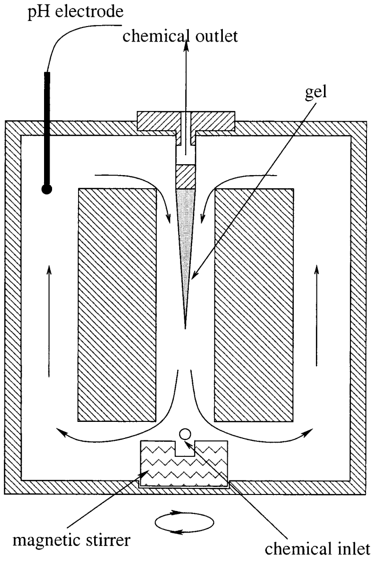

Figure 2. Cross-sectional view of the reactor.

2. Materials and Methods

Pieces of conical gel are prepared using yellow tips (200 μL) of precision pipet as a mold. A 2% agarose (Fluka, 05070) solution is heated at 80 °C during at least 30 min before pouring it into the conical mold. The solution then cools to room temperature, and the gel forms. The conical pieces of gel have typically the following caracteristics: largest radius, $R_{max} = 1.8$ mm; radius of the tip, $R_{min} = 0.055$ mm; height, $h = 40$ mm.

A reactor with a new geometry was built to enable one to feed continuously and uniformly a conical or cylindrical piece of gel. The reactor is basically a CSTR in which the piece of gel can be immersed (Figure 2). However, to ensure a good mixing along the revolution surface of the cone of gel and a relative stabilization in position of this piece of gel, the CSTR is made of three interconnected vertical cylinders. A turbine-like magnetic stirrer located at the bottom of the central cylinder creates a hydrodynamic vortice in this cylinder and pumps the fluid down, and then the fluid is pushed back to the top of the middle cylinder through the side cylinders. This introduces a strong recirculation of the bulk contents. The recirculation time is approximately 2 s. A premixed feed of chemicals is introduced at the level of the turbine. The total volume of the CSTR is 46 mL. The cone of gel (of largest diameter 3.6 mm) is glued by its base at the center of a plexiglass stopper, introduced at the top of the central cylinder (of inner diameter 15 mm). This stopper also contains the outlet port of the CSTR. The CSTR is set into a thermostated bath at $T = 25$ °C. The pH into the CSTR is monitored using a pH electrode, and patterns in the gel are revealed by the color changes of a color indicator and recorded on a time lapse VCR using a color CCD camera.

Contrary to the experiments of ref 9, the gel has to be observed through a thick amount of the solution of the CSTR which is maintained in the flow state. Thus for the patterns to be visible, it is necessary that absorbance in the F state (basic) be much weaker than in the T state (acidic). This induces a strong limitation in the choice of the pH or redox indicators that are commonly used to reveal the chemical states of the reaction. In addition, most indicators are bleached more or less rapidly during the course of the reaction, probably by reaction with chlorine dioxide. Many indicators were tested, and we eventually chose methyl red which is only slowly destroyed by the reaction. The basic form is yellow while the acidic form is red.

Sodium chlorite (Prolabo, 96% pure) and potassium tetrathionate (Fluka, 99% pure) are used without further purification. The feeding solutions are stored in four separated reservoirs containing respectively an alkaline sodium chlorite solution ([$NaClO_2$] = 2×10^{-1} M; [NaOH] = 1.5×10^{-4} M), an alkaline potassium tetrathionate solution ([$K_2S_4O_6$] = 5×10^{-2} M; [NaOH] = 1.5×10^{-4} M), and two sodium hydroxide solutions of different concentrations. The pH indicator methyl red (Aldrich) is added to the tetrathionate solution (600 mg/l). The solutions are pumped by precision piston pumps (pharmacia P500) and premixed just before being injected into the CSTR. The flows of the chlorite and tetrathionate solutions are maintained constant at 50 mL/h as well as the sum of the two sodium hydroxide solutions, while the ratio between the flows of the two sodium hydroxide solutions is varied to tune the total amount of sodium hydroxide introduced in the CSTR. So, the total feed flow is kept constant at 150 mL/h, which corresponds to a value of 18.4 min for the residence time in the CSTR.

Perturbation experiments are run as follows. The cone of gel is placed in the CSTR operated with the desired value of the parameters for at least 2 h. Then a perturbation is made, either by performing a short electrolysis at the base of the gel or by taking the gel out of the CSTR and rapidly touching it with a paper soaked in an acidic solution.

3. Results and Discussion

Experiments were performed in conditions where the contents of the CSTR remains in the F state (basic). Indeed, if the CSTR is in the T state (acidic), then the piece of gel can only be in the T state as well. If the gel is initially in the F state and in the abscence of any external perturbation, the gel remains in the F state as long as the control parameter, i.e., [OH^-] in the feed flow, is over the value of transition of the CSTR [OH^-]$_{Tcstr}$. Beyond this value both the gel and the CSTR switch to the T state.

If an acidic perturbation is made in the gel, then the system evolves to one of the following four different situations, depending on the value of [OH^-] in the feed flow. The spatiotemporal patterns are revealed by the color changes of the pH indicator.

Case 1. For a highly basic input flow, it is not possible to propagate an acidic perturbation in the gel, which consequently remains in the F state.

Case 2. At lower [OH^-] values, the perturbation propagates but dies after a transient and the whole cone remains in the F state.

Case 3. With still decreasing [OH^-] values, after the perturbation the cone is divided into three regions along its axis (Figure 3). The first region, located in the thicker part of the cone for radii $R > R_s$, is in the FT state. Beneath this first region, an oscillatory region of wave-trains propagation is observed. The waves start from the cone section of radius R_s and travel down the cone. They die when they reach the section of radius R_p, which sets the boundary between the second and the third region. The third region, located close to the tip of the cone, always remains in the F state. The velocity of the waves in the axial direction is of the order of 1.5 mm/min and their period about 20 min for a value of the input concentration [OH^-] = 4.56×10^{-3} M.

Case 4. At low values of [OH^-], after perturbation the cone remains entirely in the FT state. Most of the gel contents is acidic, except for a very thin skin of thickness $l < 0.1$ mm close to the interface of the gel.

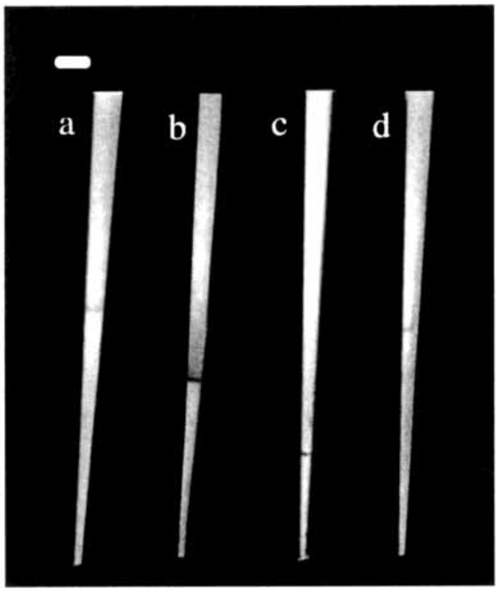

Figure 3. Snapshots of a cone of agarose gel during the propagation of an excitation wave: (a) $t = 0$; (b) $t = 3$ min; (c) $t = 4$ min, 16 s; (d) $t = 21$ min. The bar represents approximately 3 mm. Experimental conditions: [OH^-] = 4.56×10^{-3} M.

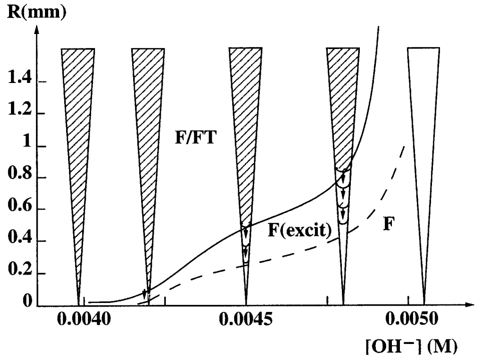

Figure 4. Schematic representation of the system behavior as a function of the value of the parameter [OH^-] in the input flow. R is the radius on the cone.

Note that as long as the thickest part of the gel is in the FT state, it is possible to change the value of the control parameter and observe the corresponding asymptotic state without making a perturbation again.

When the cone of gel is in the FT state and [OH^-] is decreased, the CSTR and the gel switch together to the T state for a value [OH^-]$_T$ slightly over [OH^-]$_{Tcstr}$. This is thought to be due to the feedback of the gel on the contents of the CSTR, which is predicted by theory and was previously observed in simulations.[12] This also makes the pH in the CSTR lower when a part of the gel is in the FT state than when the gel is in the F state for the same value of the parameter.

These observations can be gathered in a response−constraint plane (Figure 4), where the input [OH^-] is the only control parameter. The ordinate corresponds to the value of the radius R along the cone of gel. The full curve corresponds to the starting position of the wave-trains R_s, while the dash curve indicates the death location of the waves R_p. These positions along the axis of the cone are very sensitive to any change of the control parameter, which allows for a very accurate measure of the corresponding radius.

If the gel is left in the most acidic conditions (CSTR in the state F and gel wholly in the state FT) for more than 2 h, then a red precipitate forms at the interface between the gel and the

Figure 5. (a) Formation of a “skin” of methyl red precipitate over the cone. (b) Taken as the skin is partially removed to better see its heterogeneous aspect. The bar represents approximately 3 mm.

solution (Figure 5). Then, by changing slowly the control parameter toward more basic conditions, a stable front is observed at the very tip of the cone. By raising again progressively [OH$^-$] in the input flow, the stable front moves back to larger radius over the cone. We could observe a stable front up to $R = 0.9$ mm. However for the same value of the control parameter but coming from higher [OH$^-$] values, we observe wave-trains propagation. The existence of the stable front is probably due to an artifact. Indeed, a few experiments were made using bromophenol blue as a dye: only wave-trains, but no stationary front, were observed. Moreover, with methyl red as indicator, it was impossible to observe a stable front in the abscence of a thick precipitate over the surface of the cone. The formation of this stable front is thought to be due to the precipitation of methyl red over the gel, which can have at least two effects. First it might physically slow the diffusive exchange through the interface, and second the high concentration of indicator in the precipitate can reduce and even supress the domain of excitability by slowing down the effective diffusion of protons as was observed with an immobilized weak acid.[14]

In the following, we interpret the patterns selection over the cone in relation with the numerical and experimental results previously obtained with flat ring-shaped OSFR[9,10] and partly gathered in Figure 1. The decrease of the radius R along the axis of the cone is similar to a decrease of the depth l at a given value of [OH] in Figure 1.

Because of the thickness gradient in the cone, different states that were observed in previous experiments at fixed depth can now coexist in the cone. This is the case for the FT and F states which are observed either separately or simultaneously on the cone. A large domain of spatial bistability is also observed as in previous work. Indeed, the gel never switches spontaneously to the FT state, while an external perturbation enables it to reach this state. This results from the fact that the CT reaction has a quasi-infinite induction time in batch when started in basic conditions and in the range of concentrations used. The very narrow region of front oscillations that was observed at the boundary between the FT state and the excitable domain in a flat ring reactor cannot be observed here, because we do not have a cross-sectional view of the cone.

Unlike the F and FT states that are observed as such in ring-shaped OSFR, the wave-trains travelling in the axial direction are due to a coupling of neighboring states through diffusion in the axial direction. Indeed, in previous experiments, an excitatory behavior was found at the boundary of the FT state. In the cone of gel the FT state plays the role of a permanent excitation source for the underlying area which is excitable, resulting in the formation of the wave-trains. Because of the presence of this permanent excitation source, the overall system is oscillatory. The period of oscillations correspond to the lapse of time the gel needs to recover by exchange of reactants from the solution.

The determination of the wave-trains domain is very accurate. However, the coupling between adjacent states is likely to induce a small shift from the expected excitability domain in quasi-2D disks. Actually, at the boundary between the FT state and the excitability domain, the relaxation time of the waves is almost infinite. The onset of excitability would then appear for smaller values of the radius in a disk than what is observed here on the cone, so that the full line in Figure 4 is very likely to be underestimated. Note also that the wave-trains can only exist if some part of the cone remains in the FT state. By increasing [OH$^-$], the value of R_p increases up to the maximal radius of the cone. Then the excitation source disappears, and it is necessary to make a perturbation at the base of the cone to check for excitability. Even though we tried to perturb the system by making an electrolysis pulse through a small copper wire pinned into the base of the gel, it was not possible to make a precise determination of the excitability domain boundary for such high values of [OH$^-$]. The dashed line in Figure 4, showing the location of waves death (R_s), is also shifted compared to the situation in a disk. Indeed, beyond the limit of excitability, a perturbation can still propagate with damping, so that the point where waves actually vanish is more likely to be located at a value of R slightly smaller than the exact value that would be observed in a disk.

Even with those limitations, the excitability domain and the FT state extend well beyond the minimal size that can be obtained with the cone ($R < 0.055$ mm). This result is in agreement with previous calculations which predict that the minimal size for the existence of the FT state in the flat ring is around 0.047 mm [10] and that excitability could extend to even smaller values.[15]

The boundaries of the asymptotical reaction−diffusion states obtained in a cone of gel cannot be quantitatively compared to the ones for a flat ring for several reasons. First, the reactors used have different shapes, volumes, and recirculation rates, which introduce some discrepancies in the results. Besides these technical reasons, we wish to underline that a cross-section of the cone is a full disk and therefore cannot be quantitatively compared to those for a flat ring. The previous experiments in refs 9 and 10 were run using a series of flat rings of gel of depths ranging from $l = 3$ mm to $l = 0.5$ mm and of radius 12.5 mm, so that the curvature can be neglected. In the case of the disk, the diffusion gradient is radial, so the ratio of the exchange area to the volume of the gel is larger if the radius of the cone is taken as the depth of the ring. This favors the stability of the flow state, so that, in a ring, the FT as well as the excitability domains should extend to even smaller sizes. Also, we have already mentioned the coupling effects between different sections of the cone that affect the boundaries. However, the use of a cone of gel can give a good insight into pattern selection close to the boundary between the bistable and the monostable F domains, especially for the smallest sizes.

4. Conclusion

Up to now, studies of reaction−diffusion spatial and spatiotemporal patterns were essentially performed in 2D slabs of gel. Here, we show that the use of a conical piece of gel enables one to go down to much smaller radius than the flat-ring OSFR that was previously used, so that we could build a more extensive experimental phase diagram.

Also, diffusive coupling along the axis of the cone gives birth to an oscillatory behavior of the C−T reaction. Furthermore, the conical shape is a model for further studies of shape deformations in cylinders of pH-sensitive hydrogels coupled to the C−T reaction. Such experiments are currently in progress in our laboratory.

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