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Turing Structures in Simple Chemical Reactions

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I. Introduction

The British mathematician Alan Turing is best known for developing a fundamental theory of computing machines and for helping to break the Axis Enigma code during World War II.[1] In addition to his prodigious contributions to mathematics, computer science, and cryptography, Turing, shortly before his suicide at the age of 42, wrote a single paper on chemistry, entitled "The Chemical Basis of Morphogenesis".[2] This remarkable work set forth a theory by which spontaneous pattern formation might arise from the interaction of reaction and diffusion in a chemical system.

Turing's ideas have had a considerable influence on theoretical developments in pattern formation. His mechanism has been utilized to describe pattern formation in semiconductor physics,[3] star formation in galaxies,[4] biological morphogenesis,[5-7] and as we shall discuss in this Account, chemistry. The largest impact of Turing's work has been in providing a plausible explanation of how a variety of structures may emerge in living systems. Perhaps the most picturesque exposition of this approach to pattern formation can be found in the *Scientific American* article entitled "How the Leopard Gets Its Spots".[8]

Despite the considerable interest in them, Turing structures have remained experimentally elusive. It has not yet proven possible to identify in any actual biological system the minimal set of two morphogens, i.e., chemical species, responsible for generating the dynamical instability required by Turing's theory. Until 1990, attempts to find Turing structures in chemical systems had been equally unsuccessful. Although many examples of spatial pattern formation in reaction–diffusion systems are known,[9] none satisfied Turing's conditions of being convection-free and arising from a stable, homogeneous steady state through diffusion-induced instability.

In 1990, De Kepper and colleagues in Bordeaux, working with an open unstirred gel reactor, observed the first experimental evidence for Turing structures in a chemical system, the chlorite–iodide–malonic acid (CIMA) reaction.[10] Since then, this work has been verified and extended both by the Bordeaux group[11,12] and by Ouyang and Swinney[13] using several different reactor configurations. Recently, Ertl and co-workers have presented evidence that suggests the existence of Turing structures in experiments on the oxidation of carbon monoxide on the (110) face of a platinum single crystal.[14]

II. What Is a Turing Structure?

Turing-type spatial structures arise when the effects of diffusion cause a stable, homogeneous steady state of a chemical system to become unstable to infinitesimal inhomogeneous perturbations. Turing structures are stationary, that is, they do not change in time, and they have a characteristic wavelength that is independent of the size of the system. In a plane, the patterns that emerge after all transients have died away can consist of hexagons, stripes, or a mixture. Two examples in a quasi-two-dimensional system are shown in Figure 1.

Nearly all theoretical treatments of Turing structures in a chemical system employ an activator–inhibitor kinetics. The activator (e.g., an autocatalyst) accelerates the reaction, while the inhibitory species decreases the effect of the activator, making the reaction slower. In the classic Turing system, the diffusion constant of the inhibitor must be greater than that of the activator, resulting in local activation and lateral inhibition. However, as we show later, by employing the chemistry of complex formation, it is possible to circumvent this requirement on the diffusion constants and to obtain Turing structures even when the activator can diffuse faster than the inhibitor. The size of the system must be larger than the intrinsic wavelength of the pattern in order for a pattern to form. The mathematical derivation of these requirements for

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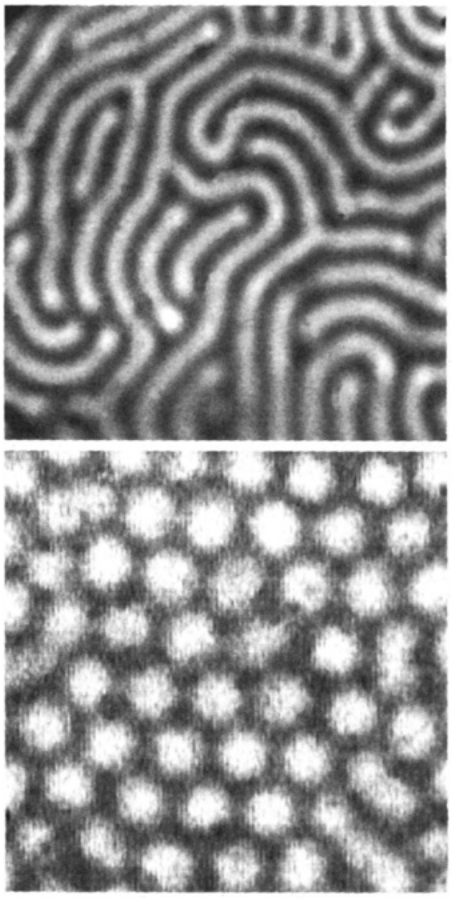

Figure 1. Quasi-two-dimensional Turing patterns in the ClO_2–I_2–MA reaction. Feed concentrations: for stripes, $[MA]_0 = 1.0 \times 10^{-2}$ M, $[ClO_2]_0 = 1.5 \times 10^{-3}$ M at one end, $[I_2]_0 = 8.0 \times 10^{-4}$ M at the other end; for hexagons, $[MA]_0 = 2.0 \times 10^{-2}$ M, $[ClO_2]_0 = 1.0 \times 10^{-3}$ M at one end, $[I_2]_0 = 8.0 \times 10^{-4}$ M at the other end.

simple model systems can be found in the books of Murray[6] and Edelstein-Keshet.[7]

III. The CIMA and Related Systems

The chlorite–iodide–malonic acid reaction was discovered, as one of a series of systematically designed oscillating chemical reactions, at Brandeis in 1982.[15] This reaction is one of the few that show nearly periodic increases and decreases in concentration in a closed (batch) system. It is derived from the ClO_2^-–I^- open system oscillatory reaction, which exhibits a remarkable variety of kinetic phenomena. A number of efforts have been made to describe mechanistically the behavior of the ClO_2^-–I^- reaction in both batch and flow reactors.[16–19] Ouyang[20] has carried out a detailed experimental study of the CIMA reaction. However, relatively little attention has been devoted to the mechanism of the batch oscillations in this reaction, despite its key role in the development of open reactors for studying spatial pattern formation[21] and the discovery of the first Turing structures in this system.[10]

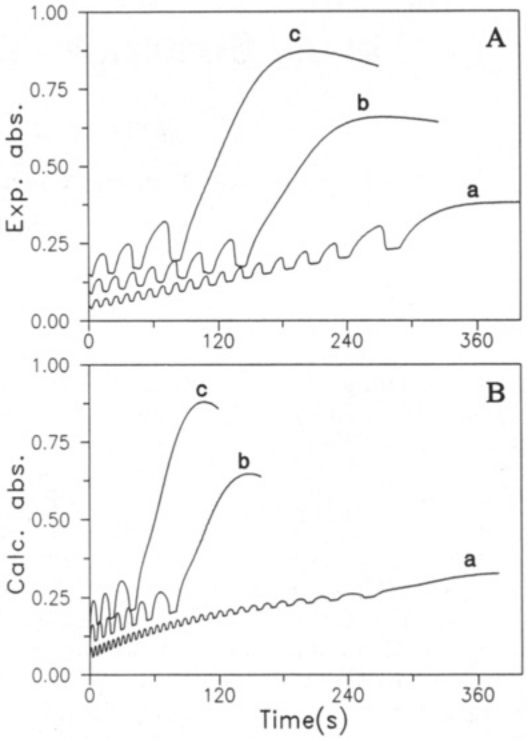

Figure 2. Experimental (A) and calculated (B) oscillations in absorbance (280 nm) in the ClO_2–I_2–MA reaction: $[ClO_2]_0 = 1.7 \times 10^{-4}$ (a), 1.0×10^{-4} (b), 7.1×10^{-5} (c), $[I_2]_0 = 5.0 \times 10^{-4}$, $[MA]_0 = 1.0 \times 10^{-3}$, $[H_2SO_4] = 5.0 \times 10^{-3}$ M. For clarity, curves b and c have been shifted upward by 0.05 and 0.10 absorbance units, respectively, since in the absence of a shift the curves overlap significantly.

After the Turing structures were found, we sought, at the suggestion of the Bordeaux and Austin groups, to develop a mechanism for the CIMA reaction and to see if that mechanism could account for the observed structures. Our efforts proved successful, yielding a mechanism for the reaction that stresses the key role of chlorine dioxide.[22] We have been able to abstract that mechanism to give a simple two-variable model that in one- and two-dimensional simulations yields Turing-type patterns of the same wavelength observed experimentally.[23] Finally, our study of the CIMA system has provided important insights into why it has been so difficult to generate Turing structures in chemical systems, why the CIMA system exhibits these patterns, and how one should be able to design new reactions that display Turing structures.[24] We present below the results of the experiments, of the mechanistic study of the CIMA system, and of the mathematical modeling of the structures.

We first found that a simple extension of the most widely used model of the chlorite–iodide reaction[19] to include the malonic acid–iodine reaction cannot account for the oscillation in batch. One or more essential species and their reactions, which are negligible in a continuous flow reactor (CSTR), must be important in batch. The earlier mechanistic studies did not take into consideration the formation of $ClO_2^\bullet$ in the chlorite–iodide reaction, since the rate of the spontaneous disproportionation of chlorite ion (the assumed source

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of chlorine dioxide) is negligible in comparison to the rates of other component reactions. The possible role of the $ClO_2^\bullet$ radical in chlorite-based oscillators was suggested first by Epstein and Orbán.[25] Later Rábai and Beck[18] demonstrated experimentally that the disproportionation of ClO_2^- to $ClO_2^\bullet$ and Cl^- is accelerated by intermediates of the I_2–ClO_2^- reaction, and that the formation rate of $ClO_2^\bullet$ can be comparable to the rate of the fast chlorite–iodine reaction. Analysis of the spectra of the CIMA system in the course of the reaction resulted in the identification of $ClO_2^\bullet$ as a key species in the batch oscillator. After an initial rapid consumption of most of the chlorite and iodide to generate $ClO_2^\bullet$ and I_2, oscillation results from the reactions of these latter species together with the reactant malonic acid. Support for this hypothesis is provided by the observation that if we start from $ClO_2^\bullet$, I_2, and malonic acid (MA), we observe oscillations with the same waveform and frequency as in the original CIMA system but without any induction period. The oscillatory behavior of this modified chlorine dioxide–iodine–malonic acid system is shown in Figure 2A.

We have employed an empirical rate law approach to describe the CIMA system and its derivatives. A minimal description requires only three component processes and their experimentally determined rate laws: the reaction between MA and I_2 to produce iodide, the reaction between $ClO_2^\bullet$ and I^-, and the reaction ClO_2^- and I^-:

$$\mathrm{MA} + \mathrm{I_2} \rightarrow \mathrm{IMA} + \mathrm{I^-} + \mathrm{H^+} \qquad r_1 = \frac{k_{1a}[\mathrm{MA}][\mathrm{I_2}]}{k_{1b} + [\mathrm{I_2}]} \tag{1}$$

$$\mathrm{ClO_2} + \mathrm{I^-} \rightarrow \mathrm{ClO_2^-} + {}^1/_2\mathrm{I_2} \qquad r_2 = k_2[\mathrm{ClO_2}][\mathrm{I^-}] \tag{2}$$

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

$$r_3 = k_{3a}[\mathrm{ClO_2^-}][\mathrm{I^-}][\mathrm{H^+}] + \frac{k_{3b}[\mathrm{ClO_2^-}][\mathrm{I_2}][\mathrm{I^-}]}{u + [\mathrm{I^-}]^2} \tag{3}$$

The values of the parameters are[22] $k_{1a} = 7.5 \times 10^{-3}\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{1b} = 5 \times 10^{-5}$ M at pH = 2 and $k_2 = 6 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$, $k_{3a} = 460\ \mathrm{M^{-2}\ s^{-1}}$, $k_{3b} = 2.65 \times 10^{-3}\ \mathrm{s^{-1}}$, and $u = 10^{-14}\ \mathrm{M^2}$ at 25 °C. Using overall stoichiometric processes rather than elementary steps for describing a complex kinetic system will yield valid results only if there is no significant interaction between the intermediates of the component processes, i.e., no cross reactions, and if no intermediates build up to high concentrations. If these conditions hold, we can preserve the accuracy and simplicity of formal kinetic rate equations without having to assume rate constants for immeasurable elementary processes. This method has proven fruitful in describing several complex systems.[26,27]

The kinetics of reaction 1 were determined by Leopold and Haim,[28] those of reaction 2 by Lengyel et al.[22] and those of reaction 3 by Kern and Kim[29] and modified by Lengyel et al.[22] This third reaction shows oscillatory behavior in a flow reactor at high input concentrations of ClO_2^- and I^- ($\sim 10^{-3}$ M), but these oscillations do not occur at the lower concentrations employed in the study of the CIMA and related systems, because the key intermediates cannot accumulate to sufficiently high levels. From a dynamical point of view, reaction 3 is the crucial feedback process; it is autocatalytic in iodine and inhibited by the reactant iodide. Under the conditions of interest, $[I_2]$ is always high and almost constant. Thus the autocatalytic feature plays no significant role in the dynamics. However, $[I^-]$ can change by several orders of magnitude, and its inhibitory role is crucial.

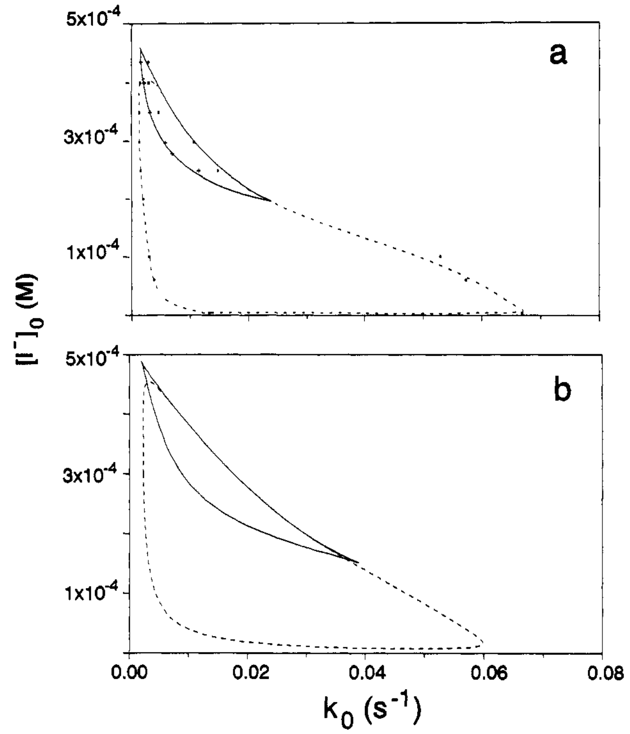

Figure 3. Experimental (a) and calculated (b) two-parameter bifurcation diagrams in the $[I^-]_0$–k_0 phase plane for the ClO_2–I^- CSTR oscillator. Dashed lines enclose regions of oscillation; solid lines bound regions of bistability. $[ClO_2]_0 = 1.0 \times 10^{-4}$ M, $[H_2SO_4] = 5.0 \times 10^{-3}$ M.

The differential rate equations corresponding to reactions 1–3 contain five variables, the concentrations of MA, I_2, $ClO_2^\bullet$, I^-, and ClO_2^-. Numerical integration yields oscillations strikingly similar to those seen in the experiments (cf. Figure 2A,B). The agreement is remarkable considering the simplicity of the model.

The model suggests that the only role of reaction 1 is to produce iodide with a moderate speed. Therefore it should be possible to replace MA by other organics that produce iodide from iodine. We find that oscillatory behavior occurs if ethyl acetoacetate is used in place of malonic acid.[22] Iodide ion can, of course, be supplied not only by a chemical reaction but also by an external input flow. We might therefore expect chlorine dioxide and iodide ion to react with oscillatory kinetics in a flow reactor even without the addition of malonic acid. Experiments[30] show oscillation in the $ClO_2^\bullet$–I^- system in a CSTR over a surprisingly broad range of input concentrations and residence time. In Figure 3a we show an experimental two-parameter bifurcation

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diagram in the [I^-] vs flow rate parameter plane. The corresponding plot calculated from reactions 2 and 3 appears in Figure 3b. Again, the agreement is excellent.

IV. Model Development for Spatial Studies

Solution of the reaction–diffusion equations that describe the spatial behavior of a chemically reacting system is an extremely demanding computational task. For this reason, it is a great advantage to have a simple model with the smallest possible number of variables. The availability of such a model, the Oregonator,[31] is one of the reasons for the popularity of the Belousov–Zhabotinsky reaction for theoretical studies of spatial phenomena.

The model consisting of reactions 1–3 for the ClO_2–I_2–MA reaction lends itself nicely to further simplification. The calculated concentrations of the reactants and intermediates suggest that, under a wide range of oscillatory conditions, [ClO_2^-] and [I^-] change rapidly by several orders of magnitude, but [$ClO_2^\bullet$], [I_2], and [MA] vary much more slowly. We can therefore reduce the above five-variable model (reactions 1–3) to a two-variable system by treating the three slowly varying concentrations as constants. The resulting "reactions" are as follows ($X = I^-$, $Y = ClO_2^-$):

$$\begin{array}{lll} \rightarrow X & r_{M1} = k'_1 & k'_1 = k_{1a}[MA]_0 \\ X \rightarrow Y & r_{M2} = k'_2[X] & k'_2 = k_2[ClO_2]_0 \\ 4X + Y \rightarrow P & r_{M3} = k'_3\dfrac{[X][Y]}{u + [X]^2} & k'_3 = k_{3b}[I_2]_0 \end{array} \qquad (4)$$

On introducing scaled variables and constants we can put the resulting system of differential equations into dimensionless form:

$$\frac{dx}{d\tau} = a - x - 4\frac{xy}{1 + x^2} \qquad (5)$$

$$\frac{dy}{d\tau} = b\left(x - \frac{xy}{1 + x^2}\right)$$

where $x = X/u^{1/2}$, $y = Yk'_3/k'_2u$, $\tau = k'_2t$, $a = k'_1/k'_2u^{1/2}$, $b = k'_3/k'_2u^{1/2}$.

The steady state of this system ($x_{SS} = a/5$, $y_{SS} = 1 + a^2/25$) is unstable if

$$b < 3a/5 - 25/a \qquad (6)$$

The Poincaré–Bendixson theorem[32] guarantees that under these conditions the system will have a periodic limit cycle solution. This inequality defines a surface in the [$ClO_2^\bullet$]$_0$–[I_2]$_0$–[MA]$_0$ plane that separates the regions of stable oscillatory and steady states. The experimental range of oscillation is well described by this equation, except when the initial concentration of $ClO_2^\bullet$ is so low that it is nearly consumed in one oscillatory period, violating the assumption that [$ClO_2^\bullet$] is a constant.

In the experiments on the CIMA system we observed that starch, used as a color indicator of I_3^- ions, and the polyacrylamide gel (PAA) have key roles in producing Turing structures. Starch and other I_3^- indicators form a very stable complex with triiodide ions. Starch and PAA do not constitute an inert medium like the solvent in the corresponding aqueous experiments. Starch and the starch–triiodide complex are nearly immobile, both in the gel and in aqueous solution, because of their high molecular weight. PAA also provides a hospitable environment for both I_2 and I_3^-. Consequently, the diffusivity of I_3^- bound to the gel and/or to the starch is effectively zero. We assume rapid, reversible formation of a starch–triiodide (SI_3^-) complex, according to

$$S + I^- + I_2 \rightleftharpoons SI_3^- \qquad K = \frac{[SI_3^-]}{[S][I_2][I^-]} \qquad (7)$$

where [S] represents the concentration of starch per 6 monomer units needed to form a complete helix.[33] If the formation and dissociation of the complex are rapid, the concentration of SI_3^- instantaneously follows that of I^-, and SI_3^- can be expressed in terms of I^-. If the complex is considered to be immobile and unreactive, which is in accord with the reactivity of I_3^- in other kinetic systems,[34] then the differential equation system that describes the spatiotemporal development of the system is, in dimensionless form,

$$\frac{dx}{d\tau'} = a - x - 4\frac{xy}{1 + x^2} + \frac{\partial^2 y}{\partial z^2} \qquad (8)$$

$$\frac{dy}{d\tau'} = (1 + K')\left[b\left(x - \frac{xy}{1 + x^2}\right) + c\frac{\partial^2 y}{\partial z^2}\right]$$

where $\tau' = (1 + K')\tau$, $K' = K[S]_0[I_2]_0$, c is the ratio of diffusion coefficients of chlorite and iodide ions, and z is the spatial coordinate. A more detailed derivation of eq 8, including the fact that complex formation does not change the composition of the steady state but does modify its stability, can be found in ref 24. If the chemical system has a single unstable steady state and hence shows oscillatory behavior in the absence of starch, complex formation can stabilize the homogeneous steady state and make possible the appearance of Turing structures at parameters which would yield oscillatory kinetics in the complex-free system. Observe that in the above partial differential equation system (8) the *effective* ratio of diffusion coefficients is $(1 + K')c$, which can be much greater than unity even if $c < 1$. Consequently, the presence of a species that forms an appropriate complex with the activator can allow Turing structures to form for a wide range of activator and inhibitor diffusion coefficients.

We may imagine that the I^- ions move not in a simple gel but in a medium with many traps (starch-, gel-bound I_2) that capture I^- for a period of time before releasing it, thereby causing I^- to diffuse and react much more slowly than in the absence of the traps. The complex formation separates the time scale of change of I^- and ClO_2^- ions by a factor of $(1 + K')$.

Several experiments have confirmed this effect of

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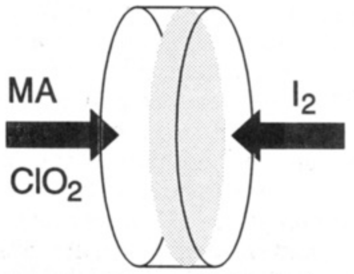

Figure 4. Schematic diagram of a typical arrangement for studying Turing patterns.

starch and the gel. Lee et al.[35] observed Turing structures in a PAA gel in the absence of starch. Experiments by Agladze et al.[12] show structures in a gel-free aqueous solution at high starch concentration. In agarose gel, which does not interact chemically with iodine species as PAA does, the presence of starch is necessary for producing the structures.[12] At low starch concentration the reaction shows traveling waves rather than Turing structures, demonstrating that the system is shifted to the oscillatory state, which is capable of producing waves. Noszticzius et al.[36] have produced Turing structures with polyvinyl alcohol instead of starch as the I_3^- indicator.

Our predictions come from an analytical treatment[6] of eq 8 based on linear stability analysis. This method gives information about the behavior of the system only in the neighborhood of the Turing bifurcation. Nonlinear analysis is more complicated and can be done either numerically or, in fortunate cases, analytically. Rovinsky and Menzinger[37] have analyzed eqs 5 with the diffusion terms, mapped the possible different patterns in the a vs b parameter space, and discussed the interaction of the Hopf[38] and Turing bifurcations in the system.

For modeling the experiments, it is necessary to consider several features of the experimental arrangement (Figure 4). In the experiments there is an inherent gradient in the concentration of the reactant species because of their different concentrations at the boundaries. The structures form perpendicular to this concentration gradient. If the thickness of the medium is small compared with the wavelength of the pattern, the structures are quasi-two-dimensional; only one layer is formed. We have developed a method based on linear stability analysis to find the position of Turing structures along the concentration gradient and the thickness of the layer in which Turing structures form.[39]

Numerical integration of the two-variable model[23,40] gives information about the type of patterns that form when the stable homogeneous steady state becomes unstable to inhomogeneous perturbation. In experiments, the most frequently seen patterns consist of mixed stripes and hexagons. The different modes can be identified by Fourier transforming the observed pattern.

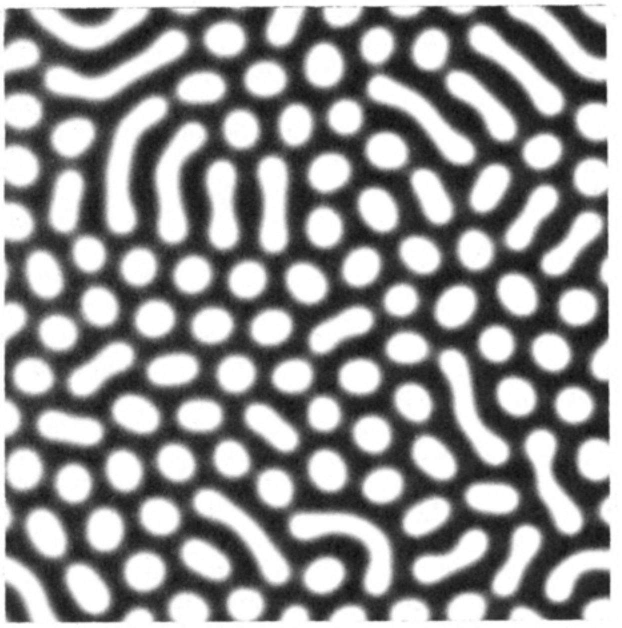

Figure 5. Calculated Turing pattern from eq 8: $a = 90.0$, $b = 4.06$, $c = 1.0$, $K' = 14.6$; number of grid points 320×320 in a total length of 80 dimensionless units. Periodic boundary conditions were applied to decrease the effect of the boundaries on the patterns.

In Figure 5 we show a calculated pattern. The calculation was started with initial perturbations around the homogeneous steady state that were random both in position and in amplitude with a maximum of 0.5%. The resulting patterns are interacting hexagons.

V. Future Prospects

In the Turing structure experiments described above, the starch, which forms an unreactive immobile complex, has a key role in slowing the diffusion of the activator iodide ions. The generalization of this effect is straightforward.[24] With any model, the same transformation used to obtain eq 8 from eq 5 can be applied. The notion of using a complexing agent to retard diffusion of the activator species can then be used to design new chemical systems capable of producing Turing structures. What type of reactions can be used? We have studied many models[5,31,41–47] that show a Turing instability. All of them exhibit homogeneous temporal oscillations for some set of parameter values close to the range of Turing instability. This observation suggests a strong connection between the propensity of

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(38) Phenomenologically, the Hopf and Turing bifurcations may be distinguished as follows. We start from a single homogeneous stable steady state at some set of conditions and then vary a control parameter (e.g., temperature or an input concentration). When a critical value of the parameter (the bifurcation point) is reached, a (normal or supercritical) Hopt bifurcation results in the continuous growth in amplitude of a spatially uniform but temporally periodic oscillation, while a Turing bifurcation leads to a spatially periodic but temporally stationary state. With the Hopf bifurcation, the initial state has become unstable to infinitesimal homogeneous perturbations, while with the Turing bifurcation, that state remains stable to homogeneous perturbation, but is unstable to infinitesimal inhomogeneous perturbations.

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a system to oscillate and its ability to exhibit Turing instability. A simple design (or search) algorithm would start from a system that shows oscillations and in which the activator species is capable of reversible complex formation. The reaction would be run with increasing amounts of complexing agent until the oscillatory state gives way to a stable steady state. The resulting concentrations would serve as a guide for carrying out experiments in a gel reactor.[10,13]

One effect of complex formation is that it decreases the range of oscillation and increases the range of stability of the steady state. An oscillatory reaction mixture can generate traveling waves in an unstirred medium. The stable steady state can lead to a Turing instability. By changing the concentration of the complexing agent in small increments, one can study the transition from traveling waves to Turing structures. This transition has not yet been studied in detail either theoretically or experimentally.

For modeling studies, the experimental arrangement causes some difficulties, because the system to be modeled has three spatial dimensions with a gradient of reactant concentrations along one of these. The structures form inside the gel at a definite distance from the boundaries. The problem requires significant computational resources, in large measure because of the stiffness of the partial differential equations. The two-variable model is a simplified version of the five-variable model based on reactions 1–3. Advances in software will be required to allow treatment of the more accurate five-variable model in three dimensions or even in two dimensions with good spatial resolution.

The model given by reactions 1–3 is based on overall component processes whose individual mechanisms may be quite complicated. Fortunately, under the conditions of interest for Turing structures, interactions between the intermediates of these processes are not significant, and the concentrations of the intermediates are much lower than those of the reactants of the individual processes. In the case of CSTR oscillation of the ClO_2^-–I^- reaction, where the concentrations of ClO_2^- and I^- are much higher, this approximation does not hold. The intermediates play a significant role. Several detailed models have been proposed for the ClO_2^-–I^- reaction,[16,18,19] but none is able to account for both the oscillations in the ClO_2^-–I^- reaction in a CSTR and the oscillations in the CIMA batch system. Further experimental and modeling studies are needed to establish a more appropriate model that accounts for all the experimental observations.

After nearly 40 years of failure, experimental progress in studying Turing structures has been rapid. We may expect further developments in the coming years. Theoretical work[48] suggests that true three-dimensional Turing patterns should show symmetries similar to those found in crystals. Such patterns will be difficult to see with the optical techniques currently employed. A promising alternative is to utilize NMR imaging,[49] which has already been applied to the study of traveling waves in reaction–diffusion systems.[50]

Most studies of Turing structures in chemical systems have employed gel reactors. While this technology has been effective, it is relatively difficult to implement. It is likely that other media that have been utilized for the study of pattern formation in reaction–diffusion systems will be adapted to the study of Turing structures. Examples include membranes[51] and sol-gel glasses.[52] We have recently obtained transient Turing-type structures in a batch gel-free reactor,[53] a configuration that should make this phenomenon far more accessible to experimentalists.

The application of Turing's ideas to fields other than chemistry is becoming a growth industry.[3–7,54] The most rapidly growing applications are likely to come in the field to which Turing originally envisioned applying his ideas, biology. For example, recent experimental advances in obtaining spatially resolved data at the subcellular level by imaging [Ca^{2+}] with calcium-sensitive dyes[55] are likely to lead to the discovery of many more experimental examples of this fascinating phenomenon.

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