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Quantitative Theoretical Study of the Speed of Propagation of Chemical Waves in the Belousov-Zhabotinskii Reaction

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A quantitative study of the wave propagation speed according to the reaction-diffusion equations governing the Belousov-Zhabotinskii reaction for both ferroin and cerium catalysis was carried out. Two types of approximations for the set of equations were made; in one, the influence of the bromide regeneration process was neglected. For ferroin, this appeared to be a correct approximation, because both sets lead to results in good agreement with experiment. For cerium systems, this process is shown to play a role in the saturation of the velocity curve at high [H^+] and [BrO_2^-].

Introduction

One of the best-studied and most visual examples of self-organization in chemistry is the formation of spatial patterns in the classic Belousov-Zhabotinskii (BZ) reaction. This reaction's overall concern is the oxidation of malonic acid by an acidic solution of bromate and bromide in the presence of a catalyst. The patterns usually appear in the form of concentric rings or spirals of oxidation propagating with constant velocity through a thin layer of the reduced reagent.

Over the past 15 years, several attempts have been made to describe BZ waves theoretically by their reaction-diffusion equations implied by the Oregonator model. Quantitatively, these attempts were not very successful, but much improvement has been made with the revised set of rate constants. Apart from two papers, a detailed systematic theoretical study of the dependence of wave velocities on reactant concentrations was, however, to our knowledge, not made. Kuhnert et al. explained the experimental parameter values of ferroin waves in a somewhat simplified analytical way. Nagy-Unvarai et al. recently presented a more accurate numerical study on cerium waves. In this paper, we will try to give a detailed quantitative description of the wave velocity as a function of reactant concentrations by numerically integrating the mass action kinetic equations that can be derived from the extended Oregonator model, taking into account the reversibility of the two partial reactions of the autocatalytic reaction. We did this by making two different approximations, one of which leads to a set of equations that differs in some important features from those recently used to describe wave propagation. Both sets will be compared with each other and with the experimental results.

BZ Waves: Summary of Experimental Results

In principle, the velocity v of BZ waves depends on three external variables: reactant concentrations, temperature, and solution viscosity.

Jorne carried out experiments varying the viscosity η of the solution at fixed temperature and found that

\[ v \sim \eta^{1/2} \]  \hspace{1cm} (1)

in agreement with theoretical dependence (at fixed concentrations):

\[ v \sim (Dk)^{1/2} \sim (K/\eta)^{1/2} \]  \hspace{1cm} (2)

| TABLE I: Activation Energy E_p for BZ Waves |
|-----------------|----------------|------------------|-----------------|
| catalyst        | E_p, kJ/mol    | temp range, °C   |
|-----------------|----------------|------------------|-----------------|
| ferroin         |                |                  |
| Kuhnert et al.  | 34.9 ± 1.2     | 11-45            |
| Wood and Ross   | 34.0           | 11.9-24.8        |
| this paper      | 38.8 ± 1.2     | 3-35             |
| theoretical     |                |                  |
| Kuhnert et al.  | 37.7 ± 2.5     | 0-40             |
| this paper      | 38.1 ± 1.5     |                  |
| Ru(bpy)_2       | 37.6 ± 3.2     | 15-40            |
| Kuhnert and Krug |              |                  |

<p>| TABLE II: Parameters of Eq 4 for Different Catalysts at T = 25 °C |
|-----------------|----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>catalyst</th>
<th>intercept A, mm/min</th>
<th>slope B, mm/(min·M)</th>
<th>concn range (H^+)[BrO_2^-])^{1/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>ferroin</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field and Noyes</td>
<td>-0.83</td>
<td>27.87</td>
<td>0.18-0.34</td>
</tr>
<tr>
<td>this paper</td>
<td>-0.999</td>
<td>27.33</td>
<td>0.11-0.15</td>
</tr>
<tr>
<td>Ru(bpy)_2</td>
<td>-0.82</td>
<td>28.2</td>
<td>0.19-0.27</td>
</tr>
<tr>
<td>Kuhnert and Krug</td>
<td>-1.2</td>
<td>27.5</td>
<td>0.15-0.22</td>
</tr>
<tr>
<td>Nagy-Unvarai et al.</td>
<td>-2.1</td>
<td>22.5</td>
<td>0.18-0.38</td>
</tr>
<tr>
<td>cerium</td>
<td>+2.3</td>
<td>10.4</td>
<td>0.38-0.52</td>
</tr>
</tbody>
</table>

*For the ferroin + bromate reaction. [Ce]_in = 0.003 M. *Estimated by us.

where D is the diffusion coefficient of the autocatalytic species HBrO_2 and k is the rate constant of the autocatalytic reaction. Varying the temperature gives Arrhenius-type dependencies for both ferroin and Ru(bpy)_2-catalyzed waves, according to

\[ v \sim (D_0 \exp(-E_0/RT) A \exp(-E_u/RT))^{1/2} \]  \hspace{1cm} \sim \exp(-E_v/RT) = \exp(-E_v/RT) \]  \hspace{1cm} (3)

with E_v activation energies.

Our experiments on ferroin waves were carried out in a closed thermostated Petri dish by enlarging the patterns on a wall with the aid of an overhead projector and marking the front propagation at discrete time intervals. For the composition of the solution the usual Winfree recipe was followed. See Figures 1 and 2. Experimental and "theoretical" values for E_v are listed in Table I. For Ce waves, no straight line was obtained by Nagy-Unvarai et al., which they attribute to the impossibility of regarding the autocatalytic process as one irreversible step in the case of cerium catalysis.

References

TABLE IV: Parameter Definitions and Their Values Used for Simulation

<table>
<thead>
<tr>
<th>parameter</th>
<th>definition</th>
<th>value for Fe</th>
<th>value for Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>$g$</td>
<td>$(2k_{R6}k_{Ba})/(k_{R6}k_{Ba})$</td>
<td>0.0002</td>
<td>0.0002</td>
</tr>
<tr>
<td>$r$</td>
<td>$(k_{R6}Y_{steady})/(k_{R4}A)A)$</td>
<td>(0.75M)/[BrO$_3^-$]</td>
<td>(0.4M)/[BrO$_3^-$]</td>
</tr>
<tr>
<td>$b$</td>
<td>$(k_{R5}/k_{R6})$</td>
<td>250[H$^+$] / M</td>
<td>250[H$^+$] / M</td>
</tr>
<tr>
<td>$M$</td>
<td>$(k_{R4}/k_{R5})$</td>
<td>0.05[H$^+$] / M</td>
<td>0.05[H$^+$] / M</td>
</tr>
<tr>
<td>$k_{R5}$</td>
<td>$(2k_{R5}k_{R5}/k_{R5}k_{R5})$</td>
<td>(1.6 * 10$^{-3}$)$^2$ / [H$^+$]$^2$</td>
<td>(16M$^2$)/[H$^+$]$^2$</td>
</tr>
<tr>
<td>$k_{R6}$</td>
<td>$(k_{R6}/2k_{R6})$</td>
<td>0.01</td>
<td>2.5</td>
</tr>
<tr>
<td>$c$</td>
<td>$(k_{R6}Z_{ concat}/(k_{R6}A)A)^2$</td>
<td>(100M[Fe(III)] / (100M[Ce(IV)])</td>
<td>(100M[Fe(III)] / (100M[Ce(IV)])</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>$k_1$([org]) / ([org] / ([org])$^2$)</td>
<td>(0.01M[org]) / (0.01M[org])</td>
<td>(0.01M[org]) / (0.01M[org])</td>
</tr>
<tr>
<td>$m$</td>
<td>$(2k_{R6}/(k_{R6}A))^2$</td>
<td>(4 * 10$^{-3}$)/[H$^+$]$^2$</td>
<td>(0.04M)/[H$^+$]$^2$</td>
</tr>
</tbody>
</table>

$Y_{steady}$ is the "steady-state" bromide concentration ahead of the wave. For Fe waves, a reasonable estimate was made by Field and Noyes, proposing $Y_{steady} = 3.0 \times 10^{-3}$ M, which is also confirmed by Showalter's experiments. For Ce waves, such an estimate was not available to us. We took it to be ca. $1.5 \times 10^{-3}$ M, giving the best comparable results. $Y_{initial}$ is taken to be independent of [H$^+$] and [BrO$_3^-$]. $Z_{initial} = 0.003$ M in Winfree's recipe. $[\text{org}] = 0.12$ M in Winfree's recipe.

model for it, called the Oregonator model$^{14}$ representing the skeleton of the FKN mechanism. In the investigation described in this paper, we shall use an extended version of the Oregonator model given by

$$A + Y \rightarrow X \quad (M1)$$
$$X + Y \rightarrow P \quad (M2)$$
$$A + X \rightarrow 2U \quad (M3a)$$
$$U + Z' \rightarrow X + Z \quad (M3b)$$
$$2X \rightarrow Q \quad (M4)$$
$$Z \rightarrow hY + Z' \quad (M5)$$

where $X = HBrO_2, Y = Br^{-}, Z = \text{cat.}^{(+)} + (\text{Ce(IV), Fe(III)}), A = \text{BrO}_3^{-}, U = BrO_2^{+}, Z' = \text{cat.}^{(+)}$ (so $[Z'] = [Z]_{initial} - [Z]$), $P$ and $Q$ are reaction products, and $h$ is some stoichiometric coefficient with rate constants $k_{M1} = k_{R6}[H^+]^2, k_{M2} = k_{R6}[H^+], k_{M3} = k_{R5}, k_{M4} = k_{R6}[H^+], k_{M5} = k_{R5}, k_{M6} = k_{R6}, k_{M7} = k_{R6}k_{M4} = k_{R6},$ and $k_{M8} = k_1[\text{org}] ([\text{org}] = [\text{malonic acid (MA)}] + [\text{bromomalonic acid (BrMA)])]$, where the subscripts R2-R6 and J correspond to the FKN reactions (see also refs 7 and 13). The rate constant values are the same as those used in ref 7 and are listed in Table III.

To obtain a mathematically manageable set of differential equations, it is convenient to nondimensionalize the variables. The set implied by the extended Oregonator model for a stirred system is

$$du/dt = qru - u^2 - u - urw + \kappa_s s^2 + (c - w) s - \kappa_{4u}w$$
$$dv/dr = -Mv - bwv + \frac{h_{eb}}{r}w$$
$$dw/dt = (c - w) s - \kappa_{4u}w - \epsilon w$$
$$mds/dt = 2u - 2\kappa_s s^2 - (c - w) s + \kappa_{4u}w$$

where

$$u = \frac{2k_{R6}X}{k_{R6}HA} \quad v = \frac{k_{R5}Y}{k_{R5}Ar} \quad w = \frac{2k_{R6}Z}{k_{R6}HA}$$
$$s = \frac{k_{R6}U}{k_{R6}A} \quad t = \frac{k_{R6}HA}{t}$$

where $H = [H^+], A = [\text{BrO}_3^{-}], X = [HBrO_2]$, etc. The definition of the parameters $g, r, b, etc., is listed in Table IV together with their explicit numerical values used for simulation.$^{15}$

Assuming that the BrO₂⁺ radical moves on the fastest time scale and its concentration instantaneously adjusts to HBrO₂ and cat.\([\text{H}^+]\) concentrations (i.e., the left-hand side of the fourth equation of set 1 is always close to zero), the resulting set of equations is

\[
\frac{du}{dt} = q(c - w) - \kappa_sw^2 \\
\frac{dv}{dt} = -Mu - bw + \frac{he}{r}w \\
\frac{dw}{dt} = (2u - 2\kappa_sw^2) - ew \\
s = \frac{-(c - w) + [(c - w)^2 + 8\kappa_sm(2 + \kappa_qw)]^{1/2}}{4\kappa_sw} \tag{II}
\]

We will compare computational results for wave velocities for two kinds of approximations to this set, which can be referred to as "Tyson's two-variable Oregonator" model and "moving-band equations".\(^{16}\)

**Tyson's Approach.** Tyson\(^{17}\) treats (II) by ignoring the time dependence of bromide with respect to that of HBrO₂ and the catalyst:

\[
L \frac{du}{dt} = q(c - w) + \frac{he}{r}w \tag{5}
\]

Introducing a dimensionless space according to

\[
x = (k_{\text{RZH}}HA/D)^{1/2} \tag{space}
\]

with \(D\) being the diffusion coefficient (of HBrO₂), substituting (5) in (II), and coupling the equations with diffusion terms, the Tyson set is obtained (assuming \(D_x = D_z = D_T\)):\(^{11}\)

\[
\frac{du}{dt} = u(1 - u) - hbw - q + \frac{d^2w}{dx^2} \\
\frac{dw}{dt} = (2u - \kappa_sw^2) - ew + \frac{d^2w}{dx^2} \tag{III}
\]

which can yield traveling-wave solutions with velocities equal to

\[
v = (k_{\text{RZH}}D[H^+][\text{BrO}_3^-])^{1/2} \tag{VI}
\]

\(\lambda\) being the dimensionless wave velocity (compare eq 2).

Tyson's approach has some important advantages. First, it reduces the (extended) Oregonator model to a two-variable model. This makes the mathematically powerful technique of phase-plane analysis possible. Furthermore, there are no problems with initial or boundary values for \(v\) (necessary for solving partial differential equations).

**Moving-Band Approach.** The moving-band equations are only concerned with the processes determining the wave propagation speed, and therefore, Field and Noyes\(^{2}\) and also Murray\(^{3}\) suggested that the bromide regeneration reaction (M5) is of minor importance in the wave front because it is a slow reaction \((\epsilon \ll 1)\). Murray further supposed \(q = 0\) and \(M = 0\) (i.e., neglecting the influence of reaction M1 (also a slow reaction)), so we obtain

\[
\frac{du}{dt} = u(1 - u) - hbw - q + \frac{d^2u}{dx^2} \\
\frac{dw}{dt} = -bw + \frac{d^2w}{dx^2} \\
\frac{dv}{dt} = (2u - \kappa_sw^2) + \frac{d^2w}{dx^2} \tag{IV}
\]

The advantages of this approach are that we do not have to make assumption 5 \((1/b \ll 1, \text{neglecting bromide diffusion})\), which might become poor at low \([\text{H}^+]\), and that we don't have to worry about the values of \(h\) and \(k_\text{p}\), which still remain very vague parameters with large uncertainties. Of course, the moving-band model is not capable of describing temporal oscillations.

There are some experimental indications that the main assumption of the moving-band approach (i.e., reaction M5 has no significant influence on the wave velocity) is acceptable. First, both ferroin and cerium waves show little or no dependence on \([\text{org}]\). This variable is only encountered in reaction M5 and in parameter \(e\) in the model. Second, and more important, for ferroin waves there is no significant difference in the velocity dependence of trigger waves on \([\text{H}^+]\) and \([\text{BrO}_3^-]\) between the BZ reaction and the ferroin oxidation by bromate without 

\[\text{malonic acid in the solution, as shown by Showalter}^{11}\] (see Table II). Therefore, we think it would be interesting to see what happens if we leave reaction M5 out, which seems to be a reasonable assumption when describing wave propagation speeds.

**Ferroin-Catalyzed BZ Reaction.** For the ferroin-catalyzed system, it is a good approximation to say that \(\kappa_s = 0\). So the Tyson set reduces to

\[
\frac{du}{dt} = u(1 - u) - hw - q + \frac{d^2u}{dx^2} \\
\frac{dw}{dt} = 2u - ew + \frac{d^2w}{dx^2} \tag{V}
\]

and we also obtain the original Murray set

\[
\frac{du}{dt} = u(1 - u) + \frac{d^2u}{dx^2} \\
\frac{dw}{dt} = -bw + \frac{d^2w}{dx^2} \tag{VI}
\]

Both sets are relatives of the classic Fisher equation:

\[
\frac{du}{dt} = kw(1 - u) + D \frac{du}{dx^2} \tag{7}
\]

which can be shown to have solutions with the wave speed \(\lambda = 2(kD)^{1/2}\).

In the case of the Tyson set, the lower boundary conditions, i.e., the concentrations of the reduced steady state ahead of the wave, are easily calculated by setting the nondiffusional equations equal to zero, giving (for \(h\) larger and not to close to 0.5)

\[
u_{\text{red}} = \frac{h + 0.5q}{h - 0.5q} \quad w_{\text{red}} = \frac{h + 0.5q}{h - 0.5} \epsilon \tag{8}
\]

with \(h \approx 1.5\) for a reduced excitable medium, as suggested by Tyson. For the Murray set, the lower and upper conditions are given by \(0 \leq u \leq 1\) and \(0 \leq v \leq 1\).

Both the Tyson and Murray sets were integrated numerically by Euler integration with a finite difference approximation for the Laplace operator \((d/dx^2)\), in the case of the Tyson set by initiating a trigger wave at the end of a line and in the case of the Murray set by taking the initial conditions equal to Heaviside initial conditions. In most of our simulations, the spatial step size was 50/300 dimensionless spatial units and the temporal step size was 0.01 dimensionless temporal unit. The accuracy of many
For calculating dimensionlized wave velocities, we have to use eq 6. Here we are confronted with a problem if we want an accurate description of the velocities: the need for an accurate value of $D$. This $D$ reflects the diffusibility of the autocatalytically generated species HBrO$_3$. Unfortunately, its accurate value is not available. Estimates in the literature vary from $1.2 \times 10^{-5}$ to $2.0 \times 10^{-5}$ cm$^2$ s$^{-1}$, extrapolated from known values of related chemicals ($D_{\text{ClO}_3} = 1.3 \times 10^{-5}$, $D_{\text{Br}_2} = 2.08 \times 10^{-5}$). Such an uncertainty is often used as an opportunity to adjust the numerical value to the best agreement with experiment. We will do the same and even make use of the situation by using two different values of $D$. When presenting the results of the Tyson set, we have used $D = 1.5 \times 10^{-5}$ cm$^2$ s$^{-1}$, as Tyson suggests, and in the case of the moving-band model, we used $D = 1.8 \times 10^{-5}$ cm$^2$ s$^{-1}$, as Field and Noyes originally suggested. We admit that this is somewhat uncomfortable situation, permitted (or better, not prohibited) by the large uncertainty of $D$. However, we see no other way of making a comparison between the possible approaches, because by taking one single value of $D$, one of the two approaches would immediately pay off.

So we obtain for the Tyson set

$$v (\text{mm/min}) = -0.62 + 27.6X$$

for $0.18 < X < 0.35$, with $X = ([\text{H}^+][\text{BrO}_3^-])^{1/2}/M$, and for the Murray set

$$v (\text{mm/min}) = -1.05 + 27.4X$$

for $0.10 < X < 0.40$, both in excellent agreement with experiment.

A graphical representation of (9) and (10) is depicted in Figures 5 and 6.

The solutions of the Murray set are, of course, not dependent on the total catalyst concentration or the (MA + BrMA) concentration, as experimentally observed. The Tyson set is also not dependent on the total catalyst concentration (no $c$ in (V)) but slightly dependent on $[\text{org}]$. For the same values of $H = 0.40$ M and $A = 0.30$ M, we calculate $\lambda = 1.70$ for $[\text{org}] = 0.12$ M and $\lambda = 1.62$ for $[\text{org}] = 0.36$ M. This means that according to Tyson’s equations $v$ should slow down a bit with increasing $[\text{org}]$, whereas experimentally $v$ seems to speed up very slightly with increasing $[\text{org}]$.

One poor feature of the Tyson set is that it is not capable of explaining the dependence as observed in the ferroin + bromate reaction. In that situation, $\epsilon = 0$, so the Tyson set reduces to the Fisher equation with $\lambda = 2$, with no negative intercept in the velocity curve. We feel that this is caused by neglecting bromide diffusion through assumption 5.

In the literature, there is no agreement about the cause of the negative intercept, which is significant in the experiment. We subscribe to Kuhnert’s point of view that in ferroin systems this is the result of the inhibition by bromide through reaction M2 in the Oregonator model ((R2) in the FKN mechanism). Neglecting this reaction would reduce the Murray set (VI) to the Fisher equation. In the Tyson set, reaction M1 still plays a role. However, we expect it to be small because this reaction is first order in [BrO$_3^-$] but second order in [H$^+$] and this deviating dependence is not observed in experiment. This is also an argument for leaving out (M1), as is done in the moving-band approach.

**Cerium-Catalyzed BZ Reaction.** Ce-catalyzed BZ waves require a numerical solution of sets III and IV. The Tyson set (III) was integrated by Nagy-Unvár et al. with boundary values (8), the moving-band set by us with boundary values $u_{\text{red}} = 0$, $v_{\text{red}} = 1$, and $w_{\text{red}} = 0$. The results are given in Figures 7 and 8.

In both figures, [BrO$_3^-$] is taken as a constant (0.30 M). The reason for this is that the model is not capable of giving the correct dependence of $\lambda$ and $v$ on [BrO$_3^-$]. This is a direct consequence of reaction M3b, not present in the original Oregonator model. Its reaction rate depends on [H$^+$] but not on [BrO$_3^-$].

---

of the saturation effect lies in the competition between reactions on \([\text{BrO}^-,\]) of the (-M3a) reaction rate is hardly competitive with (M3b) and in doing so reduces the autocatalytic concentrations of HBrO, and Ce(IV) in the resting excitatory solution increase and in that manner inhibit the autocatalytic production of HBrO by speeding up reaction -M3b. In the moving-band model, both [HBrO2] and [Ce(IV)] in the reduced medium are zero, because of the absence of reaction M5 in this model. Thus, reaction M5 plays a role, in an indirect way, in the determination of the wave speed of Ce waves. In ferron systems, this role is negligible because the ratio of the reaction rates \(k_{R5}/k_{R6}\) is much smaller (see Table III).

Although the value of \(\tau\) is highly uncertain in the case of cerium waves, Figure 8 nevertheless shows that bromide should be accounted for completely in the model if one wants to make an accurate calculation of the wave speed (at low \([\text{H}^+])\). In our opinion, the cause of the negative intercept of the solutions of (III) and (IV) finds its origin not only in the absence of reaction M5 in (IV) but also in assumption 5 in the derivation of (III).

Both sets describe the dependence of \(u\) on the total cerium concentration satisfactorily. For the results of (III), we refer to ref 7. We will not show our calculations of (IV) here. Set IV shows, of course, no dependence on [org], as experimentally observed. Set III shows a slight dependence on [org]. For the same values of \([\text{H}^+]\) = 0.40 M and \([\text{BrO}^-]\) = 0.30 M, we calculate \(\lambda = 1.15\) for [org] = 0.12 M and \(\lambda = 1.06\) for [org] = 0.36 M.

Conclusions

Jahneke et al.\(^{(19)}\) have remarked rightly that computations from reaction–diffusion equations for BZ systems still remain to some degree "an exercise in curve fitting", because of the uncertainty of some of the parameter values. However, by using Tyson's Lo rate constants together with a reasonable estimate for the diffusion coefficient of HBrO\(_2\), the Oregonator model appears to be able to account for the wave speed dependence on reactant concentrations in quantitative detail. Both the intercept and slope are in good agreement with experimental values, especially in the case of ferron waves.

Such a quantitative description also exposes some deficiencies of the Oregonator model. First, there is the incorrect theoretical dependence of the speed of Ce waves on \([\text{BrO}^-]\), caused by reaction R6. Because the FKN mechanism seems quite settled on this point, it is not clear how to correct the model. Second, there is the much criticized process J. Although it accounts surprisingly well for the saturation effect in the Ce velocity curve and also gives a qualitative good reproduction of the Ce concentration profiles (but not quantitative),\(^{(20)}\) its parameter values \(k_J\) and especially \(h\) remain uncertain. It is not even clear if it is correct to give \(h\) a unique value. Tyson himself has used two different values of \(h\) in one of his papers.\(^{(21)}\) Such an approach would, of course, dramatically change the results of sets III and V. Our calculations also show that the wave process J defines the role of Mn and Br:Mn in the bromide regeneration is probably too simplified. Both Fe and Ce waves are predicted by the model to slow down a bit with increasing [org], whereas experimentally there is no dependence of [org], or at least no reduction of \(u\) with increasing [org].

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