Reports

Modeling of Turing Structures in the Chlorite–Iodide–Malonic Acid–Starch Reaction System

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Recent experiments on the chlorite–iodide–malonic acid–starch reaction in a gel reactor give the first evidence of the existence of the symmetry breaking, reaction-diffusion structures predicted by Turing in 1952. A five-variable model that describes the temporal behavior of the system is reduced to a two-variable model, and its spatial behavior is analyzed. Structures have been found with wavelengths that are in good agreement with those observed experimentally. The gel plays a key role by binding key iodine species, thereby creating the necessary difference in the effective diffusion coefficients of the activator and inhibitor species, iodide and chlorite ions, respectively.

DAILY EXPERIENCE SUGGESTS THAT diffusion always causes a smoothing that eliminates chemical gradients and leads to uniform spatial distributions. In a remarkable paper entitled "The chemical basis of morphogenesis," Turing (*1*) predicted in 1952 that the coupling of diffusion with suitable chemical reaction kinetics could destabilize a homogeneous stationary state and result in the formation of temporally stationary, spatially inhomogeneous structures. He suggested that this process might lead to a variety of morphogenetic phenomena. The possibility of such diffusion-induced instabilities has been widely investigated in the chemical and biological literature (*2–4*).

Only very recently, however, was the first clear experimental evidence of stationary Turing structures reported (*5*). A strip of gel loaded with starch indicator was fed with constant concentrations of malonic acid (MA) at one end and of chlorite (ClO_2^-) and iodide (I^-) ions at the other end. The patterns, which are nonuniform both parallel and perpendicular to the direction along which the reactants diffuse toward each other (the starch is immobile on the gel), were observed in the color of the starch-I_3^- complex.

Lengyel *et al.* have recently demonstrated (*6, 7*) that in a closed, homogeneous reaction mixture temporal oscillations in the ClO_2^--I^--MA reaction arise from the simpler chlorine dioxide (ClO_2)–I_2–MA system. The reaction of ClO_2-I_2-MA accounts for all events taking place after the initial fast consumption of ClO_2^- and I^- to produce ClO_2 and I_2. The ClO_2-I_2-MA reaction can be described with a five-variable model consisting of three reactions, whose rate laws are known (*6*):

$$\mathrm{MA} + I_2 \rightarrow \mathrm{IMA} + I^- + H^+$$

$$-d[I_2]/dt = k_{1a}\,[\mathrm{MA}]\,[I_2]/(k_{1b}+[I_2]) \quad (1)$$

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

$$-d[ClO_2]/dt = k_2\,[ClO_2]\,[I^-] \quad (2)$$

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

$$-d[ClO_2^-]/dt = k_{3a}\,[ClO_2^-]\,[I^-]\,[H^+] + k_{3b}\,[ClO_2^-]\,[I_2]\,[I^-]/(u+[I^-]^2) \quad (3)$$

The inhibition (*8*) by the reactant I^- in the second term of the rate law for Eq. 3 is of particular significance. Under typical experimental conditions, $[I^-] \approx 10^{-5}$ M, $[H^+] \approx 10^{-4}$ M, and $[I_2] \approx 10^{-3}$ M, so that, with the kinetic parameters given in Table 1, the first term in that rate law is negligible compared with the second.

Numerical integrations, which reproduce both the number of oscillations and the concentration dependences found in the experiments, show that, although the concentrations of ClO_2^- and I^- vary by several orders of magnitude during an oscillation, the concentrations of ClO_2, I_2, and MA are slowly varying functions of time; they are well approximated as constants during an oscillatory period. By taking $[ClO_2]$, $[I_2]$, and [MA] as time-independent parameters and making other chemically reasonable simplifications, we find that the five-variable model can be reduced to a two-variable model (*7*) ($X = I^-$, $Y = ClO_2^-$, $A = I_2$):

$$A \rightarrow X \qquad r_{M1} = k_1'$$

$$k_1' = k_{1a}\,[\mathrm{MA}]_0\,[I_2]_0/(k_{1b}+[I_2]_0) \quad (4)$$

$$X \rightarrow Y \qquad r_{M2} = k_2'\,[X]$$

$$k_2' = k_2\,[ClO_2]_0 \quad (5)$$

$$4X + Y \rightarrow P \qquad r_{M3} = k_3'\,[X][Y]/(u+[X]^2)$$

$$k_3' = k_{3b}\,[I_2]_0 \quad (6)$$

A homogeneous system governed by Eqs. 4 through 6 has only one steady state, which for certain values of the parameters loses stability through a supercritical Hopf bifurcation. The two-variable model is amenable to simple analytical investigation of the necessary and sufficient conditions for Turing instability. Similar studies have been carried out on two similar inhibitory models, the Degn-Harrison model (*9*) by Velarde and co-workers (*10*) and the Thomas model (*11*) by Murray (*2, 12*).

Our system of reaction-diffusion equa-

Table 1. Model parameters.

Rate or diffusion constant	Value at 25°C	EA (kJ mol^{-1})	Value at 7°C	Reference
k_{1a} (s^{-1})	7.5×10^{-3}	81.5	9×10^{-4}	This work
k_{1b} (M)	5×10^{-5}		5×10^{-5}	
k_2 (M^{-1} s^{-1})	6×10^3	62.0	1×10^3	This work
k_{3a} (M^{-2} s^{-1})	460	51.4	120	(*8*)
k_{3b} (s^{-1})	2.65×10^{-3}	110.0	1.5×10^{-4}	(*8*)
u (M^2)	1×10^{-14}		1×10^{-14}	
$10^5 \times D_{ClO_2^-}$ (cm^2 s^{-1})	1.5		0.75	Estimated from mobility data
$10^5 \times D_{I^-}$* (cm^2 s^{-1})	1.4		0.70	(*25*)
$10^5 \times D_{ClO_2}$ (cm^2 s^{-1})	1.5		0.75	As ClO_2^-
$10^5 \times D_{I_2}$ (cm^2 s^{-1})	1.2		0.60	Estimated from values for I^- and I_3^- (*25*)
$10^5 \times D_{MA}$ (cm^2 s^{-1})	0.8		0.4	Estimated from mobility data

*In the calculations D_{I^-} was taken as 5×10^{-7} cm^2 s^{-1} because of the binding of I_2 and I_3^- to the gel (see text).

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tions is

$$\partial x/\partial t = k_1' - k_2'x - 4k_3'xy/(u + x^2) + D_x\,(\partial^2 x/\partial z^2) \qquad (7)$$

$$\partial y/\partial t = k_2'x - k_3'xy/(u + x^2) + D_y\,(\partial^2 y/\partial z^2) \qquad (8)$$

where z is the spatial variable, and D_x and D_y are the diffusion coefficients of x and y, respectively. It is useful to define the following dimensionless constants:

$$\alpha = k_1[\mathrm{MA}]_0/(k_2u^{1/2}\,[\mathrm{ClO_2}]_0) \qquad (9a)$$

$$\beta = k_{3b}\,[I_2]_0/(k_2u^{1/2}\,[\mathrm{ClO_2}]_0 \qquad (9b)$$

When applied to Eqs. 7 through 9, the necessary and sufficient conditions (*13, 14*) for diffusion-induced instability in a two-variable system can be summarized as follows, where the a_{ij} are the elements of the Jacobian matrix, and ss signifies steady state {as with $a_{12} = [\partial(\partial x/\partial t)/\partial y]|_{ss}$}:

1) The homogeneous system must have a steady state $\{x_{ss} = u^{1/2}\alpha/5,\ y_{ss} = (u^{1/2}/\beta)\,[1 + (\alpha/5)^2]\}$ that is stable to homogeneous perturbations. This condition is fulfilled if

$$a_{11} + a_{22} < 0 \qquad (10)$$

and

$$a_{11}a_{22} - a_{12}a_{21} > 0 \qquad (11)$$

In our case, inequality 11 always holds, and inequality 10 becomes

$$\beta > 3\alpha/5 - 25/\alpha \qquad (12)$$

2) The stability of the homogeneous steady state against inhomogeneous perturbations can be investigated with either Neumann or Dirichlet boundary conditions. The following inequality is a necessary condition for diffusive instability (*14*):

$$a_{11}D_y + a_{22}D_x > 2[D_xD_y\,(a_{11}a_{22} - a_{12}a_{21})]^{1/2} > 0 \qquad (13)$$

Comparing inequalities 10 and 13, we observe that a_{11} and a_{22} must have opposite signs. In our case $a_{22} < 0$ at any parameter values, whereas $a_{11} > 0$ if

$$\alpha > 5(5/3)^{1/2} \qquad (14)$$

In the standard terminology used to discuss Turing structures (*12*), the activator has a positive sign ($a_{11} > 0$) and the inhibitor has a negative sign ($a_{22} < 0$) in the Jacobian; consequently, I^- is the activator and ClO_2^- is the inhibitor. In the chemical sense, X (I^-) is a self-inhibitor (*15*) in the crucial process (*3*); that is, the higher the concentration of I^-, the slower the reaction. However, X indirectly stimulates its own buildup by inhibiting its own destruction. Chemically, Y (ClO_2^-) acts directly neither as an activator nor as an inhibitor, but, by removing X, it serves as an inhibitor for the Turing instability.

The necessary condition, Eq. 13, requires that the diffusion coefficients of the reactants be different and that the inhibitor (ClO_2^-) diffuse more rapidly than the activator (I^-). With plausible values for the other parameters, we find that the ratio D_y/D_x must be at least 10 for Eq. 13 to hold. In aqueous solution, diffusion coefficients of typical small ions are of the order of 10^{-5} cm^2 s^{-1}, and the diffusion coefficient of ClO_2^- cannot be ten times greater than that of I^-. In general, diffusion-induced instability with nearly equal diffusion coefficients (*16*) can occur only under very special conditions, which are unlikely to be realized in practice.

In the Turing structure experiments, the gel is not an inert medium like the solvent in the corresponding aqueous experiment. The starch cannot diffuse in the gel, nor can the starch-I_3^- complex; their diffusion coefficients are zero (*17*). More importantly, the polyacrylamide gel is typically 10 to 30% by weight (2 to 6 mol/dm^3) in the acrylamide monomer, which provides a hospitable environment for both I_2 and I_3^-. Specific interactions of I_2 and I_3^- with organic polymers such as polyvinylacetate (*18*) and starch (*19*) are well known. Such interaction with the $-CONH_2$ side groups of the polymer is highly likely and would reduce the effective diffusion constant of I^-. In particular, the relatively low electron density of the NH_2 moiety would facilitate Lewis acid-base interactions with I_3^-. Simple experiments in which ClO_2^- and I_2 solutions are poured through a column of polyacrylamide gel show that the latter do have significantly longer retention times.

We may picture the I^- ions moving not in a simple gel but in a medium with many traps (gel-bound I_2, starch) that capture I^- for a period of time before relasing it, thereby causing I^- to diffuse much more slowly than in the absence of the traps. The effective diffusible concentration and concentration gradient of I^- are lower than the corresponding stoichiometric quantities. Thus the rate of I^- diffusion decreases as if its diffusion coefficient were lower. The required tenfold difference between the diffusion coefficients of I^- and ClO_2^- is easily achieved by this mechanism. In fact, polyacrylamide gels have been used for the analytical separation of halogen-containing species (*20*). For reaching a qualitative picture (*21*), we estimated $D_y/D_x = 15$. Figure 1 shows the phase diagram in the α-β phase plane obtained from the inequalities 12 through 14. The domain of diffusive instability broadens as D_y/D_x is increased.

The parameters used to calculate the structures are given in Table 1. The rate constants were determined at 25°C, but the Turing structures were found at 7°C. Energies of activation (EA) of the component reaction are available, so rate constants at 7°C can be estimated. We were unable to find a direct determination of the diffusion coefficient of ClO_2^-, but from ion mobility data (*22*) it must be similar to those of chlorate and perchlorate ions, that is $\approx 1.5 \times 10^{-5}$ cm^2 s^{-1} at 25°C. With the Stokes-Einstein relationship (diffusion coefficient $D = kT/6\pi\eta a$, where η is viscosity, a is the particle radius, and k is the Boltzmann constant), the temperature (T) dependence of the diffusion coefficients can be calculated. The absolute temperature changes only slightly, but the viscosity of water approximately doubles as the temperature drops from 25° to 7°C.

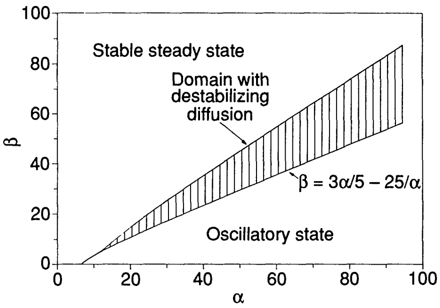

Fig. 1. Stability diagram of the two-variable model and the domain of diffusion-induced instability with $D_y/D_x = 15$ in the (α, β) plane.

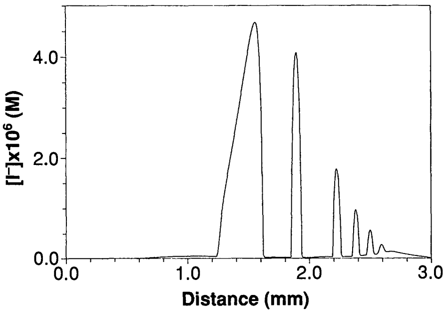

Fig. 2. Stationary structures in the five-variable model with parameters given in Table 1. Initial concentrations in the gel were zero for all components. Fixed boundary conditions: all concentrations (in M) are zero at the gel ends, except $[MA] = 1.0 \times 10^{-2}$ at the left and $[I_2] = 1.0 \times 10^{-3}$, $[ClO_2] = 6.0 \times 10^{-4}$ at the right.

The wavelength of the structures can be calculated from:

$$d = 2\pi/q$$

where

$$q = \tfrac{1}{4}(a_{11}/D_x + a_{22}/D_y)^{1/2} \qquad (15)$$

Using the parameters in Table 1, we find that the wavelength is ≤0.15 mm, which is close to the experimental result (0.2 mm). Numerical integration of Eqs. 4 through 6 confirmed the existence of Turing structures, but the amplitude was only a few percent of the total concentration of I^-, too small to be observed visually as in the original experiment.

To describe the system more realistically, we must use the five-variable model, Eqs. 1 through 3, because in the experiments the concentrations of the initial reactants at the gel boundaries are a key factor in determining the nature (amplitude and wavelength) of the solution. The relevant case is that in which ClO_2 and I_2 diffuse from one end and MA from the other. We used a finite difference method with 500 mesh points in the 3-mm gel length. With much coarser meshes the inhomogeneity (*23*) (related to the number of peaks) was much larger than with 500 points, but above 400 mesh points the structures were independent of the resolution and were stable in space and time after 7 hours of reaction time. The wavelength, location, and number of peaks are much more sensitive to the diffusion coefficients of I^- and ClO_2^- than to those of ClO_2, I_2, and MA. An example of a calculated stationary structure is shown in Fig. 2.

The experiments of Castets *et al.* (*5*) were conducted on the ClO_2^--I^--MA reaction, whereas the present model treats the simpler ClO_2-I_2-MA system. As Lengyel *et al.* have shown (*6*), ClO_2 and I_2 are formed in the ClO_2^--I^- reaction and then dominate the reaction with MA. However, the generation of ClO_2 and I_2 takes place at some distance into the gel. Unfortunately, there is not yet a detailed mechanism that accounts for the formation of ClO_2 in the ClO_2^--I^- reaction at high ClO_2^- excess. Recent experiments (*24*) show evidence of very similar Turing structures in a ClO_2-I^--MA mixture in the same reactor, lending support to the contention that the model presented here adequately describes the original system.

In retrospect, the discovery of Turing structures in the ClO_2^--I^--MA-starch system appears somewhat fortuitous, in that it is the "inert medium," the gel, by binding key iodine species, that makes it possible to establish the crucial difference in the effective diffusion coefficients of activator and inhibitor. Such circumstances may be rare in inorganic chemical systems. In biological systems, on the other hand, membrane-bound species play key roles, and substrate inhibition, rather than the autocatalysis found in most chemical oscillators, is a common means of dynamical regulation. In such systems, as Turing recognized, diffusion-induced instability is likely to be a major mechanism for pattern formation.

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Potassium in Clinopyroxene Inclusions from Diamonds

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Analytical transmission electron microscopy, electron microprobe analyses, and single-crystal x-ray diffraction data support the conclusion that high potassium contents, up to 1.5 weight percent K_2O, of some diopside and omphacite inclusions from diamonds represent valid clinopyroxene compositions with K in solid solution. This conclusion contradicts the traditional view of pyroxene crystal chemistry, which holds that K is too large to be incorporated in the pyroxene structure. These diopside and omphacite inclusions have a high degree of crystal perfection and anomalously large unit-cell volumes, and a defect-free structure is observed in K-bearing regions when imaged by transmission electron microscopy. These observations imply that clinopyroxene can be a significant host for K in the mantle and that some clinopyroxene inclusions and their diamond hosts may have grown in a highly K-enriched environment.

THE QUESTION OF WHERE SUBSTANTIAL K resides in the mantle is fundamental for understanding the source for K in basalts that originate from partial melting of the mantle, the distribution of K in the mantle, the role of K in mantle metasomatism and diamond formation, and the mantle's heat budget (because of radioactive decay of ^{40}K). Garnet peridotites are thought to have compositions typical of the upper mantle, and among the nominally anhydrous solid phases in these rocks, diopsidic clinopyroxene (approximately $CaMgSi_2O_6$) has the highest K level, is stable over a large range of pressures, and is reasonably abundant. However, measured levels of K in clinopyroxene (cpx) from garnet peridotite xenoliths in kimberlites and other extrusive rocks are too small to account for the K levels in basalts produced by partial melting (*1*). Eclogites are closer to basalts in composition, and their K-bearing phases may include sanidine as well as omphacite (a cpx with a nominal composition of $Na_{0.5}Ca_{0.5}Al_{0.5}Mg_{0.5}Si_2O_6$). Although eclogites may be important reservoirs for K, they are not considered to be the source of most mantle-derived basalts. Moreover, the relatively high K contents of omphacite from Group I eclogite xenoliths (0.10 to 0.33% K_2O by weight) have not been demonstrated to be in the cpx crystal structure (*2*). In order to evaluate accurately the potential for cpx as a K reservoir in the mantle and as a possible source for K in the genesis of mantle-derived igneous rocks, the crystal chemistry of K in pyroxene must be understood better and reconciled with measurements on xenolith suites.

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