N(1), NH_2(6), and N(7) of AMP adenine rings. The bond distances determined from the ^{15}N investigation clearly show that the metal–nucleotide ring interaction is an *inner-sphere* coordination effect. Evidence for two separate binding sites is presented and serves to explain an anomalously short Mn^{2+}–C(8) bond distance.

Extension of these multinuclear studies to ^{15}N-enriched nucleotides will allow investigation of 1:1 metal–nucleotide complexes at physiologically significant nucleotide concentrations, <0.01 M; such studies will be initiated in this laboratory.

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Role of Diffusion in Trigger Wave Propagation in the Belousov–Zhabotinskii Reaction

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Abstract: The role of diffusion is investigated in the ferroin-catalyzed Belousov–Zhabotinskii reaction. Trigger wave patterns are formed and the velocity of propagation of the front bands is correlated to the diffusion coefficients of the participating species. The diffusion coefficients are varied by adjusting the viscosity of the solutions. The propagation velocity is proportional to the reciprocal of the square root of the viscosity, hence it depends linearly on the square root of the diffusion coefficient. This behavior is in agreement with theoretical predictions based on the coupling between the kinetic model and diffusion.

Introduction

The Belousov–Zhabotinskii reaction is the only known chemical reaction exhibiting both temporal and spatial oscillations. Belousov[1] first reported temporal oscillations during the cerium ion catalyzed oxidation of citric acid by bromate ion. Zhabotinskii[2,3] demonstrated oscillations in similar systems where the cerium ion can be replaced by Mn^{2+} and $Fe(phen)_3^{2+}$ and the citric acid can be replaced by malonic and maleic acid derivatives.

Busse[4] observed the formation of horizontal bands in solutions subjected to concentration gradient. Zaikin and Zhabotinskii[5] observed oxidation bands propagating through the thin layer of the solution. Winfree[6] observed two types of spatial structures. Phase waves occur under concentration gradient and trigger waves which initiate in local centers and propagate owing to diffusion-reaction coupling.

The mechanism of the Belousov–Zhabotinskii reaction has been investigated extensively by Noyes, Koros, and Field.[7,8] The concentration of the intermediate bromide ion Br^- controls two mechanisms, and the bromous acid concentration switches rapidly between the two limits.

The mechanism of the spatial oscillations in the trigger waves cases has been explained by various authors. Field and Noyes[9,10] have shown that their mechanism for temporal oscillations coupled with diffusion can explain trigger waves. The waves move by destroying Br^- in front of the wave and leaving a high concentration of Br^- behind, which is the domain for the next wave to propagate.

The governing equations are given by[10]

$$\frac{\partial C_A}{\partial t} = D_A\left(\frac{\partial^2 C_A}{\partial x^2}\right) + k_3[H^+][BrO_3^-]C_B - k_2[H^+]C_AC_B + k_5[H^+][BrO_3^-]C_A - 2k_4C_A^2 \quad (1)$$

$$\frac{\partial C_B}{\partial t} = D_B\left(\frac{\partial^2 C_B}{\partial x^2}\right) - k_3[H^+][BrO_3]C_B - k_2[H^+]C_AC_B \quad (2)$$

where $C_A = [HBrO_2]$ and $C_B = [Br^-]$. Experimentally the bands move with a constant velocity, v

$$v = (\partial x/\partial t)_{C_A,C_B} \quad (3)$$

and

$$\partial C_A/\partial t = v(\partial C_A/\partial x) \quad (4)$$

Approximated solution is given for maximum sharpness[10]

$$v = \{4D_Ak_5[H^+][BrO_3^-]\}^{1/2} \quad (5)$$

From the rate constant $k_5 = 1 \times 10^4$ M^{-2} s^{-1} and the diffusion coefficient $D_A \sim 1.8 \times 10^{-5}$ cm^2/s, the velocity is given by

$$v\ (\text{mm/min}) = 509[H^+]^{1/2}[BrO_2^-]^{1/2}$$

Experimentally the velocity was found to be

$$v\ (\text{mm/min}) = 24.75[H^+]^{1/2}[BrO_3^-]^{1/2}$$

obviously representing large numerical discrepancy.

Recently, Reusser and Field[11] numerically solved the partial differential equations describing the dynamics of interaction of reaction and diffusion of the trigger wave propagation. Their calculations reduce the quantitative discrepancy with the experimental velocities measured by Field and Noyes.[10] Reusser and Field[11] attribute the discrepancies to two approximations in the Oregonator model and the possibility of air presence in the thin layer experiments.

Dreitlein and Smoes[12] analyzed the velocity of trigger wave propagation. They claimed that all waves must propagate with at least the velocity

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$$v_c = 2(D/E)^{1/2} \tag{6}$$

where D is the diffusion coefficient, and E is a parameter depending upon the temperature and concentrations.

Murray[13] obtained traveling wave solutions for the Belousov–Zhabotinskii reaction based on the kinetic model of Field, Koros, and Noyes[8] and showed that the velocity λ_d is given by

$$\lambda_d = \{k_5 D[\mathrm{H}^+][\mathrm{BrO}_3^-]\}^{1/2}\lambda(b,r) \tag{7}$$

where $\lambda(b,r)$ is the dimensionless wave speed evaluated numerically and depends on

$$b = \frac{k_2}{2k_4}[\mathrm{H}^+], \qquad r = \frac{[\mathrm{BrO}_3^-]k_5}{[\mathrm{Br}^-]k_2}$$

A simplified model for the Belousov–Zhabotinskii reaction is given by Tomita, Ito, and Ohta,[14] and the theoretical results compare reasonably well with experimental results.

Kuramoto and Yamada[15] developed a dynamic theory of patterns for two-component dissipative medium. Target patterns, spiral waves, self-locking of phase, and solitary wave propagation are discussed from a unified point of view.

All previous models are based on a coupling between the kinetics and diffusion, and the propagation velocity is proportional to the square root of the diffusion coefficient. Field and Noyes[10] showed experimentally that the velocity is proportional to $([\mathrm{H}^+][\mathrm{BrO}_3^-])^{1/2}$ and is not significantly affected by changes in the concentration of other major reactants. However, the dependence of the propagation velocity on $D^{1/2}$ has not been proved yet.

The purpose of the present work is to show that coupling between the kinetics and diffusion can be responsible for the trigger wave propagation and that the velocity of propagation is proportional to $D^{1/2}$.

The diffusion coefficients were changed by changing the viscosity of the solution. Inert and viscous polyether has been added in various concentrations and changed the viscosity without affecting the kinetics. The viscosities were measured and it was assumed that to a good approximation the product of the viscosity μ and the diffusion coefficient D is constant (Walden's rule):

$$D \cdot \mu = \text{constant}$$

Therefore, if the theoretical models are correct, the propagation velocity is approximately proportional to $\mu^{-1/2}$:

$$v \propto \mu^{-1/2}$$

Experimental Section

The wave propagation velocity was measured in the ferroin-catalyzed Belousov–Zhabotinskii reaction. The velocity of band propagation was measured in a thin layer (1 mm deep) of solution, placed between two glass plates, in a specially constructed thermostated 9-cm diameter dish. The floor of the dish was maintained in contact with circulating water at 25 °C and the solution was covered with a glass plate, resting on a 1-mm thick Teflon ring. The solution was prepared from commercial Analyzed Reagent grade materials. The composition of the solution followed generally the Winfree[16] composition for spatial oscillations: 0.01 M $\mathrm{H_2SO_4}$, 0.05 M $\mathrm{KBrO_3}$, 0.04 M $\mathrm{CH_2(COOH)_2}$, and 0.0029 M ferroin. The pH of the solution was adjusted at pH 0.25 by $\mathrm{H_2SO_4}$. A drop of 1 g/L Triton X-100 detergent was added. The viscosities of the solutions were adjusted by adding various quantities of polyether polyol (Pluracol V-10, BASF Wyandotte Corp.). The presence of the polyol did not interfere significantly with the frequency of homogeneous oscillations in a well-stirred container. The viscosities were measured in Ostwald viscometers (Fisher Scientific) at 25 °C.

The reaction was started by adding the ferroin (iron phenanthroline) to the dish and swirling until the mixture was homogeneous and one bulk oscillation has occurred. Oxidizing blue bands appeared and moved through the solution. The solutions were photographed at known intervals and the velocities were measured relative to the center of the concentric traveling bands. Velocity measurements were made on the outer bands propagating into the red solution.

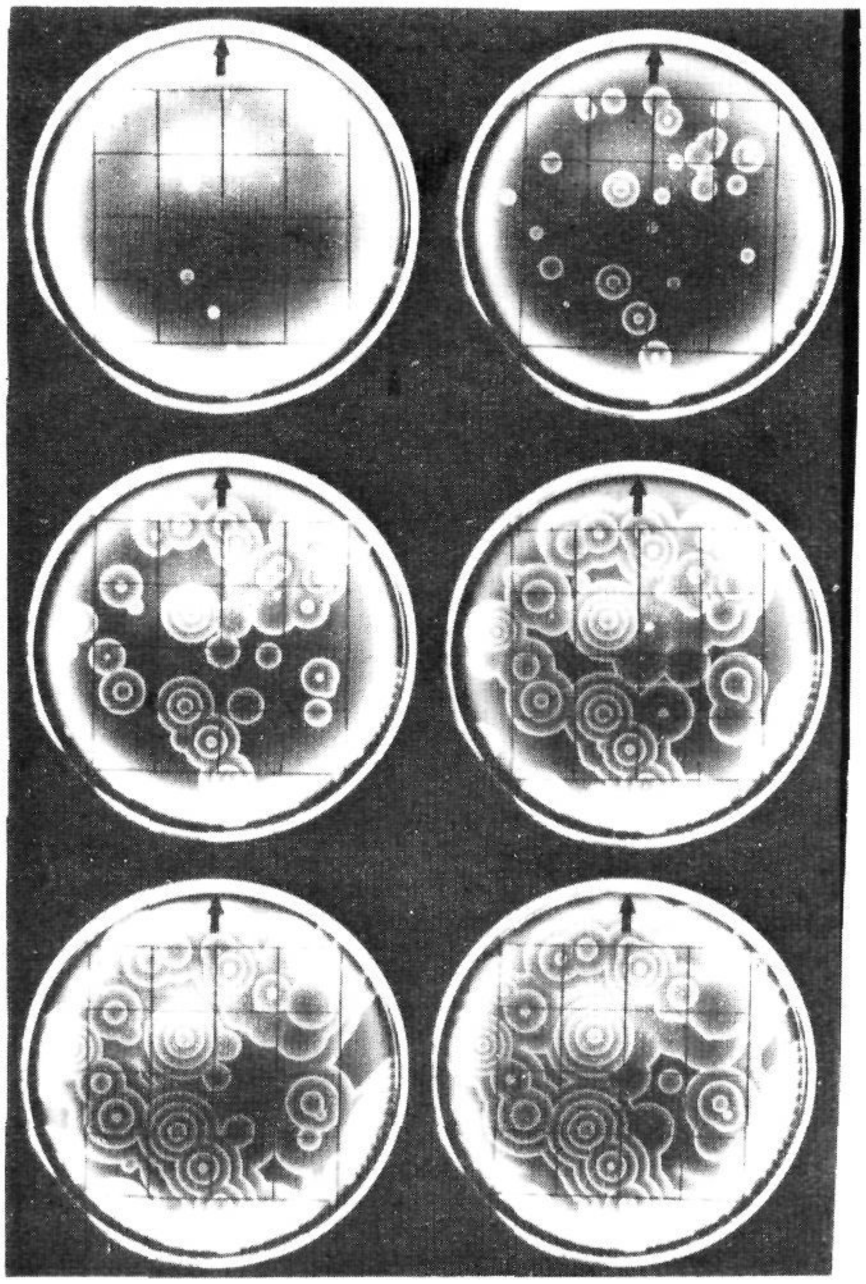

Figure 1. Sequence of trigger-wave propagation in ferroin-catalyzed Belousov–Zhabotinskii reaction: 25 °C; time interval, 45 s; scale, 1 cm.

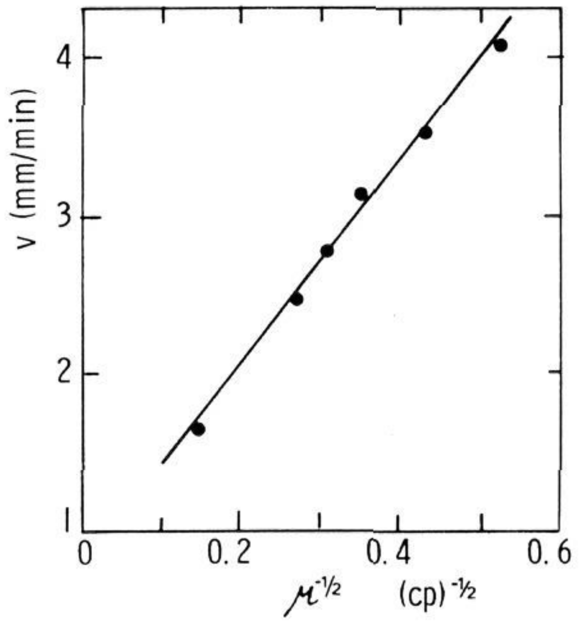

Figure 2. Validation of the kinetics-diffusion coupling. The dependence of the propagation velocity on the viscosity of the solution.

Results and Discussion

Figure 1 show a typical sequence of traveling bands in the ferroin-catalyzed Belousov–Zhabotinskii reaction. The photographs were taken at intervals of 45 s, and the average velocities were measured for solutions of viscosity range of 3.67 to 48.3 cP.

Figure 2 shows a plot of the average velocity of propagation vs. the viscosity to the $-^1/_2$ power. A straight line is observed, indicating that the velocity of propagation is proportional to the square root of the diffusion coefficient, in agreement with the various theoretical and experimental models.[10–12]

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The chemical inertness of the polyether Pluracol toward the solution was checked by measuring its effect on the temporal frequencies in stirred solutions. Concentrations of the oscillatory solution differed from the excitable solutions; however, the content and the mechanisms are similar. The oscillatory composition followed the suggestion of Field and Noyes.[10] The addition of the polyether Pluracol did not affect significantly the period of the oscillation, 70 ± 5 s. Although this is not a proof that the polyether is inert in the Belousov–Zhabotinskii reaction, it nevertheless indicates that the interactions are small and the main effect is the change in the viscosity of the solution. It is possible that the change in viscosity affects the rate of diffusion of oxygen from the atmosphere. However, the experiments were performed in a thin layer between two glass plates; hence oxygen diffusion is minimal during the trigger wave experiments.

Quantative comparison of the experimental data and theoretical models of Field and Noyes,[10] Reusser and Field,[11] and Murray[12] indicates large numerical discrepancies. The rate constants are $k_5 = 1 \times 10^{-4}$ M^{-2} s^{-1}, $k_4 = 4 \times 10^7$ M^{-1} s^{-1}, and $k_2 = 2 \times 10^9$ M^{-2} s^{-1}.[8] The diffusivity can be estimated for the nonviscous solution as 1.8×10^{-5} cm^2/s.[8] Hence the velocity of propagation is given by Field and Noyes[10] and Murray.[13]

$$v \text{ (mm/min)} = 509(\mathrm{H}^+)^{1/2}(\mathrm{BrO_3}^-)^{1/2}$$

In the present investigation $(\mathrm{H}^+) \sim 0.02$ M and $(\mathrm{BrO_3}^-) = 0.05$ M; therefore, the propagation velocity is on the order of $v = 16$ mm/min, an order of magnitude larger than the experimental data. The numerical discrepancy is probably due to uncertainties in the rate constants and the effects of various physical parameters such as the depth of the layer and exposure to oxygen.

The mechanism of Field and Noyes[7-10] essentially consists of three intermediate species, Br^-, $HBrO_2$, and Fe^{3+}. The orange region in front of the propagating front contains a modest amount of bromide ion which reacts according to

$$\mathrm{BrO_3 + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr} \qquad \text{(R3)}$$

$$\mathrm{HBrO_2 + Br^- + H^+ \rightarrow 2HOBr} \qquad \text{(R2)}$$

The product HOBr is destroyed by the brominating malonic acid, and the bromous acid is maintained at very low steady-state concentration. When the bromide concentration becomes low so reaction R2 is slow, then bromous acid can react with bromate ion to initiate a second sequence of reactions:

$$\mathrm{BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2\cdot + H_2O} \qquad \text{(R5)}$$

$$\mathrm{BrO_2\cdot + Fe^{2+} + H^+ \rightarrow HBrO_2 + Fe^{3+}} \qquad \text{(R6)}$$

$$\mathrm{BrO_2\cdot \rightarrow BrO_3^- + HOBr + H^+} \qquad \text{(R4)}$$

Step R5 is the rate-determining step and $HBrO_2$ is autocatalytically generated as ferroin (red) is rapidly oxidized to ferriin (blue). The bromide ion is consumed therefore triggering the autocatalytic formation of bromous acid. The color change is due to the oxidation of ferroin Fe(II) to ferriin Fe(III) by the radical $BrO_2\cdot$. In the oxidation band (blue) the ferriin reacts with the bromomalonic acid to form bromide again which in turn inhibits the autocatalytic formation of the bromous acid.

From the present work and previous theoretical and experimental studies it appears that trigger wave propagation is caused by the coupling between the autocatalytic mechanism and diffusion. Field and Noyes[10] verified experimentally that the propagation is proportional to

$$v = k[\mathrm{H}^+]^{1/2}[\mathrm{BrO_3}^-]^{1/2}$$

The present study shows that for given composition and temperature

$$v \propto D^{1/2}$$

Therefore there is good reason to believe that the velocity is given by

$$v = K\{D[\mathrm{H}^+][\mathrm{BrO_3}^-]\}^{1/2}$$

in a qualitative agreement with the theoretical prediction[10-12] based on kinetics–diffusion coupling.

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Theoretical Study of the Optical Absorption and Magnetic Circular Dichroism Spectra of Cyclopropane

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Abstract: Ab initio configuration interaction calculations have been carried out for the absorption and magnetic circular dichroism (MCD) spectra of cyclopropane. Since the MCD was computed to result from the interference of several states, the calculated results were fitted to Gaussian line-shape functions with experimental widths. The resultant calculated spectrum is in good agreement with the observed, although the interpretation afforded by these calculations differs in many respects from that obtained through a moment analysis of the experimental spectrum. The advantages and dangers of the moment analysis approach to the interpretation of MCD spectra are epitomized and discussed.

A. Introduction

Although cyclopropane is the smallest of the cyclic hydrocarbons, it is atypical of the series in that it often behaves more like a conjugated than a saturated molecule. It has long been noted, for instance, that it resembles ethylene in many of its chemical reactions and that its first major ultraviolet absorption band displays a maximum at 7.8 eV, far to the red of most saturated absorbers and in the region of the $\pi \rightarrow \pi^*$ transitions of unsaturated molecules.

This behavior can be rationalized[1] from the observation that its HCH angles are not far from 120°, a fact which implies something approaching sp^2 hybridization at the carbons. Two of these hybrids are directed toward the hydrogens, while the third points into the center of the equilateral triangle forming the so-called "internal" system of in-plane valence orbitals. The remaining p orbital lies perpendicular to both the C_3 axis and the

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