Front velocity in models with quadratic autocatalysis

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Front propagation is studied in several reaction–diffusion models based on the Oregonator model of the Belousov–Zhabotinsky reaction. Each system involves autocatalysis (X→2X), termination (2X→0) and consumption of the autocatalyst (X→0, X+Y→0), augmented with interconversion (X→R) between the autocatalyst X and a rapidly diffusing unreactive species R. We investigate the dependence of the front velocity on the diffusion coefficients of X and R, the interconversion rates, and the other kinetic parameters, when the system possesses either one or two stable steady states.


I. INTRODUCTION

Recent discoveries of standing waves, accelerating waves, antispirls, and packet waves in the Belousov–Zhabotinsky (BZ) reaction dispersed in aqueous nanodroplets of water-in-oil Aerosol OT microemulsion (BZ–AOT system)1–3 call attention to the need for deeper understanding and analysis of this system, one of whose most significant features is the presence of species which can diffuse at very different rates. A simple model of the BZ–AOT system4 accounts for many of the experimentally observed phenomena. The model is obtained by augmenting the well-known Oregonator model (O1)–(O5) of the BZ reaction4 with two new reactions (O6) and (O7).

A+Y→X \hspace{1cm} k_1 \hspace{1cm} (O1)
X+Y→P \hspace{1cm} k_2 \hspace{1cm} (O2)
A→2X+2Z \hspace{1cm} k_3 \hspace{1cm} (O3)
2X→P \hspace{1cm} k_4 \hspace{1cm} (O4)
B+Z→hY \hspace{1cm} k_5 \hspace{1cm} (O5)
X→R \hspace{1cm} k_f \hspace{1cm} (O6)
R→X \hspace{1cm} k'_f \hspace{1cm} (O7)

where A=BrO_3^-, X=HBrO_2, Y=Br^-, Z is the oxidized form of the catalyst, B is the sum of malonic and bromomalonic acids, R is BrO_2 radical (or Br_2O_4) in the oil phase, and P represents unreactive products. The overall forward reaction (O6) consists of production of R in a water droplet [HBrO_2+HBrO_3→2BrO_2^- (or Br_2O_4)+H_2O] followed by interfacial transfer of the product from the droplet to the oil phase through the surfactant shell. The overall back reaction (O7) involves interfacial transfer from the oil phase into a droplet and then reaction of R with the reduced form of the catalyst, Cat (Br_2O_4→2BrO_2^-BrO_3^-+Cat→HBrO_2), inside (or at the interface of) the droplet. In most studies of the Oregonator, the concentrations of A and B are taken to be constant, and X, Y, and Z serve as the variables.

The diffusion coefficients of the water-soluble species (X, Y, Z, A, and B) are equal to the diffusion coefficient $(10^{-8}–10^{-7}$ cm$^2$/s) of entire droplets or clusters of droplets, while the diffusion coefficient of the oil-soluble species (R) is about $10^{-5}$ cm$^2$/s.5 The very different diffusion coefficients of X and R, $D_X$ and $D_R$, respectively, raise the question of how the velocity of reaction–diffusion waves in the BZ–AOT system depends on these parameters. For the Oregonator model (O1)–(O5), the wave velocity $c$ is essentially determined by the rate of the autocatalytic step (O3) and is given by the Fisher–Kolmogorov equation6,7 for the minimum velocity, $c_{\text{min}}$, of a propagating front with quadratic autocatalysis (see also Ref. 8).

$$c_{\text{min}} = 2(D_Xk_3[A])^{1/2}.$$

In the full system (O1)–(O7), we have the additional species R with a diffusion coefficient $D_R$ much larger than $D_X$. What effect does the presence of this species have on the velocity of front propagation?

This problem has implications beyond the BZ–AOT system. Therefore we reformulate it more generally. A species X is formed autocatalytically. There are reactions in which this autocatalyst is consumed. Another form of the autocatalytic species, R, is unreactive, i.e., R does not take part in any reactions other than interconversion with X. R can diffuse much more rapidly than X. A biological analog is the production by organisms such as mushrooms, bacteria or plants of inactive forms, e.g., spores or seeds, which can be rapidly spread by the wind. We have not found in the literature, including a recent comprehensive review on chemical waves,9 a treatment of the generic behavior of systems with fast inactive and slow active forms of the autocatalyst or activator species.

In this paper we analyze how front propagation depends on $k_f$ and $k'_f$, which characterize the transformation between the reactive and unreactive forms of the autocatalyst, as well as on the other parameters of system (O1)–(O7). To focus the problem more clearly, we neglect for the moment the dynamics of Y, i.e., step (O5), which is responsible for the negative feedback in the BZ system, and step (O1), in which Y acts to generate X. We take $[Y]$ in step (O2), the decay reaction, to be constant. Under these assumptions, we obtain the following scheme:
with corresponding equations for front propagation in the case of quadratic autocatalysis with “slow” X and “fast” R species:

\[
\frac{\partial X}{\partial t} = k_a^f[X] - k_b[X] + D_X \Delta [X],
\]

(2)

\[
\frac{\partial X}{\partial t} = k_a[X] - k_b[X] - k_d[X] + k_b[R] + D_X \Delta [X],
\]

(3)

where \( k_a = k_1[A] \) is the effective rate constant of autocatalysis, \( k_r = k_2 \) is the termination constant, and \( k_d = k_2[Y] \) is the effective decay rate constant. In one spatial dimension, the Laplacian \( \Delta \) is \( \frac{\partial^2}{\partial x^2} \), where \( \partial \) is the coordinate along the direction of front propagation. The system (2), (3) has one unstable steady state, \( [X] = [R] = 0 \), and one stable steady state, \( [X] = [R] = [Y] = k_1[X]_x / k_b \) (\( [X]_x \) will appear later). This system is an intriguing one, because it gives rise to a large average displacement of \( R(=(D_Xt)^{1/2}) \) and a small shift of the X-front \( (=t(D_Xk_a)^{1/2}) \) for times \( t \ll D_R/(D_Xk_a) \) that significantly exceed the characteristic time of autocatalysis, \( k_a^{-1} \). Transition of R into X far beyond the front and the possibility of autocatalytic growth of X for small initial values of X may lead to a significant increase in the velocity of the propagating front, which transforms \( [X]_1 \) into \( [X]_2 \), above the value predicted by Eq. (1). We analyze this problem in Sec. II.

Another model, which is more faithful to the Oregonator, takes into account the effects of the negative feedback by introducing an additional term, \( -k_{out}[X]/(K_m + [X]) \), replacing Eq. (3) by Eq. (4):

\[
\frac{\partial [X]}{\partial t} = k_a[X] - k_b[X] - k_d[X] + k_{out}[X]/(K_m + [X])
\]

(4)

This modification transforms the unstable steady state \( [X]_1 = 0 \) into a stable steady state \( [X]_1 = 0 \) and an unstable steady state \( [X]_2 \). The resulting bistable system (2), (4) is analyzed in Sec. III.

Finally, by making the steady state approximation, \( d[Y]/dt = 0 \), we obtain \( Y = (k_{out}/k_b)((X) + K_m) \), where \( k_{out} = k_4[X]/[Z] \), and \( K_m = k_1[A]/k_2 \). Using this expression and including all steps in the Oregonator model (O1)–(O7), we have

\[
\frac{\partial [X]}{\partial t} = k_a[X] - k_b[X] - k_d[X] + k_{out}[X]/(K_m + [X] + K_m)
\]

(5)

The system (2), (5) is also bistable, but with nonzero stable steady states \( [X]_1 \) and \( [X]_2 \). It, too, is studied in Sec. III.

System (2), (3) corresponds to the so-called “pulled case” of front propagation in the classification suggested by Ben-Jacob10 and employed in subsequent publications.11–14 In this case, the front propagates into an unstable steady state \( [X]_3 \) \( = [R]_3 \) \( = 0 \) for Eqs. (2), (3), and any velocity \( v \) greater than or equal to a minimum value \( v_{\text{min}} \) yields a solution to the corresponding differential equations. The simplest one-variable example of front propagation, described by the following general equation:

\[
\frac{\partial [X]}{\partial t} = F([X]) + \Delta [X],
\]

(6)

where \( dF([X])/d[X] = F'(0) \) \( = 1 \) at \([X] = 0\), was studied by Aronson and Weinberger.15 They showed that the front velocity asymptotically approaches the value \( v_{\text{min}} = 2 \) [more exactly, \( v_{\text{min}} = 2F'(0)^{1/2} \)] for a localized initial perturbation of the unstable steady state.

Based on a “linear marginal stability” hypothesis, Dee and Langer16 and then van Saarloos12,13 showed how the front velocity \( v_{\text{min}} \) can be found for more complex (usually one-variable) equations, as long as the front still propagates into an unstable steady state. The “marginally stable” velocity \( v_{\text{min}} \) has the property that all fronts with velocity \( v > v_{\text{min}} \) are stable to perturbations, but fronts with \( v < v_{\text{min}} \) are unstable.

Systems (2), (4) and (2), (5) belong to the “pushed case,”11 in which the propagating front switches one stable state to another (an unstable steady state lies between the two). For this case, simple linear stability analysis is insufficient.17 We will compare our computer simulations with linear stability analysis for both cases.

II. SYSTEM WITH A SINGLE STABLE STEADY STATE

A. Linear stability analysis

If there is no interconversion of autocatalyst, \( k_f^f = k_b \)

\( = 0 \), then the velocity of front propagation for Eq. (3) is

\[
c = c_{\text{min}}(1 - k_f^f/k_a)^{1/2},
\]

(6)

where \( c_{\text{min}} \) is given by Eq. (1). For the two-variable system (2), (3), the front velocity, \( v \), may be found by linear stability analysis8,18,19 of the steady state solutions of the ordinary differential equations obtained by introducing the moving coordinate \( \eta = \rho - vt \).

First, we rewrite Eqs. (2), (3) in dimensionless form, substituting new variables \( \tau = k_f^f t, \ x = (k_f^f/k_a)[X], \ r = (k_a/D_R)[R] \), and \( \rho = (k_a/D_X)^{1/2} \rho' \).

\[
\frac{\partial x}{\partial \tau} = f(x) - k_f x + k_b r + \Delta \tau,
\]

(7)

\[
\frac{\partial r}{\partial \tau} = k_f r - k_r r + d \Delta \tau,
\]

(8)

where \( f(x) = (1 - k_d x - x^2, \ k_f = k_f/k_a, \ k_b = k_f/k_a, \ k_d = k_d/k_a, \ d = D_R/D_X, \ \Delta = \partial^2/\partial \rho^2) \). In this dimensionless notation, \( c_{\text{min}} = 2 \).

The linear stability analysis of (7), (8), which involves converting the two partial differential equations to four first-order ordinary differential equations by first introducing the moving frame \( \eta = \rho - vt \) and then defining variables equal to the \( \eta \) derivatives of the concentrations, is identical to that found in Ref. 19 and gives the following characteristic equation:

\[
g(\lambda, \nu) = \lambda^4 + \lambda^3 \nu (1 + 1/\nu)
\]

\[
+ \lambda^2 (d f(x)/d x - k_f - v^2 l - k_b l)
\]

\[
- \lambda (v / l)(k_b + k_f - d f(x)/d x)
\]

\[
- (k_f / l) d f(x)/d x = 0.
\]

(9)
The system has two steady states, \( x_{ss}^{(1)} = 0 \) and \( x_{ss}^{(3)} = (1 - k_0) \), corresponding, respectively to the steady states \([X]_1\) and \([X]_3\) of Eqs. (2), (3). State \( x_{ss}^{(1)} \), on which we focus, gives exactly one positive (\( \lambda_1 \)) and one negative eigenvalue for all values of the parameters.\(^{19}\) The other two eigenvalues may be either complex or real. The second steady state \( x_{ss}^{(3)} = (1 - k_0) \) gives four real eigenvalues, two negative and two positive [Fig. 1(b)].

If Eq. (9) were to possess a pair of complex eigenvalues for \( x_{ss}^{(1)} \), the system would oscillate around \( x_{ss}^{(1)} = 0 \), which would result in negative concentrations, which is physically impossible. The values of \( \nu \) at which complex eigenvalues emerge [points \( A \), \( B \), and \( C \), corresponding to velocities \( \nu_A \), \( \nu_B \), and \( \nu_C \) in Fig. 1(a)] are therefore of special interest, since they allow us to determine the physically allowed range for the velocity of front propagation. The physically meaningful values of \( \nu \), where all eigenvalues \( \lambda \) are real (and all but \( \lambda_1 \) are negative), fall between points \( A \) and \( B \) or to the right of point \( C \) in Fig. 1(a).

The variation of \( \nu_A \) and \( \nu_C \) with some of the system parameters is shown as the bold lines in Fig. 2 (Table I). We see that when \( k_f < 1 \) [actually, when \( k_f + k_d < 1 \), see Fig. 2(f)] and \( k_b < d/2 \) \( k_b < k_d d/2 \), see Figs. 2(e) and 2(h)], the velocities \( \nu_A \) and \( \nu_C \) coexist. The smaller \( k_b \), the more pronounced the difference between \( \nu_A \) and \( \nu_C \). At higher values of \( k_f \) (when \( k_f > 1 \)), points \( A \) and \( B \) coincide with the origin in Fig. 1(a), and all values of \( \nu \) less than \( \nu_C \) give complex eigenvalues. The slower velocity \( \nu_A \) is very close to \( c/e \) in Eq. (6) with \( k_d/k_f \) replaced by \( k_d + k_f \), i.e., \( \nu_A \) is proportional to \( D_X^{1/2} \). The faster velocity \( \nu_C \) attains its maximum, \( \nu_{max} \), at \( k_f = k_b \). More detailed analysis reveals that

\[
\nu_{max} = c_{min} d^{1/2}. \tag{10}
\]

Figures 2(g) and 2(h) show that \( \nu_C/c_{min} \) is proportional to \( d^{1/2} \) (i.e., \( \nu_C \) is proportional to \( D_X^{1/2} \)) at \( k_b < d/2 \), but with a coefficient of proportionality that depends on \( k_f \) and \( k_b \). For example, these coefficients are 0.496, 0.391, and 0.315 for curves 1, 2, and 3, respectively, in Fig. 2(g) (when \( k_f = 1 \)), and 0.495, 0.21, and 0.068 for curves 1, 2, and 3, respectively, in Fig. 2(h) (when \( k_f = 0.1 \)). Figure 2(f) demonstrates that \( \nu_C \) and \( \nu_A \) depend on \( k_d \) as \( \nu_A = v_0 (1 - k_d)^{1/2} \) and \( \nu_A = v_0 (1 - k_f - k_d)^{1/2} \), where \( v_0 \) and \( v_0 \) are equal to \( v_0 \) and \( v_0 \), respectively, at \( k_f = 0 \). These relationships are analogous to Eq. (6) and have a simple explanation. For quadratic autocatalysis, the front velocity is proportional to \( (Dk_{auto}^{1/2} \) [see Eq. (1)], where \( D \) is the relevant diffusion coefficient.

<table>
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<th>TABLE I. Parameters ( k_f ), ( k_b ), ( k_d ), and ( d ) of models (2), (3) and (2), (4) used in Fig. 2.</th>
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\(^{19}\)var=variable.
and $k_{\text{auto}}$ is the effective pseudo-first-order rate constant for autocatalysis. Velocities $v_C$ and $v_A$ may be written as $v_C = \text{constant} \times [D_R h(k_f,k_b)(1-k_d)]^{1/2}$ and $v_A = \text{constant} \times [D_x(1-k_f-k_b)]^{1/2}$, where $h(k_f,k_b)$ is some function of $k_f$ and $k_b$. The dependence of $v_C$ on $k_f$ is more complex than that of $v_A$ [see Figs. 2(a)–2(d)]. For $k_f<k_b$, $v_C$ [i.e., $h(k_f,k_b)$] increases with $k_f$. When $k_f>k_b$, $v_C$ begins to decrease, and for $k_f\approx k_b$, $v_C$ varies as $k_f^{-1/2} [h(k_f,k_b) = \text{constant} \times (k_f/k_b)^{1/2}]$. In contrast, $v_A$ always varies with $k_f$ and $k_d$ as $(1-k_f-k_d)^{1/2}$, because reactions $X \rightarrow 0$ and $X \rightarrow R$ play the same role for $X$.

If we define $k_d^C$ and $d^C$ as the values at which $v_C$ and $v_A$ merge [see Figs. 2(e) and 2(h)], we find that $k_d^C = c(k_f)d^C$, as shown in Fig. 2(i), where for large $d(d>10)$, $c(k_f)$ is of order 1 and depends only on $k_f$; for example, $c(k_f)=0.4$, 0.6, 1.2, 1.5, 1.6 at $k_f=0.01$, 0.1, 0.5, 0.8, 0.9, respectively. For $k_f>1$ or $k_d^C>c(k_f)d$, $d^C$ linear stability analysis gives only a single velocity of front propagation.

The limiting case of Eqs. (2) and (3) when $D_x=0$, which is formally equivalent to $d=\infty$ in Eqs. (7) and (8), provides some insight into the significance of the analysis.\(^{19}\) which is similar to that of Eqs. (7) and (8) (though here we have only three coupled first-order equations to deal with), gives the following characteristic equation:

$$\lambda^3 + \lambda^2(\nu + (1-k_d-k_f)/\nu) + \lambda(1-k_d-k_f-k_f) - k_b(1-k_d)/\nu = 0.$$  

Again, one eigenvalue, $\lambda_1$, is always positive, and its dependence on $\nu$ resembles curve 1 in Fig. 1(a); i.e., $\lambda_1$ monotonically decreases with $\nu$. Now, however, curve 2a is absent, and complex eigenvalues appear only between the analogs of points $v_C$ and $v_B$ (which we designate $v_{CL}$ and $v_{BL}$, respectively). When $k_f<1$, the imaginary part of the complex eigenvalues looks like curve 2b in Fig. 1(a), while for $k_f>1$, only point $v_{CL}$ is present, i.e., a pair of complex eigenvalues exists for all $\nu<v_{CL}$. Numerical solution reveals that $v_{CL}$ and $v_{BL}$ coincide with $v_C$ and $v_B$, except when $\nu$ is close to $v_C$.\(^{20}\) We see in Figs. 2(d) and 2(e) that $v_{CL}$ (curves $L$) is smaller than $v_C$ and $v_A$ at small $k_f$ ($k_f<1$) [Fig. 2(d)] and large $k_d(k_d>2)$ [Fig. 2(e)]. In the limit of $k_f \rightarrow 0$ or $k_b \rightarrow \infty$, the front velocity vanishes for $D_x=0$; it equals $v_A$ (or $v_{min}$) for positive $D_x$. We conclude that the velocity $v_C$ found by linear stability analysis of system (2) and (3) is the front velocity for the limiting case $D_x=0$ and depends only on $D_R$; i.e., when $D_X=0$ the front is “carried by” the species $R$.

B. Computer simulations

In addition to the linear stability analysis, we also integrated the partial differential equations (PDE) (7) and (8) using FlexPDE,\(^{21}\) in which a Newton–Raphson iteration process is used with a variable time step and mesh. FlexPDE refines the triangular finite element mesh until the estimated error in any variable is less than a specified tolerance, which we chose as $10^{-6}$, at every cell of the mesh. Calculations were performed on a quasi-one-dimensional rectangle of width 1 and length $L$, where $L=100$, 200, or 400; the longer rectangles being used for broader fronts. The initial conditions were chosen as $\lfloor X \rfloor_0=k_f\lfloor X \rfloor_0/k_b$, $\lfloor X \rfloor_0=\lfloor X \rfloor_1$ at $0<\rho<L/100$ and $\lfloor X \rfloor_0=\lfloor X \rfloor_1$ at all other points. No-flux boundary conditions and fixed-value boundary conditions with $\lfloor X \rfloor=\lfloor X \rfloor_3$, $\lfloor R \rfloor=k_f\lfloor X \rfloor_1/k_b$ were used at the left boundary and $\lfloor X \rfloor=\lfloor R \rfloor=0$ at the right boundary (the front propagates from left to right). Using no-flux boundary conditions at both borders yields the same result, since the length $L$ is large relative to the characteristic length scales of the system.

At $k_f=0$, the calculated front velocity coincides with the theoretical value, Eq. (1), and the front is quite sharp (Fig. 3, curve 1). The width of the front increases with $k_f$ (Fig. 3, curve 2). Simulations of system (2) and (3) reveal that at any $k_f$ and $k_b$, the calculated velocities (open diamonds in Fig. 2) coincide with the theoretical values $v_C$. Even at $k_f<1$, when two velocities $v_A$ and $v_C$ coexist [see Figs. 2(a), 2(b), and 2(e)], the front velocity is equal to $v_C$ and depends on $D_R$ rather than on $D_X$.

Calculations on system (2) and (3) at large $d(d=100)$ and at $D_X=0$ give nearly identical values of $v$, except at small $k_f$ and large $k_b$. Results for this case are shown in Figs. 2(d) and 2(e) by crosses, which lie on the theoretical curves $L$ ($v_{CL}$).

III. BISTABLE SYSTEMS

A. System (2), (4)

We first modify Eq. (3) by introducing the small additional term $k_{out}[X]/(K_m+[X])$ to produce Eq. (4). This term mimics reaction (O2) if we set $[Y]=(k_{out}/k_2)/(k_m+[X])$, but unlike the more complete Eq. (5), which includes the term arising from reaction (O1) which we consider below, it maintains the steady state at $[X]=0$. The significance of this state is that it allows one to invoke the argument that velocities leading to complex eigenvalues in the linear stability analysis are not physically meaningful, since the system cannot oscillate about a zero concentration. Coupled with the dependence of the positive eigenvalue $\lambda_1$ on $\nu$, this situation allows us to employ linear stability analysis to select $v_A$ and $v_C$ as the stable velocities for wave propagation. We expect the wave front for system (2), (4) to have the same dependence on the system parameters as the front in system (2), (3) as $k_{out}\rightarrow 0$, except when the existence of a threshold concentration of $[X]$, below which autocatalysis cannot start, becomes significant.

FIG. 3. Front profiles for stationary regimes of front propagation in system (2), (3). Parameters $k_a=1$, $k_1=0.01$, $k_0=0$, $k_s=1$, $L=100$, $D_X=0.01$, $D_R=1$, $k_f=(1)\ 0$, (2) 20.
1. Linear stability analysis

The effect on the steady states of adding this new term with relatively small $k_{\text{out}}$ and $K_m$, and $k_{\text{out}}/(k_a - k_d) > K_m$ is shown in Fig. 4(a). The unstable steady state $[X]_1 = 0$ is transformed into a stable state $[X]_1 = 0$ and an unstable steady state $[X]_2$. Under these conditions, $[X]_3 \approx k_{\text{out}}/(k_a - k_d) - K_m$. The difference between $[X]_2$ and $[X]_1$ is the threshold concentration of $X$. In the calculations below, we take $k_d = 0$, so we can replace $k_f$ by $k_f$, $k_b$ by $k_b$, $k_d$ by $k_d$, and $\tau$ by $t$.

We carried out a linear stability analysis of system (2), (4) analogous to that performed for system (2), (3), but with $d(f(x)/dx) = k_a - k_d - 2k_c[X]_2 - k_{\text{out}}K_m/(K_m + [X]_2^2)$ in the characteristic Eq. (9). For the stable states $[X]_1 = [X]_2$, the dependence of the eigenvalues $\lambda$ on $\nu$ resembles that shown in Fig. 1(b) in that all eigenvalues are real and vary monotonically with $\nu$. For the unstable state $[X]_3 = [X]_2$, the behavior of the eigenvalues is analogous to that shown in Fig. 1(a), and the dependence of $\nu_A$ and $\nu_C$ on the parameters mirrors that shown in Fig. 2. For small $k_{\text{out}}$ and very small $K_m$, when $k_{\text{out}}/K_m > 100$, $\nu_A$ and $\nu_C$ depend on the parameters as they do in the monostable case. At small $k_{\text{out}}$ and $K_m$, when $k_{\text{out}}/K_m$ only slightly exceeds 1 (e.g., $k_{\text{out}} = 0.02$, $K_m = 0.01$), $\nu_A$ and $\nu_C$ show qualitative differences (e.g., $\nu_C$ decreases at $k_j < 1$), but the qualitative behavior does not change. Although the steady state concentration $[X]_2$ is positive, and when $\lambda$ is complex small amplitude oscillations around $[X]_2$ are possible in principle, $[X]_2 = [X]_1 = 0$ as $k_{\text{out}} \to 0$, and the velocities $\nu_A$ and $\nu_C$ may still give a good approximation to the actual velocity of the front, despite the fact that the argument regarding complex eigenvalues is applied here to the nonzero steady state $[X]_2$. We analyze this question numerically in the next section. To find exact expressions for the velocity of the front that connects two stable steady states, other mathematical methods may be applied,16,17 which yield a discrete spectrum of possible velocities $\nu_{\text{front}}$. These techniques (analogous to solution of the Schrödinger equation) are beyond the scope of the present paper.

2. Computer simulation

The quasi-one-dimensional partial differential equations (2), (4) were numerically integrated on a rectangle of length $L$ and width 1 with initial conditions $[R]_0 = k_f[X]_0/k_b$, $[X]_0 > [X]_2$ for $0 < \rho < L/100$ and $[X]_0 < [X]_2$ at all other points. Zero-flux boundary conditions were used at the left boundary and $[X] = [R] = 0$ at the right boundary (the front propagates from left to right).

The front velocity depends strongly on $k_f$ and $k_b$. The simulated velocity $\nu$ (shown in Fig. 2 as “24,” filled symbols) coincides with $\nu_C$ when $k_f > 1$ ($k_f > k_b$) or $k_b > c(k_j)d$, and, also in agreement with the results of linear stability analysis, $\nu_{\text{max}} = (D_Xk_d)^{1/2}$ at $k_f = k_b$. However, when $k_f < 1$ and $k_b < c(k_j)d$ [see Figs. 2(a), 2(b), and 2(e)], $\nu$ is significantly smaller than $\nu_C$, lies between $\nu_A$ and $\nu_C$, and $\nu \to c_{\text{min}}$ at very small $k_f$. This behavior differs dramatically from that found for system (2), (3). We conclude that the threshold $[X]_2 = [X]_1$ plays a crucial role for small $k_f$ and $k_b$ $[k_f < k_b, k_b < k_f < c(k_j)d]$ and that the velocity found by linear stability analysis of the unstable steady state $[X]_2$ is not a good approximation to the actual velocity. However, for large $k_f$ or large $k_b$, this threshold is not important.

The inequality $k_f > k_b$ $[k_f > 1]$ is similar to the condition $k_f > k_a$. The forward interconversion reaction $X \to R$ and decay reaction $X \to 0$ both consume the autocatalyst, but differ in that the latter reaction is irreversible. The inequality $k_f > k_a$ implies termination of autocatalysis and leads to a zero front velocity [propagation failure, see Eq. (6)]. The inequality $k_f > k_a$ means that the autocatalytic species $X$ is unable to serve as the front-propagating species, because its interconversion to $R$ outpaces its autocatalytic production. Thus, the front propagation now depends critically upon the diffusion of $R$. Therefore, the calculated $\nu$ coincides with $\nu_C$ at $k_f > 1$.

The inequality $k_f > k_a c(k_j)d$ arises from the competition between the interconversion reaction $R \to X$ and the diffusion of $X$ and $R$. The characteristic diffusion length for $X$ may be estimated as $l_X = (D_X/k_d)^{1/2}$. The characteristic time for $R$ to diffuse a distance $l_X$ is $l_X^2/D_R$. This time may be compared with the characteristic time for transformation of $R$ into $X$, $(k_f)^{-1}$. If $(k_f)^{-1} < l_X^2/D_R$ [which is equivalent, within a factor of order unity, to $k_f > k_a c(k_j)d$], we have equilibrium between $X$ and $R$. Under these conditions, linear stability analysis gives the correct results and the profile of $[X]$ coincides with that of $k_b[R]/k_f$, while for small $k_b$ $[k_f < k_a c(k_j)d]$ and small $k_f(k_f < k_a d)$, the equilibrium condition $k_f[R] = k_b[R]$ does not hold.

The dependence of $\nu$ on $k_d$ [Fig. 2(f)] is well described by the expression $\nu = \nu_0(1 - k_d/k_f)^{1/2}$, where $k_d$ is a small constant that depends on $K_m$ and $k_{\text{out}}$, and $\nu_0 = \nu$ at $k_d = 0$. Figures 2(g) and 2(h) demonstrate that $\nu$ is proportional to $d^{1/2}$, as predicted by linear stability analysis, for $k_f/k_a < c(k_j)d$.

B. System (2), (5)

If we assume that $[Z]$ = constant and make the steady state approximation with respect to $Y$ in the full system (O1)–(O7),22 we obtain system (2), (5) with $k_{\text{out}} = h k_d^2 [B] X[Z]$. System (2), (5) differs from system (2), (4) primarily in that the stable steady state $[X]_1$ now occurs at a nonzero concentration. We expect the dependence of $\nu$ on $k_f$ and $k_b$, and $d$ to resemble that shown in Fig. 2 for system (2), (4), if $[X]_2$
is close to \([X]_1\). In this section, we focus on the dependence of \(\nu\) on \(k_{\text{out}}\) and \(K_m\), which determine the unstable steady state concentration \([X]_2\).

The steady states of this system are given by Eq. (12). The behavior for a typical set of parameters is shown in Fig. 4(b).

\[
d[X]/dt = k_a[X] - k_f[X]^2 - k_{\text{out}}(X - K_m)/([X] + K_m) = 0.
\]

When \([X]_2\) and \([X]_3\) \(\gg K_m\), they may be approximated as \([X]_2 \approx 0.5(k_a + [k_a^2 - 4k_aout]^{1/2})/k_f\). When \([X] \approx k_a/k_f\), \([X]_1\) and \([X]_2\) are given by \([X]_1,2 \approx 0.5([X]_{\text{out}}[k_a - K_m] - 4[X]_{\text{out}}[k_a - K_m])^{1/2}\). Bistability can occur only when \(k_{\text{out}}\) lies between \(k_{\text{out, min}} = K_m(3 + 8/12)^{1/2}\) and \(k_{\text{out, max}} = k_a^2/4k_f\). For this range of \(k_{\text{out}}\), Eq. (12) may be written in the form

\[
d[X]/dt = k_f([X] - [X]_f)([X] - [X]_f)
\]

\[\times ([X]_3 - [X])/([X] + K_m).\]

Note that for the one-variable system described by the cubic equation: \(\partial^3 x/\partial t^3 = (x - x_1)(x - x_2)(x - x_3) + \partial^2 x/\partial x^2\) (where \(x_1 < x_2 < x_3\)), the front velocity \(v_{\text{front}}\) is given by (see, for example, Refs. 8 and 14)

\[
v_{\text{front}} = (x_1 + x_3 - 2x_2)/(2^{1/2}).
\]

We studied the dependence of \(\nu\) on \(k_{\text{out}}\) at a single value of \(K_m\). Our results are summarized in Fig. 5 (Table II). Curve 1 in Fig. 5 is a reference curve for \(k_f = k_b = 0\) [and can be compared with Eq. (14), see curve 0 in Fig. 5]. In all cases, \(\nu\) decreases with \(k_{\text{out}}\) or, equivalently, with the threshold for transition, \([X]_2 - [X]_1\). The sensitivity of \(\nu\) to changes in \(k_{\text{out}}\) (measured as \(\partial \nu/\partial k_{\text{out}}\)) depends on \(k_f\) and \(k_b\). If \(k_f\) is less than 1, but not so small that the diffusivity of \(R\) makes no contribution to front propagation (curves 2 and 5), then \(\partial \nu/\partial k_{\text{out}}\) is large at small \(k_{\text{out}}\); when \(k_f > 1\) (curves 4 and 6), \(\partial \nu/\partial k_{\text{out}}\) is small at small \(k_{\text{out}}\). This behavior arises from the different modes of wave propagation at small and large \(k_f\). When \(k_f > 1\) and \([X]_2\) is small \((k_{\text{out}}\) is small), the velocity \(\nu\) coincides with \(\nu_c\), which is determined primarily by the diffusion of \(R\), for which there is essentially no threshold or barrier. When \(k_f < 1\), the contribution of \(\nu_A\) or, more precisely, of the diffusion of \(X\), to the total velocity \(\nu\) is significant. Therefore the barrier to switching between states, \([X]_2 - [X]_1\), which depends upon \(k_{\text{out}}\), plays an important role. We obtain nearly identical results (curve 5) for \(k_b = 0.04\) or 1 with \(k_f = 0.2\), which suggests that the equilibrium constant \(k_f/k_b\) does not affect the dependence of \(\nu\) on \(k_{\text{out}}\) (or on \([X]_2\)). This conclusion is supported by the fact that curves 3, 5, and 6, all of which have \(k_f/k_b = 5\), show quite different behavior.

IV. CONCLUSION

We have shown that introducing an inactive, rapidly diffusing form, \(R\), of the activator species, \(X\), causes significant changes in the propagation velocity given by the Fisher–Kolmogorov equation (1).

In general, the velocity of the propagating front depends on both diffusion coefficients \(D_X\) and \(D_R\). If \(k_f > k_a\), the wave is “carried” largely by the rapidly diffusing species, and \(\nu\) depends mainly on \(D_R\). When \(k_f < k_a\) and \(k_f < k_a\) \(\ll k_f\), only a small amount of the activator is transformed to \(R\), and wave propagation should depend primarily on \(X\) and \(D_X\). This is indeed the case for the bistable system (2), (4), but, for the monostable system (2), (3), which does not possess a threshold of \([X]\) for initiating autocatalysis, the velocity still depends on \(D_R\). Very small concentrations of \(X\) far beyond the main visible front can lead to autocatalysis and acceleration of the front in system (2), (3). The existence of a threshold \([X]_2 - [X]_1\) in the bistable system (2), (4) wipes out this effect. The analogous result was obtained for discrete systems,19,23–25 and so-called “cutoff” fronts,26 where a threshold was present.

For system (2), (4), at intermediate transformation rates \((k_f < k_a)\) and at \(k_b < k_{\text{act}}(k_f)d\), the velocity lies between the limits \(\nu_A\) and \(\nu_C\) determined by the diffusion rates of pure \(X\) and pure \(R\). We have not obtained analytical expressions for \(\nu\) in this range of parameters, where linear stability analysis is not sufficient.

The velocity attains its maximum value when \(k_f = k_b\), because the system is then able to balance the two “forces” that tend to drive the wave forward. If \(k_f\) is much larger than \(k_b\), the system is depleted of the activator \(X\), and the autocatalytic reaction slows down, much as occurs if the rate of the decay reaction increases [see Fig. 2(f)]. If, on the other hand, \(k_b\) is too large, \(k_b > k_{\text{act}}(k_f)d\), not enough \(R\) is present, and the system cannot “take advantage” of that species’ more rapid diffusion rate. If \(k_f\) and \(k_b\) exceed the character-

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**TABLE II.** Parameters \(k_f\) and \(k_b\) for model (2), (5) used in Fig. 5.

<table>
<thead>
<tr>
<th>Curve</th>
<th>(k_f)</th>
<th>(k_b)</th>
</tr>
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<tr>
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<td>0</td>
</tr>
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<td>0.2</td>
</tr>
<tr>
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<td>1</td>
</tr>
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</tr>
<tr>
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<td>5</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>
istic reaction and diffusion rates of the system \( k_f^r > k_a, k_b^r > k_a c(k_f^r) d \), then X and R reach (pseudo)-equilibrium, and the results of linear stability analysis describe both systems (2), (3) and (2), (4) well.

Analysis of the full system (O1)–(O7) shows standing waves only when \( k_f^r < k_a \) and \( k_b^r < k_a c(k_f^r) d \). It is an open question whether there is an inherent connection between the existence of two possible velocities \( v_A \) and \( v_C \) for traveling waves and the ability to support standing waves.

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20 Note that the maximum value of \( v_C \) is 1, at \( k_f=k_b \). In Fig. 2 it appears that \( v_{CA} \) is \( v_{CL} \), because, to compare \( v_{CL} \) with \( v_{CA} \), we present \( v_{CL} \) as \( v_{CL}/(4D_X) \). With \( D_X \) set to 0.01, the value used for simulation of the full system (2), (3).
22 Making the steady state approximation with respect to Z, as opposed to treating \( Z \) as a parameter, yields a system that resembles (2), (3) in having two non-negative steady states, an unstable one at \( Z = 0 \) and a stable one at positive \( X \). This version of the model has an additional, unphysical steady state at negative \( X \).