Spatial periodicity induced by a chemical wave train

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An all-chemical analog of clock-wave-front model for somitogenesis is proposed. The spatial periodicity can be obtained by arresting the homogeneous oscillations in a typical two-component reaction-diffusion system in the Hopf region by interacting with a chemical wave front. The patterns can be controlled by tuning the wave speed of the front.

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The theory of morphogenesis [1] proposed by Turing in the middle of the last century is based on the search for symmetry breaking of a homogeneous steady state of a dynamical system governed by the reaction-diffusion equations. The underlying instability owes its origin to short-range activation and long-range diffusion of two interacting species obeying activator-inhibitor reaction kinetics and the resulting symmetry-broken state is characterized by various spatial regions with distinct physical and chemical features or conspicuous patterns. The theory and its variants have found extensive applications in several areas of natural sciences, particularly, in developmental biology [2–11], where the growth of sequential space-periodic structures along the anterio-posterior axis of the vertebrate embryo has remained a focus of major attraction. Somitogenesis [3–15] provides a typical example of how such spatial periodicity forms during embryogenesis. Several models [8–14] of somitogenesis are now known. Among them the clock and wave front model [14] has gained a good testing ground for further experiment. The model assumes the existence of a biochemical oscillator within the band of paraxial mesodermal cells. The oscillator of all the neighboring cells oscillates synchronously. The model further postulates that a wave front of cell change sweeps posteriorly through the cells slowly, halting the oscillations and thereby inducing maturation of somatites which are essentially blocks of cells of paraxial mesoderm arranged as spatially periodic structures.

In the present Brief Report we look for a chemical analog of the clock-wave-front model of somitogenesis. Chlorine dioxide-iodine-malonic acid (CDIMA) system [16–21], which has remained as a classic paradigm for a wide class of far-from-equilibrium phenomena in spatially extended system, offers itself as an excellent candidate for the model. With CDIMA systems it has been shown that progressive arrest of homogeneous oscillations can control the symmetry as well as the wavelength of spatial structures when the reaction medium is illuminated with a constant or periodic source of light [22,23]. Our endeavor in this Brief Report is to suggest an all-chemical analog for exploring the possibility of formation stationary pattern out of homogeneous oscillations in the Hopf region by interaction with a progressive chemical wave front or pulse rather than light field. We exploit the sensitivity of CDIMA system to the concentration of some external reducing agent to demonstrate how the wavelength of the produced patterns changes with the velocity of the traveling wave and frequency of the temporal oscillations.

To begin with we consider the following chemical reactions that are involved in the CDIMA model [16,17];

$$MA + I_2 \rightarrow IMA + I^- + H^+,$$

$$ClO_2 + I^- \rightarrow ClO_2^- + \frac{1}{2}I_2,$$

$$ClO_2^- + 4I^- + 4H^+ \rightarrow Cl^- + 2I_2 + 2H_2O.$$

When starch is added from outside in the reaction medium, we have the additional equilibrium between starch and iodide ions;

$$S + I_3^- \leftrightharpoons SI_3^-.$$

Ideally the reaction schemes imply a many variable model for CDIMA system. However in the course of reaction the concentrations of all the species but I^- and ClO_2^- remain more or less constant. This effectively reduces the model into a two-variable one with concentrations of I^- and ClO_2^- playing the role of activator and inhibitor respectively. With $[I^-] \equiv u$ and $[ClO_2^-] \equiv v$ and treating concentrations of all other species as constants Lengeyl and Epstein have suggested the governing reaction-diffusion dynamics of these two variables as follows:

$$\frac{\partial u}{\partial \tau} = a - u - 4\frac{uv}{1+u^2} + \nabla^2 u, \tag{1}$$

$$\frac{\partial v}{\partial \tau} = \sigma\left[b\left(u - \frac{uv}{1+u^2}\right) + d\nabla^2 v\right]. \tag{2}$$

Here the parameters a and b are proportional to the concentration ratios $[MA]/[I_2]$ and $[ClO_2]/[I_2]$, respectively, and are related to kinetic parameters. d refers to the ratio of the diffusion coefficients $d=[D_{ClO_2^-}]/[D_{I^-}]$. σ is the concentration of starch which forms a complex with I_3^- such that $\sigma = 1 + K[S]$, where K is the equilibrium constant for the complexation reaction and $[S]$ is the concentration of starch.

The complexation thus separates the time scales for the

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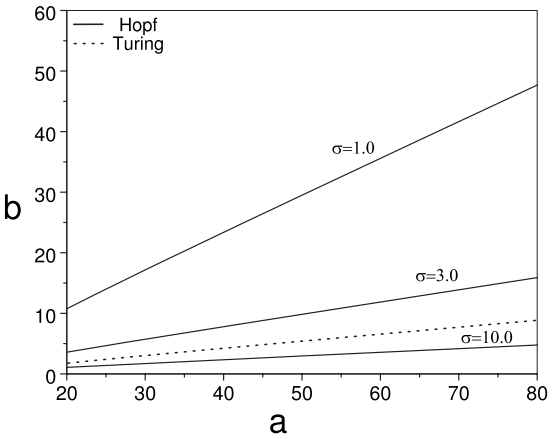

FIG. 1. Bifurcation diagram for CDIMA system exhibiting Hopf-Turing transition for $a=18.0$, $b=1.5$, and $d=1.6$.

evolution of the activator and inhibitor by a factor σ. This exerts a stabilizing influence upon the steady state without affecting, however, the steady-state composition. The Hopf curve given by

$$\sigma b = \frac{3a}{5} - \frac{25}{a} \tag{3}$$

separates a,b phase space into two regions (Fig. 1). Above the curve the steady state is stable, below it gives rise to homogeneous oscillation. With increasing σ the curve takes a downward shift. The criterion for the diffusion-induced instability on the other hand can be had from Turing bifurcation condition which for the present system reads as

$$(3da^2 - 5ab - 125d)^2 \geq 100abd(25 + a^2). \tag{4}$$

The plot of a vs b according to Eq. (4) gives the Turing line. Below the Turing curve the state loses its stability due to diffusion. Thus the Turing condition is met in a parameter zone above the Hopf and below the Turing curve. As apparent from Fig. 1 such a situation can only be realized if σ is sufficiently high. Thus controlling starch concentration by stabilizing the steady state opens up the possibility of pattern formation.

The aforesaid condition may be manipulated by application of external agencies [24–28]. For example application of electric field [24,25] shifts the Hopf curve upwards and results in condition for instability at low σ. Similar situations can also be realized due to external additive noise [29]. The motivation of our present work differs from earlier studies on the following issue. Here we choose the system in a parameter zone below the Hopf line where the entire system oscillates homogeneously. Since the system is spatially extended, we let a chemical gradient flow from one boundary to another. This may be realized by producing a suitable traveling wave in the same medium or simply passing some reactive gas through it. This traveling wave or the gas has the characteristic that it interacts with the oscillatory system in a way that the oscillations are stopped in the region where wave passes. We thus explore the possibility of generating spatially inhomogeneous pattern in an oscillatory medium due to the

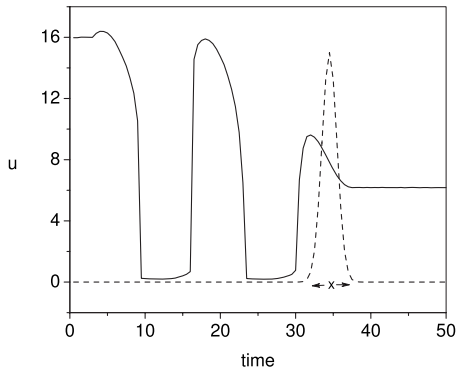

FIG. 2. Scheme of development of inhomogeneous spatial pattern.

interaction between the oscillations with a progressing chemical wave front/propagating pulse. For the purpose we exploit the sensitivity of CDIMA system to the concentration of ClO_2 and a typical wave front that has the ability to interact with it. The reacting medium is so chosen that the diffusivities of the species throughout the medium are small enough. So the dynamics of the species at various points are effectively uncoupled. The traveling wave moves across the medium and arrests the oscillations at different points at different phases of oscillation. So as the wave passes by an inhomogeneous spatial distribution results in. The scheme is illustrated by Fig. 2.

It is well known that the coupling of chemical reaction with diffusion may give rise to propagating chemical waves provided the reaction contains some appropriate form of kinetic feedback such as autocatalysis. Many different types of reaction-diffusion waves have been observed in isothermal chemical systems such as propagating pulses or propagating fronts. The chemical waves that are observed in excitable Belousov-Zhabotinsky reaction are the examples of propagating pulses. Here as the pulse propagates through a point the reaction intermediates undergo an excursion to return to its original state as the wave passes through. However in case of a propagating front the system after the excursion does not return to the original state but settles down to a new kinetic state. Such propagating waves were generated in the iodate oxidation of arsenous acid [30]. In this reaction the front typically converts the reaction-mixture from one kinetic state (with an initial state where very little reaction has occurred) to the state of thermodynamic equilibrium. The net reaction (5) describing the iodate-arsenous acid reaction when arsenous acid is in stoichiometric excess to iodate ($[\mathrm{As(III)}]_0 > 3[\mathrm{IO_3^-}]_0$) is given by

$$\mathrm{IO_3^-} + 3\mathrm{H_3AsO_3} = \mathrm{I^-} + 3\mathrm{H_3AsO_4}. \tag{5}$$

When iodate is in stoichiometric excess to arsenous acid ($[\mathrm{As(III)}]_0 < 5/2[\mathrm{IO_3^-}]_0$), the system is described by net reaction (6);

$$2\mathrm{IO_3^-} + 5\mathrm{H_3AsO_3} + 2\mathrm{H^+} = \mathrm{I_2} + 5\mathrm{H_3AsO_4} + \mathrm{H_2O}. \tag{6}$$

If initially IO_3^- is taken in excess over AsO_3^- the wave of I^- produced is Gaussian [30] in nature. As the wave is made to pass through the CDIMA reaction medium the system is

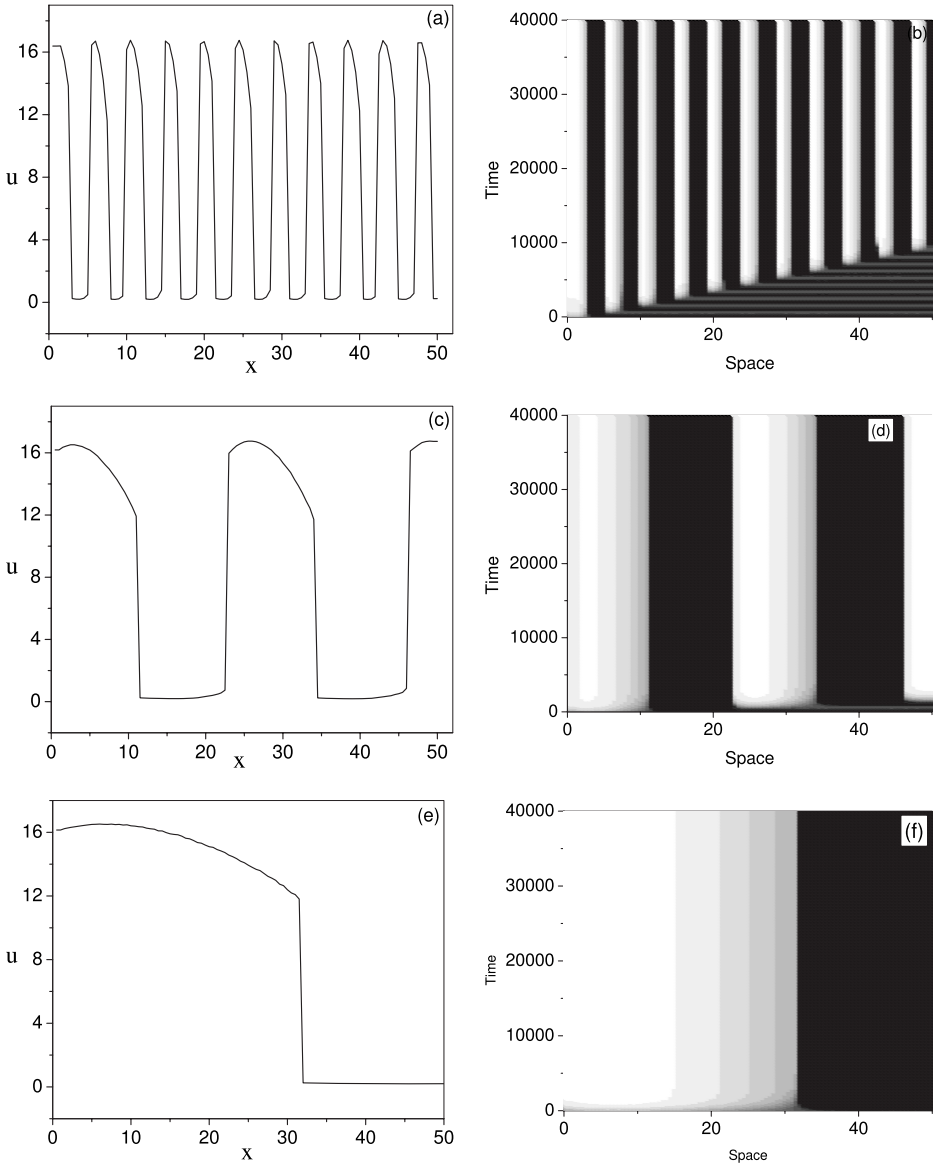

FIG. 3. Spatial [(a), (c), and (e)] and spatiotemporal [(b), (d), and (e)] evolution of concentrations while passing a wave train having speed of 0.003 [(a) and (b)], 0.0087 [(c) and (d)], and 0.0765 [(e) and (f)] unit or time, the parameters chosen are $a=18.0$ and $b=1.5$ in absence of wave train and $b=0$ in presence of wave, $d=1.6$, $\sigma=4.0$ (grid size 100×100 with $\Delta x=\Delta y=1.0$ and $\Delta t=0.005$).

likely to feel the high iodide concentration in such a way that the ClO_2 gets reduced by it. This arrests the oscillation immediately as the multiplicative parameter b in Eq. (2) is turned off. To capture such a scenario we numerically simulate the system described by Eqs. (1) and (2) at a parameter zone just below the Hopf line. This ensures a homogeneous time periodic oscillation throughout the space. We then let the iodide wave (we assume it to be Gaussian as suggested by the experiment) to pass through the medium. To realize spatial periodicity induced by wave train we have carried out numerical simulations of Eqs. (1) and (2) in two dimensions using explicit Euler method. The computations have been performed on 100×100 array with grid spacings $\Delta x=\Delta y=1.0$ and a time step $\Delta t=0.005$ and zero flux boundary condition. The parameter b is set to a value 0 or 1.5 at some given space point depending upon whether the wave train has passed through it or not. Figure 3 illustrates the space-time description corresponding to such a situation for several values of wave speed. It demonstrates how the temporal homogeneous oscillation is translated into spatial pattern as the wave passes through the medium.

In Fig. 4 we have demonstrated how the wavelength of spatial pattern changes with velocity of traveling wave. The spatial wavelength increases with the velocity. As the wave

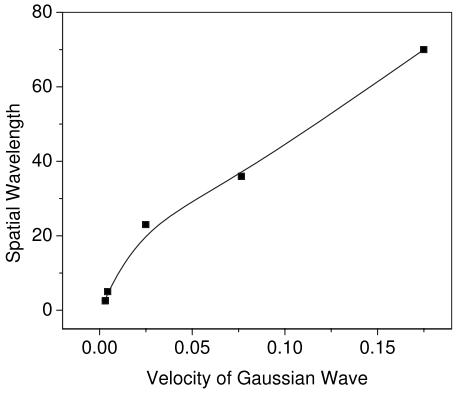

FIG. 4. Variation in wavelength as a function of the velocity of the wave train with the parameter set $a=18.0$, $b=1.5$, $d=1.6$, and $\sigma=4.0$.

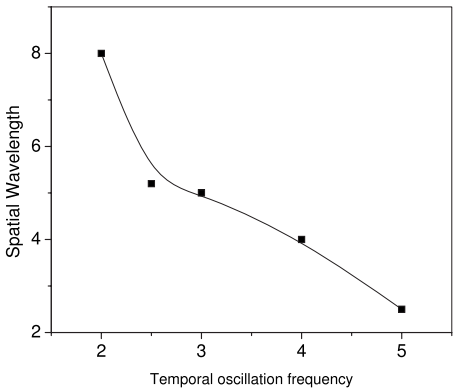

FIG. 5. Variation in wavelength of spatial pattern as a function of the frequency of temporal oscillation with the parameter set $a=18.0$, $b=1.5$, $d=1.6$, and $\sigma=4.0$.

moves fast through the medium it cannot feel the difference in phases of oscillation at various space points and above a critical value of velocity which depends on the system size the inhomogeneity vanishes. This fact is also consistent with the results from biology. Similarly with increase in temporal frequency of the oscillation the spatial wavelength decreases (Fig. 5).

However with regard to the experimental realization this scheme requires a critical arrangement. This is because the iodide ions initially present uniformly in space may react with the ClO_2 of CDIMA system and disturb the oscillation over the entire space even before the generation of iodide wave. Also this iodide may react with other oxidizing agents present in the system such as ClO_2^-. A simpler scheme could be to pass some gaseous reactant through the reaction medium that can selectively react with ClO_2. HBr gas can serve the purpose very well as it can only reduce ClO_2 but does not affect the salt of its lower halogen, I^- under the same condition. With a passing gas there is another additional advantage that the velocity can be tuned by adjusting some external condition such as pressure difference.

In conclusion, we have suggested an all-chemical analog of clock-wave-front model for somitogenesis. It has been shown that by exploiting the sensitivity of CDIMA system to the concentration of some reducing agent it is possible to arrest homogeneous oscillations in the Hopf region by interaction with a chemical wave front and thereby generating patterns without application of any light source or external agency. The patterns are sensitive to the variation in wave speed or frequency of the temporal oscillations.

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