

# Oscillations in Chemical Systems. V. Quantitative Explanation of Band Migration in the Belousov-Zhabotinskii Reaction

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**Abstract:** During the ferroin-catalyzed oxidation of malonic acid by acid bromate, successive bands of oxidation advance through reduced regions. Rates of band motion have been measured at 25° as a function of concentrations of reactants. These rates are nearly proportional to  $[H^+]^{1/2}[BrO_3^-]^{1/2}$  and almost independent of the concentrations of the other species in the system. The mechanism previously developed to explain temporal oscillations in homogeneous solution has been modified to include diffusion, and the equations have been examined analytically and numerically. The results agree with the observed kinetic behavior, although the calculated constant of proportionality is somewhat greater than that observed. These calculations indicate that the concentration of bromous acid in an advancing band front increases by several orders of magnitude in a distance of about 2  $\mu$ .

During the course of most chemical reactions proceeding by complex mechanisms, the concentrations of intermediates either pass through a single maximum or else attain a steady state concentration that changes only slowly and monotonically with time. However, in systems where feedback in one or more of the component reactions leads to certain types of nonlinear rate laws, the expected steady state may be unstable to small fluctuations in intermediate concentrations. A system must contain two or more intermediates for such an instability to occur. In these cases it is theoretically possible that the concentrations of some intermediates do not attain their steady state values but instead approach a stable oscillatory trajectory around the steady state. Such trajectories are called *limit cycles*.<sup>1</sup> The literature of chemical oscillations has been reviewed by Nicolis and Portnow.<sup>2</sup>

Belousov<sup>3</sup> first observed such *temporal* oscillations in intermediate concentrations during the cerium ion catalyzed oxidation of citric acid by acid bromate in a stirred solution. Zhabotinskii<sup>4</sup> demonstrated the range of different organic acids and metal ions that could be used in the reaction. The detailed chemical mechanism of the reaction has been elucidated by Field, Körös, and Noyes,<sup>5,6</sup> and computer simulation has confirmed the limit cycle behavior of the spatially homogeneous system.<sup>7</sup>

Zaikin and Zhabotinskii<sup>8</sup> reported the development of spatial structure in an initially homogeneous but unstirred Belousov reagent containing ferroin and bromomalonic acid as the catalyst and organic acid, respectively. The spatial structure appears as traveling bands of oxidation that are clearly supported by the free energy of the chemical reactions taking place.

For reasons discussed below, the temporal and spatial

oscillations occur at somewhat different optimum reactant concentrations. The dramatic behavior of two<sup>9</sup> and three<sup>10,11</sup> dimensional traveling bands of oxidation in a similar reagent has been described by Winfree. His observations led to an explanation<sup>10,11</sup> of the complex but highly systematic shapes of the traveling bands. The explanation is based upon the existence of a rotating three dimensional scroll band of oxidation in the reagent. The exact relationship between the scroll bands of Winfree and the plane bands to be discussed here undoubtedly involves the refractory region following each band of oxidation.<sup>9,12,13</sup>

We have previously<sup>12</sup> explained plane band propagation in this system qualitatively by extending the chemical mechanism of the temporal oscillations. In the present paper we report the experimental rates at which the traveling bands migrate and show that the concentration dependence of those rates is quantitatively consistent with the mechanism as previously developed.

## Experimental Section

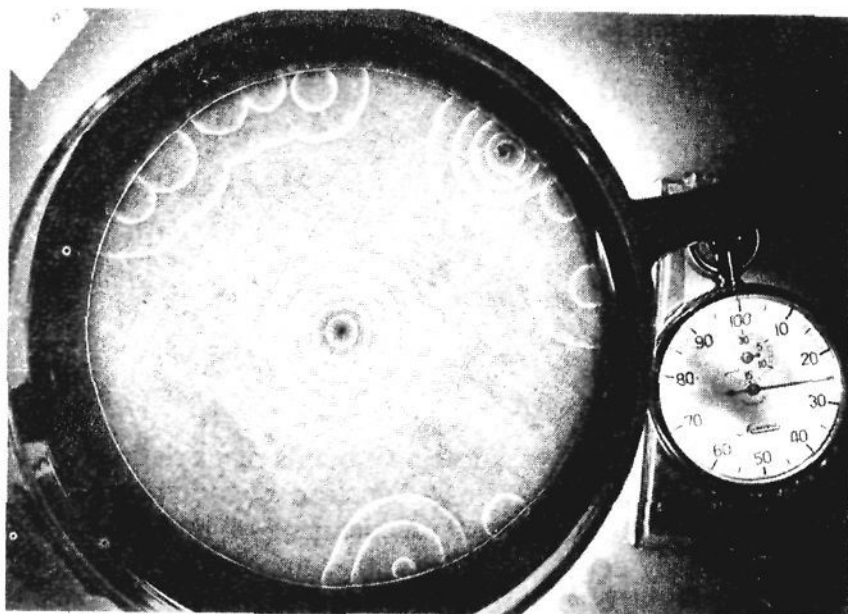
**Reagents.** The NaBrO<sub>3</sub>, NaBr, Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O, malonic acid, and 1,10-phenanthroline monohydrate were commercial Analyzed Reagent grade materials; they were used without further purification. Triton X-100, a nonionic detergent manufactured by Rohm and Haas, Co., Philadelphia was used to lower the surface tension of the solutions. All solutions were prepared with triply distilled water, the final two distillations being from acidic dichromate and basic permanganate, respectively.

**Apparatus.** Velocity of band propagation was measured in a thin layer of solution in a specially constructed thermostated Petri dish. The bottom consisted of two pieces of plate glass with a translucent millimeter grid paper sandwiched between. The dish was surrounded with a jacket so that walls and floor could be maintained in contact with circulating water at 25.0 ± 0.1°. The system was supported on three adjustable legs so the floor could be leveled to maintain the reagent at a constant depth less than 2 mm.

A piece of No. 22 Nichrome wire made contact with the solution through a hole drilled in the center of the dish, and a platinum wire penetrated the edge of the floor in the same manner. After the

- (1) G. Nicolis, *Advan. Chem. Phys.*, **19**, 209 (1971).
- (2) G. Nicolis and J. Portnow, *Chem. Rev.*, **73**, 365 (1973).
- (3) B. P. Belousov, *Sb. Ref. Radiats. Med., Moscow*, **1958**, 145 (1959).
- (4) A. M. Zhabotinskii, *Dokl. Akad. Nauk SSSR*, **157**, 392 (1964); A. M. Zhabotinskii, *Biofizika*, **9**, 306 (1964).
- (5) R. M. Noyes, R. J. Field, and E. Körös, *J. Amer. Chem. Soc.*, **94**, 1394 (1972).
- (6) R. J. Field, E. Körös, and R. M. Noyes, *J. Amer. Chem. Soc.*, **94**, 8649 (1972).
- (7) R. J. Field and R. M. Noyes, *J. Chem. Phys.*, in press.
- (8) A. N. Zaikin and A. M. Zhabotinskii, *Nature (London)*, **225**, 535 (1970).

- (9) A. T. Winfree, *Science*, **175**, 634 (1972).
- (10) A. T. Winfree in "Science and Humanism: Partners in Human Progress," H. Mel, Ed., University of California Press, Berkeley, Calif., in press.
- (11) A. T. Winfree, *Science*, **181**, 937 (1973).
- (12) R. J. Field and R. M. Noyes, *Nature (London)*, **237**, 390 (1972).
- (13) A. M. Zhabotinskii and A. N. Zaikin, *J. Theor. Biol.*, **40**, 45 (1973).



**Figure 1.** Typical set of concentric traveling bands of oxidation developing in the thermostated Petri dish. A Nichrome wire at the center is serving as pacemaker:  $[\text{H}_2\text{SO}_4]_0 = 0.26 \text{ M}$ ,  $[\text{NaBrO}_3]_0 = 0.23 \text{ M}$ ,  $[\text{malonic acid}]_0 = 0.024 \text{ M}$ ,  $[\text{bromomalonic acid}]_0 = 0.075 \text{ M}$ ,  $[\text{ferroin}]_0 = 5.45 \times 10^{-3} \text{ M}$ , temperature =  $25.0 \pm 0.1^\circ$ .

Nichrome had become "activated" by passage of one moving oxidation band, the wire became a pacemaker<sup>8,9</sup> and triggered other bands at a regular frequency. This pacemaking activity could be suppressed by making the Nichrome more than 1.5 V negative with respect to the platinum.

At first bubbles tended to form on the floor of the Petri dish when reagent was added. This problem was minimized by treating the dish for several days with 6 M sulfuric acid. Winfree<sup>11</sup> has suggested that nucleation of bubbles can also be reduced by coating the surface with silicone.

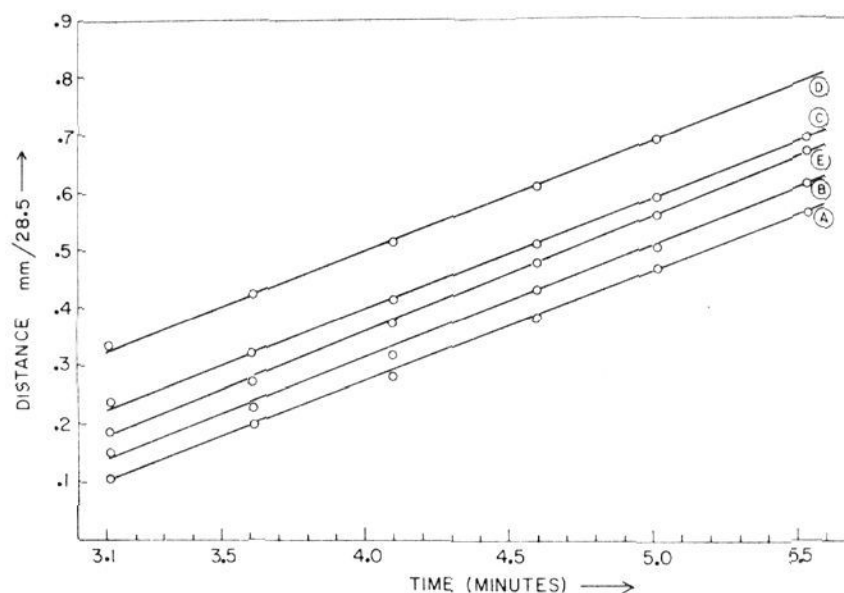
Migration of bands was followed by photographing the system at suitable intervals with a camera mounted above the Petri dish. The focal plane of the camera was maintained parallel to the floor of the dish. Illumination came from below the solution, and a running stopwatch was included in the field of the camera.

**Procedure.** All stock solutions were stored and mixed in a thermostat maintained at the  $25^\circ$  temperature of the Petri dish. The  $\text{H}_2\text{SO}_4$ ,  $\text{NaBrO}_3$ , malonic acid, and NaBr solutions were added in that order. Much of the malonic acid was brominated by free bromine liberated by the bromide-bromate reaction. After the free bromine had disappeared, one drop of 0.1% Triton X-100 was added for each 30 ml of reagent solution; uniform spreading of reagent over the bottom of the Petri dish was thus facilitated.

Reaction was started by adding the ferroin (iron phenanthroline) solution and swirling until the mixture was homogeneous and one bulk oscillation had occurred. This oscillation appeared to be necessary before the moving bands behaved in a reproducible manner. Usually, the oscillation was complete and the solution had taken on the bright orange color of  $\text{Fe}(\text{phen})_3^{2+}$  by the time it had settled from the initial swirling.

The homogeneous solution was poured into the Petri dish, and oxidizing bands colored with blue  $\text{Fe}(\text{phen})_3^{3+}$  formed and moved through the solution. These bands do not appear spontaneously but rather form at heterogeneous centers such as gas bubbles, motes of dust, surfaces of certain metals, etc. All moving bands except the first one triggered by the Nichrome electrode were considered interferences as far as the present work was concerned. Therefore, all solutions were filtered through 0.8- $\mu$  Millipore filters, Type AAWP, 25 mm, from the Millipore Corp., Bedford, Mass. 01730.

The solution was photographed at known times, and the distance (of bands) from a fixed reference point was measured in each photograph with dividers and vernier calipers. The band was usually circular about the central Nichrome wire, and distance vs. time measurements were made in all four quadrants. Figure 1 shows a typical photograph of the system and Figure 2 shows data plots of position against time for a typical run. Linearity of these plots indicates that velocity of the band depends little on time since homogenization or on curvature of the band. Using a somewhat different reaction mixture, Tatterson and Hudson<sup>14</sup> found similar



**Figure 2.** Typical plots of distance vs. time for bands traveling in different areas of the Petri dish in the same experiment: velocity =  $5.5 \pm 0.1 \text{ mm/min}$ ,  $[\text{H}_2\text{SO}_4]_0 = 0.26 \text{ M}$ ,  $[\text{NaBrO}_3]_0 = 0.23 \text{ M}$ ,  $[\text{malonic acid}]_0 = 0.074 \text{ M}$ ,  $[\text{bromomalonic acid}]_0 = 0.075 \text{ M}$ ,  $[\text{ferroin}]_0 = 0.0038 \text{ M}$ , temperature =  $25.0 \pm 0.1^\circ$ .

results for bands traveling down 2 and 4 mm capillary tubes. Velocities of bands propagating in different directions and areas during the same run usually had standard deviations of about 2%. Standard deviations of average velocities from duplicate runs were usually about 3%.

Velocity measurements were always made on bands moving into the bright orange area where no other band had passed since the solution was last homogenized. These velocities are easier to interpret than those when bands may be interacting.<sup>8-11</sup> After the Petri dish had become full of bands, the solutions could be rehomogenized by swirling. A bulk oscillation often accompanied swirling. Band velocity remained constant within experimental error throughout several rehomogenizations.

## Results

Winfree<sup>9</sup> has proposed a set of reagent concentrations that was considered a standard. It results in an orange (reduced) solution that is marginally stable to temporal oscillation but will still propagate blue (oxidizing) bands once they have been initiated. The composition of this solution is presented in Table I; it is calculated

**Table I.** Representative Concentrations (M) Exhibiting Spatial and Temporal Oscillations and Concentration Ranges Used in This Work<sup>a</sup>

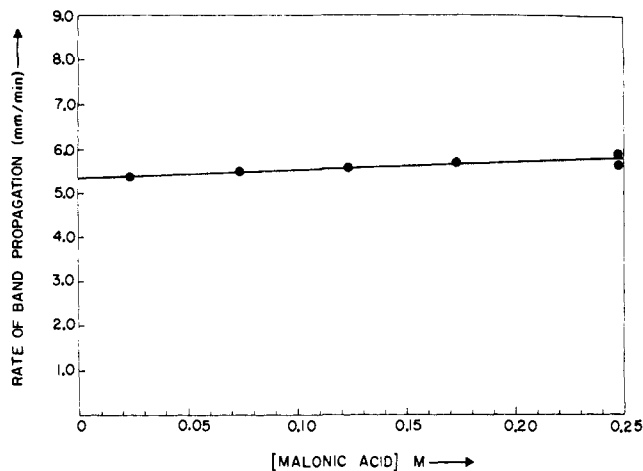
Reactant	Spatial		Temporal Field <sup>c</sup>
	Winfree <sup>b</sup>	This work	
$\text{H}_2\text{SO}_4$	0.2917	0.1744–0.5067	1.25
$\text{NaBrO}_3$	0.3055	0.1275–0.3812	0.07
$\text{CH}_2(\text{COOH})_2$	0.02736	0.02440–0.2476	0.375
$\text{BrCH}(\text{COOH})_2$	0.08574	0.03738–0.1495	0.045
Ferroin	0.00294	0.00129–0.00545	0.00025

<sup>a</sup> Solutions showing spatial oscillations also contained 1 drop of 1 g/1000 ml Triton X-100 per 30 ml of final reagent. <sup>b</sup> A. T. Winfree, *Science*, **175**, 634 (1972). <sup>c</sup> R. J. Field, *Chem. Ztg.*, **7**, 171 (1973).

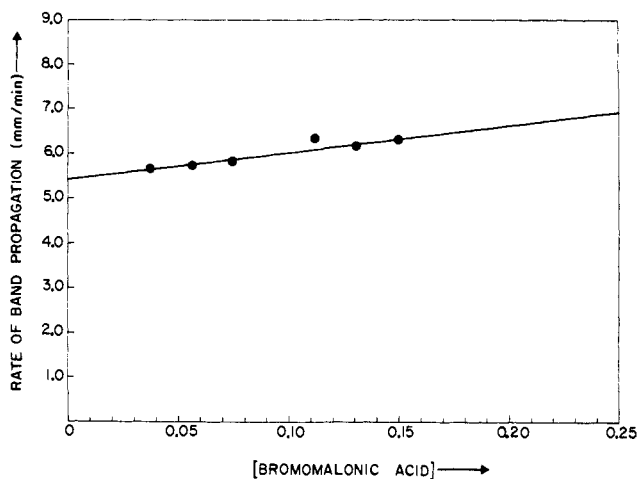
for the time when the free bromine initially generated has all reacted with malonic acid. Table I also contains a composition that conveniently exhibits sustained temporal oscillations. This reagent will also exhibit traveling bands of oxidation, but they are short lived because of the occurrence of bulk temporal oscillations. The differences in concentration are discussed below.

Each of the components of the solution was varied

(14) D. F. Tatterson and J. L. Hudson, *Chem. Eng. Commun.*, **1**, 3 (1973).



**Figure 3.** Plot of the velocity of band propagation *vs.* the initial concentration of malonic acid:  $[\text{H}_2\text{SO}_4]_0 = 0.26 \text{ M}$ ,  $[\text{NaBrO}_3]_0 = 0.23 \text{ M}$ ,  $[\text{bromomalonic acid}]_0 = 0.075 \text{ M}$ ,  $[\text{ferroin}]_0 = 0.0038 \text{ M}$ ,  $[\text{malonic acid}]_0 = 0.024 \sim 0.25 \text{ M}$ , temperature =  $25.0 \pm 0.1^\circ$ .

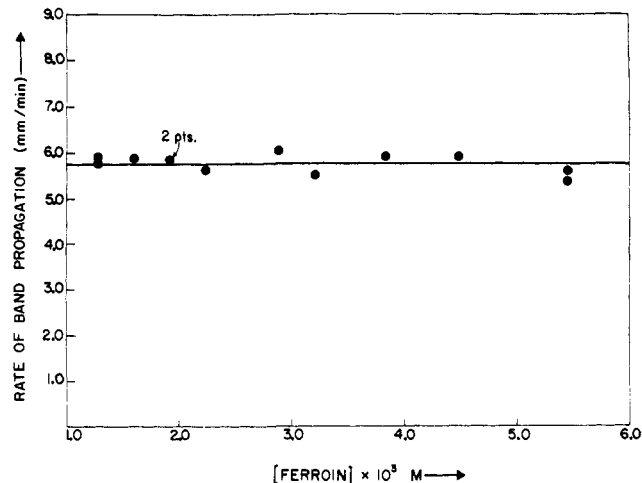


**Figure 4.** Plot of the velocity of band propagation *vs.* the initial concentration of bromomalonic acid:  $[\text{H}_2\text{SO}_4]_0 = 0.26 \text{ M}$ ,  $[\text{NaBrO}_3]_0 = 0.23 \text{ M}$ ,  $[\text{malonic acid}]_0 = 0.024 \text{ M}$ ,  $[\text{ferroin}]_0 = 0.0038 \text{ M}$ ,  $[\text{bromomalonic acid}]_0 = 0.037 \sim 0.1495 \text{ M}$ , temperature =  $25.0 \pm 0.1^\circ$ .

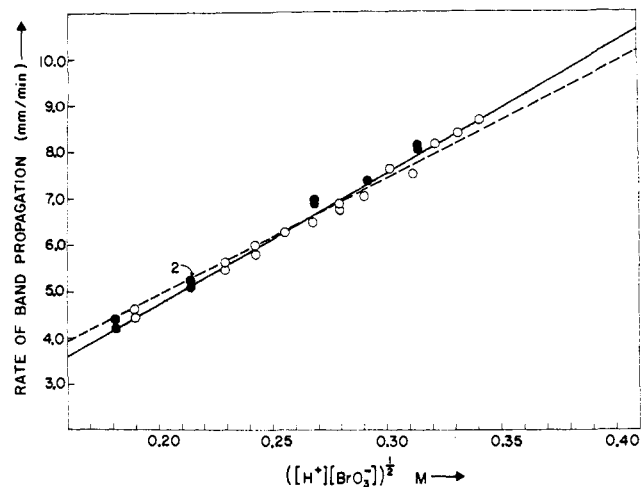
over a considerable concentration range while the other components were maintained at a concentration near that of the Winfree<sup>9</sup> standard. The concentration ranges are also presented in Table I and always bracket the Winfree composition for that component. The possible concentration limits were defined either by the reagent becoming so excitable that the entire area of the Petri dish almost immediately became full of bands or else by the reagent becoming unstable to bulk oscillations. Either occurrence made it impossible to follow a given band long enough to determine its velocity accurately.

The results of these measurements are plotted in Figures 3–6. The rate of band propagation is clearly almost independent of the concentrations of ferroin and of malonic acid and is only slightly affected by that of bromomalonic acid. Figure 6 demonstrates that the rate is almost directly proportional to the product  $([\text{H}^+][\text{BrO}_3^-])^{1/2}$ . The best two-parameter least-squares line through the points is

$$v(\text{mm/min}) = -0.832 + 27.87[\text{H}^+]^{1/2}[\text{BrO}_3^-]^{1/2} \quad (1)$$



**Figure 5.** Plot of the velocity of band propagation *vs.* the initial concentration of ferroin:  $[\text{H}_2\text{SO}_4]_0 = 0.26 \text{ M}$ ,  $[\text{NaBrO}_3]_0 = 0.23 \text{ M}$ ,  $[\text{malonic acid}]_0 = 0.024 \text{ M}$ ,  $[\text{bromomalonic acid}]_0 = 0.075 \text{ M}$ ,  $[\text{ferroin}]_0 = (1.28 \sim 5.45) \times 10^{-3} \text{ M}$ , temperature =  $25.0 \pm 0.1^\circ$ .



**Figure 6.** Plot of velocity of band propagation *vs.* square root of product of initial concentrations of sulfuric acid and sodium bromate:  $[\text{malonic acid}]_0 = 0.023 \text{ M}$ ,  $[\text{ferroin}]_0 = 0.0038 \text{ M}$ ,  $[\text{bromomalonic acid}]_0 = 0.075 \text{ M}$ . Filled circles are for  $[\text{H}_2\text{SO}_4]_0 = 0.2576 \text{ M}$  and  $[\text{NaBrO}_3]_0 = 0.13 \sim 0.38 \text{ M}$ . Open circles are for  $[\text{NaBrO}_3]_0 = 0.2290 \text{ M}$  and  $[\text{H}_2\text{SO}_4]_0 = 0.17 \sim 0.51 \text{ M}$ . Temperature =  $25.0 \pm 0.1^\circ$ . The solid line corresponds to eq 1, and the dashed line corresponds to eq 2.

while the best line constrained to pass through the origin is

$$v(\text{mm/min}) = 24.75[\text{H}^+]^{1/2}[\text{BrO}_3^-]^{1/2} \quad (2)$$

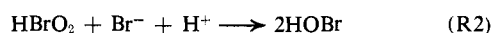
Both lines are presented in Figure 6. The standard deviations are 0.224 and 0.164 mm/min for the one- and two-parameter lines, respectively. These values do not allow a choice to be made between the lines. However, the correlation coefficient<sup>15</sup> between  $([\text{H}^+][\text{BrO}_3^-])^{1/2}$  and the residuals for both lines indicates that there is a proportional deviation in the one-parameter fit. The values of this correlation coefficient are 0.6906 and 0.0146 for the one- and two-parameter lines. There is only a 0.1% probability that for 27 points the correlation coefficient will exceed 0.6 if there is no functional dependence between the

(15) Hugh D. Young, "Statistical Treatment of Experimental Data," McGraw-Hill, New York, N. Y., 1962, p 130 ff and Table V, p 164.

variables.<sup>15</sup> We conclude that the one-parameter line is unlikely to be the true form of the data. There is no evidence for a more complicated relationship than eq 1.

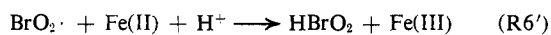
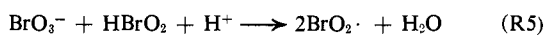
## Discussion

**Equations Describing Band Motion.** The mechanism as developed previously<sup>5-7,12</sup> predicts that band propagation can be described in terms of the three intermediate species  $\text{Br}^-$ ,  $\text{HBrO}_2$ , and  $\text{Fe(III)}$ . The orange region in front of a moving band contains a modest amount of bromide ion that reacts by the sequence of steps R3 and R2.<sup>16</sup> The resulting  $\text{HOBr}$  is destroyed



by brominating malonic acid, and the bromous acid is maintained at a very low steady state concentration given by  $[\text{HBrO}_2] = (k_3/k_2)[\text{H}^+][\text{BrO}_3^-] = 1.05 \times 10^{-9} [\text{H}^+][\text{BrO}_3^-]$ . The bromomalonic acid formed plays an important role in the mechanism.

If the concentration of bromide ion becomes low enough so that reaction R2 is sufficiently slow, then bromous acid can also react with bromate ion to initiate another sequence of reactions.



Step R5 is rate determining, and the sequence  $\text{R5} + 2 \times \text{R6}'$  has the net effect of generating  $\text{HBrO}_2$  autocatalytically as ferriin (red) is rapidly oxidized to ferriin (blue). In the band front the concentration of bromous acid can approach a steady state given by  $[\text{HBrO}_2] = (k_3/2k_4)[\text{H}^+][\text{BrO}_3^-] = 1.25 \times 10^{-4} [\text{H}^+][\text{BrO}_3^-]$  while the bromide ion concentration is driven to very low values.

An area of oxidation increases its size by consuming the bromide ion around it and triggering the autocatalytic formation of bromous acid. When an area becomes oxidizing, however, ferriin is quickly produced and reacts with bromomalonic acid to generate sufficient bromide ion to end the autocatalytic formation of bromous acid. Additional reactions of ferriin with organic species are complicated and not elucidated in detail; they are not germane to the propagation of an oxidation front. The rapid poisoning of an area of oxidation by its own products leads to formation of the moving bands of oxidizing activity that are observed. These bands propagate by destroying the bromide ion in front of them, but they leave a much higher concentration of bromide ion behind them. The high bromide ion concentration directly behind a band makes that region refractory to the passage of other bands. It is to a large extent this refractory region that is responsible<sup>12</sup> for the complex behavior observed when traveling bands interact with each other or are broken.<sup>8-11</sup> The following analysis is concerned with the propagation of bands into a region not perturbed by the passage of previous bands. It is assumed that the velocity of band propagation is controlled by the concentration of bromide ion and bromous acid in the band front and that the trailing band of bromide ion does not affect the velocity of band propagation.

(16) R equation numbers refer to the equations in ref 6.

If the migration of the oxidizing band in the  $x$  direction can be described by these processes, then Fick's second law permits us to set up two simultaneous differential equations in terms of the concentrations  $c_A \equiv [\text{HBrO}_2]$  and  $c_B \equiv [\text{Br}^-]$ .

$$\left(\frac{\partial c_A}{\partial t}\right)_x = D_A \left(\frac{\partial^2 c_A}{\partial x^2}\right)_t + k_3[\text{H}^+][\text{BrO}_3^-]c_B - k_2[\text{H}^+]c_A c_B + k_5[\text{H}^+][\text{BrO}_3^-]c_A - 2k_4 c_A^2 \quad (3)$$

$$\left(\frac{\partial c_B}{\partial t}\right)_x = D_B \left(\frac{\partial^2 c_B}{\partial x^2}\right)_t - k_3[\text{H}^+][\text{BrO}_3^-]c_B - k_2[\text{H}^+]c_A c_B \quad (4)$$

Since  $c_A$  and  $c_B$  are always small in this system, the diffusion coefficients  $D_A$  and  $D_B$  can be assumed to be independent of these concentrations.

The experimental observations indicate that the band moves with a constant velocity,  $v$ , defined by the convention

$$v = -(\partial x / \partial t)_{c_A, c_B} \quad (5)$$

$$(\partial c_A / \partial t)_x = v(\partial c_A / \partial x)_t \quad (6)$$

Substitution of eq 6 and its  $c_B$  analog into eq 3 and 4 generates two nonlinear second order differential equations describing the instantaneous profiles of  $c_A$  and  $c_B$  in the dynamic system. These equations do not solve in terms of analytical functions, but they are obviously consistent with the experimental observation that the velocity depends only upon the concentrations of  $\text{H}^+$  and  $\text{BrO}_3^-$  and not on those of other chemical species.

**Approximate Analytical Solution.** Although eq 3 and 4 are not rigorously soluble, it can be noted that in the face of an advancing band the  $k_5$  autocatalytic term will be much more important than any of the others. Then eq 3 can be approximated by eq 7. The solution

$$D_A \frac{d^2 c_A}{dx^2} - v \frac{dc_A}{dx} + k_5[\text{H}^+][\text{BrO}_3^-]c_A = 0 \quad (7)$$

of this equation is of the form

$$c_A = B_1 e^{\alpha_1 x} + B_2 e^{\alpha_2 x} \quad (8)$$

where the  $B$ 's are constants determined by the boundary conditions. Of course this solution requires the concentration to increase indefinitely behind the front, and eq 7 is intended to model only the leading edge of the band.

If the  $\alpha$ 's in eq 8 are real, then

$$v \geq (4D_A k_5 [\text{H}^+][\text{BrO}_3^-])^{1/2} \quad (9)$$

If eq 9 is an equality, the  $\alpha$ 's are equal and the wave front has maximum sharpness.

Equation 9 is gratifyingly consistent with the kinetic form observed in Figure 6. We have previously<sup>6</sup> estimated that  $k_5 = 1.0 \times 10^4 \text{ M}^{-2} \text{ sec}^{-1}$ , and it seems a reasonable estimate that  $D_A = 1.8 \times 10^{-5} \text{ cm}^2/\text{sec}$ . Then the coefficient multiplying the concentration term becomes  $509 \text{ M}^{-1} \text{ mm min}^{-1}$  or about 20 times the experimental values in eq 1 and 2.

The numerical discrepancy is somewhat larger than is comfortable. A similar but smaller discrepancy arose previously<sup>6</sup> when the critical bromide concentration for the start of autocatalysis was found to be 3.6 times the value of  $(k_3/k_2)[\text{BrO}_3^-]$  calculated from the estimated

rate constants. Part of this discrepancy may be associated with the approximation of eq 7. Equation 9 predicts the rate at which a band would move into a medium containing nothing that reacted with bromous acid. However, the medium in front of an advancing band contains bromide ion at a concentration several orders of magnitude above that of the bromous acid in the approaching wave front. Reaction of this bromide ion with the diffusing bromous acid may explain some of the quantitative discrepancy.

**Numerical Solution of Moving Band Equations.** An attempt was also made to solve the equations numerically. Four dimensionless variables were defined related to  $c_A$ ,  $c_B$ ,  $dc_A/dx$ , and  $dc_B/dx$ , and the two second order differential equations were converted to four simultaneous first order equations in the four variables. These could be solved numerically by a Runge-Kutta started predictor-corrector technique for any initial set of boundary conditions. The initial  $c_B$  was chosen to be  $3 \times 10^{-5} M$  (about 20 times the critical bromide concentration for homogeneous temporal oscillations). The initial  $c_A$  was calculated as the steady state bromous acid concentration that would be associated with that bromide ion concentration in homogeneous solution. An effort was then made to select initial  $dc_A/dx$ ,  $dc_B/dx$ , and  $v$  values such that the numerical solution would pass through a wave front with  $c_B$  approaching a limiting value of zero and  $c_A$  simultaneously approaching the limiting bromous acid concentration in an oxidizing band. Both diffusion coefficients were assumed to be  $1.8 \times 10^{-5} \text{ cm}^2/\text{sec}$ .

The numerical solutions were so sensitive to small changes in boundary conditions that it became impracticably tedious to search for a full solution. However, something very close to a satisfactory solution was obtained for  $[H^+] = 0.2575 M$  and  $[BrO_3^-] = 0.2797 M$  with a velocity exactly half that predicted by eq 9. Figure 7 is a composite plot that is certainly very close to the concentration profiles in a real wave front.

Figure 7 shows predictable deviations from the concentration profiles calculated previously<sup>7</sup> for temporal oscillations in homogeneous solution. Thus diffusion of bromous acid ahead of the advancing band front causes bromide concentration to decrease rapidly even when it is several times the critical concentration. On the other hand, because the  $c_A$  plot is concave up in the leading edge of a band, the slope  $dc_A/dx$  is about three times as steep as would be expected if the rate in homogeneous solution were divided by the velocity.

Figure 7 indicates that all except a few per cent of the change in bromous acid concentration takes place in a distance of the order of  $2 \mu$  and that most of the depletion of bromide ion takes place in about  $5 \mu$ . Computer modeling of the homogeneous system<sup>7</sup> indicates that the concentration of oxidized indicator rises almost as sharply as that of bromous acid. The rise in a real system may be less steep because our computational methods do not recognize that step R6' is somewhat reversible and that step R5 ceases to be strictly rate determining as oxidized metal ion accumulates.<sup>17</sup> However, Figure 7 certainly agrees with the photographic evidence of Figure 1 that advancing bands have very sharp leading edges!

(17) (a) R. C. Thompson, *J. Amer. Chem. Soc.*, **93**, 7315 (1971);  
(b) R. M. Noyes, R. J. Field, and R. C. Thompson, *ibid.*, **93**, 7315 (1971).

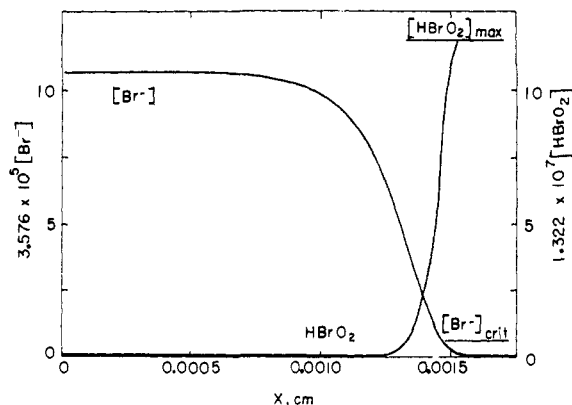


Figure 7. Instantaneous concentration profiles of bromide ion and bromous acid for a band front migrating to the left into a region with  $[Br^-] = 3.0 \times 10^{-5} M$ . Calculations are for  $[H^+] = 0.2575 M$  and  $[BrO_3^-] = 0.2797 M$ , and band velocity is  $0.11386 \text{ cm/sec}$ . Plots represent numerical solutions of eq 3 and 4 for assumed constant velocity.

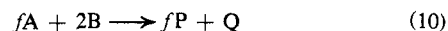
### Comparison of Temporal and Spatial Oscillations.

Table I indicates that somewhat different solution compositions are optimum for temporal and spatial oscillations although both phenomena can occur in the same solution. The Winfree<sup>9</sup> solution for spatial band migrations has much more bromomalonic than malonic acid and uses the ferroin-ferriin couple as catalyst. The solution for temporal oscillations has much more unbrominated acid and the most dramatic examples use the cerium(III)-cerium(IV) couple to catalyze the reaction. The oxidizing bands in the spatial system advance into a marginally stable solution containing metal ion in reduced form. The temporal oscillations commence after an induction period during which the metal ion is in oxidized form.

These differences can be rationalized by means of the model mechanism previously developed<sup>7</sup> for calculations on this system.



The net reaction is



This model can be related to the present system by setting  $A = B = BrO_3^-$ ,  $X = HBrO_2$ ,  $Y = Br^-$ , and  $Z = 2Fe(III)$ .

As was pointed out before,<sup>7</sup> when  $f < 1$  the steady state solution corresponds to large concentrations of  $X$  and  $Z$  and to an oxidizing state. This is the situation during the induction period before temporal oscillations commence. Much of the organic matter is unbrominated malonic acid which does not liberate bromide ion when oxidized, and the strong oxidant  $Ce(IV)$  attacks most organic species in the system so that distinctly less than one bromide ion is generated by each  $Ce(IV)$ .

The reduced steady state observed in the Winfree<sup>9</sup> solution seems to require that  $f$  be slightly greater than unity. It is hard to accommodate this requirement to the mechanism unless the  $Fe(III)$  species react so as to



liberate at least one-half a bromide ion apiece. Such behavior could be observed if the radicals from attack of Fe(III) on bromomalonic acid can disproportionate without further reaction with Fe(III) and if organic oxidation products generate radicals that can further attack bromomalonic acid.<sup>18</sup> Alternatively, slow acid hydrolysis of the organic bromine species may occur rapidly enough to maintain a steady state bromide ion concentration greater than the critical value at which bromous acid formation becomes autocatalytic. Finally, bromous acid may react directly with bromomalonic acid so that autocatalytic generation is made somewhat more difficult.

Although these mechanistic fine points are not yet resolved, the main features of band migration are certainly well accommodated by eq 3 and 4.

**Additional Comments.** Winfree<sup>19</sup> has clearly recognized two very different mechanisms by which oxidizing bands could propagate through a medium like this. If different regions oscillate at the same frequency but with different phase, or if frequencies are different in different regions because of gradients in concentra-

(18) J. J. Jwo, unpublished observations.

(19) A. T. Winfree in "Lecture Notes on Biomathematics," P. van den Driessche, Ed., Springer-Verlag, West Berlin, 1974, in press.

tion, temperature, etc., regions of oxidation would propagate even if there were no diffusion whatsoever. Winfree calls such propagation a "pseudo-wave," and it is this phenomenon which Kopell and Howard<sup>20</sup> have examined recently.

In the system we are studying here, oxidizing bands advance into a uniform medium that is marginally stable to homogeneous oscillation. Diffusion in the region ahead of the band front triggers the reaction that advances the oxidized region. Winfree calls such propagation a "trigger-wave."

Pseudo-waves may propagate at velocities greater than trigger-waves could move. However, a hypothetical system consisting of pseudo-waves moving more slowly than trigger-waves would propagate into the medium in front of each oxidizing region would evolve into one in which band velocities were determined by the trigger-wave mechanism.

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(20) N. Kopell and L. N. Howard, *Science*, **180**, 1171 (1973).

## Circularly Polarized Luminescence Spectrum of Camphorquinone<sup>1</sup>

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**Abstract:** The absorption, total luminescence, circular dichroism (CD), and circularly polarized luminescence (CPL) spectra of the  $\alpha$ -diketone, *d*-camphorquinone, were measured in solution at room temperature. The CPL and lowest energy CD bands exhibit a near mirror-image relationship as do the total luminescence and lowest energy singlet-singlet absorption bands. The dissymmetry factors measured in the emission experiments are an order of magnitude smaller than those observed in the absorption experiments. These results lead to the conclusions that: (1) the chirality of the dicarbonyl group in the fluorescent state is the same as that in the ground state; (2) except for the dihedral twist angle ( $\phi$ ) in the dicarbonyl group, molecular structural parameters are similar in the ground and fluorescent states; (3) the dihedral twist angle ( $\phi$ ) is smaller in the fluorescent state than in the ground state; and (4) the fluorescent state and the singlet excited state responsible for CD and absorption in the 480-nm region are identical.

The chiroptical properties, circular dichroism (CD) and optical rotatory dispersion (ORD), have been of great value in obtaining information about the more subtle aspects of molecular stereochemistry and electronic structure. The signs and magnitudes of CD bands and of the Cotton effects observed in ORD spectra exhibit an extraordinary sensitivity to the stereochemical features of chiral systems in their electronic ground states. Furthermore, with the aid of theoretical models, the relative shapes, frequencies, and inten-

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sities of CD bands have been used to elicit information about the spectroscopic states responsible for the chiroptical observables. In most cases, this information is qualitative and consists of the orbital nature and symmetries of the electronic, or vibronic, excited states connected to the ground state by direct radiative absorption. In accordance with the Franck-Condon principle, the symmetries of these states are defined with respect to the geometry and point-group symmetry of the molecular ground state. Neither CD nor ORD can provide information concerning the stereochemistry and electronic structure of thermally equilibrated or relaxed electronic excited states, or of excited states inaccessible by direct radiative absorption. Generally,