Critical size and curvature of wave formation in an excitable chemical medium

(Belousov–Zhabotinskii reaction/nucleation size/dispersion/wave propagation)

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ABSTRACT The critical radius for the outward propagation of waves in an excitable solution of the Belousov–Zhabotinskii reaction was experimentally analyzed and found to be $\approx 20 \mu\text{m}$, being in a range predicted by theory. Thus, the wave initiation depends on the critical radius in an all-or-none fashion. For waves having high positive curvature of wave fronts, a linear relationship between the curvature and their normal velocity was established, allowing computation of a diffusion coefficient of $1.9 \times 10^{-5} \text{ cm}^2/\text{s}$ for the autocatalytic species, which agrees well with results previously obtained for negatively curved wave fronts. The analysis of the dispersion of wave velocity yielded the decrease of wave velocity for small initiation periods as predicted theoretically.

The Belousov–Zhabotinskii (BZ) reaction is one of the most frequently studied examples for self-organization in nonlinear chemical systems under far from thermodynamic equilibrium conditions (1). The mechanism of this reaction, in which malonic acid is catalytically oxidized and brominated by acidic bromate, has been investigated in detail in several laboratories (2, 3). The BZ system exhibits temporal oscillations and spatial patterns (4, 5). Propagating waves arise by local perturbation of the system, and the results of such a perturbation are treated in this communication. We provide experimental evidence for the existence of a critical radius that must be exceeded to induce outward propagation of circular waves. Furthermore, there are two important relationships that have to be considered for the understanding of the geometry and dynamic behavior of spatial waves. One is the dependence of the normal velocity on front curvature, which expresses the correlation between the shape and the propagation velocity of the wave fronts (6–9); the other is the dispersion relation, which expresses the dependence of the propagation velocity on the frequency of wave initiation (6, 7, 10). We have measured both relationships in the same excitable medium with high precision by applying computerized spectrophotometric video techniques with microscopic resolution.

Theory

The description of the BZ reaction kinetics on the basis of the so-called Oregonator model (19) leads, after supplementing the resulting rate equations by diffusion terms, to the following reduced dimensionless reaction diffusion equations (6)

$$\begin{aligned}\varepsilon \frac{\partial u}{\partial t} &= \varepsilon^2 \Delta u + f(u, v) \\ \frac{\partial v}{\partial t} &= \varepsilon \Delta v + g(u, v),\end{aligned}\quad [1]$$

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where u is proportional to $[\text{HBrO}_2]$, v is proportional to the oxidized form of the catalyst ferroin (v), t is a scaled time, Δ is the Laplacian operator, $f(u, v)$ and $g(u, v)$ describe the kinetics of the reaction, and ε is a time scale factor (the spatial scale has been chosen such that the diffusion coefficients of u and v become identical to ε).

Because $\varepsilon \ll 1$, the system can be treated by singular perturbation arguments. After changing variables into a moving coordinate system, the application of these arguments leads to the following two results for the wave solutions of the equation system.

The first is the relationship between the normal velocity N and the curvature K of a wave front (6–9)

$$N = c - D \cdot K \quad [2]$$

or, in detail:

$$\frac{\partial y / \partial t}{(1 + (\partial y / \partial x)^2)^{1/2}} = c - D \cdot \frac{\partial^2 y / \partial x^2}{(1 + (\partial y / \partial x)^2)^{3/2}}.$$

Here, c denotes the velocity of plane waves, D is the diffusion coefficient of the autocatalytic species, and x and y are the spatial coordinates.

The main statements of Eq. 2 are the following, as illustrated in Fig. 1: (i) For negative curvature the normal velocity increases with increasing curvature. (ii) For positive curvature, it decreases with increasing curvature. (iii) The relationship predicts a minimal radius

$$R_{\text{crit}} = \frac{D}{c}, \quad [3]$$

below which propagation of circular waves will not take place.

Furthermore, treatment of Eq. 1 allows us to derive a dispersion relation for wave propagation

$$c = \sigma(T), \quad [4]$$

as described in detail (6, 10). This relation expresses the dependence of the speed of plane waves c on the initial period T of wave initiation or on the frequency ω of the wave trains. It shows a decrease of the velocity of the wave propagation when the frequency of wave initiation is increased.

Methods

Reaction mixtures were prepared as described (11) and contained 48 mM sodium bromide, 340 mM sodium bromate, 95 mM malonic acid, and 380 mM sulfuric acid. As soon as the solution had become colorless, ferroin (3.5 mM) was added. The solution was filtered by using $0.45\text{-}\mu\text{m}$ Millipore filters to eliminate dust particles. Measurements were carried out in an optically flat Petri dish containing a solution layer $0.5\text{--}0.6 \text{ mm}$ thick at room temperature (usually $25^\circ\text{C} \pm 1^\circ\text{C}$).

Abbreviation: BZ, Belousov–Zhabotinskii.

FIG. 1. Schematic illustration of the relation between the normal velocity N and the front radius R according to Eq. 2, for $D = 2 \times 10^{-5}$ cm^2/s and $c = 100$ $\mu\text{m}/\text{s}$.

For the investigation of positive curvatures, small circular waves were produced. These were initiated by immersing very thin glass capillaries (slightly conically shaped; minimum diameter at the tip of the electrode, 12 μm) spattered with a silver film ≈ 0.5 μm thick. Silver dissolved in the solution reacts with bromide ions, thus reducing the bromide ion concentration to a low value, which acts as a chemical stimulus for a wave. Capillaries of different sizes were tested to find the minimum radius necessary for wave initiation. Subsequently, a capillary with a tip diameter of 32 μm was used for circular wave initiation to measure the velocity of the outward propagation as a function of wave radius. For the detection of the wave evolution, the probe was illuminated with diffuse light of 490 nm (maximum absorption of the catalyst ferroin) in an inverse microscope (Zeiss IM 35) connected to a video camera (Hamamatsu C 1000) with 512×512 pixel raster resolution. Video movies with a frequency of 25 images per s were recorded and subsequently evaluated frame by frame by digital methods (12). From these frames isoconcentration or isointensity lines were extracted at the steep edge of the propagating circular waves. Their shape was subsequently fitted by circles. Velocities of wave propagation were calculated from the time derivative of smoothed radius vs. time data.

For the investigation of the dispersion relation, we triggered repeatedly the chemical wave trains by automatically immersing a silver wire (diameter, 100 μm) into the solution. The time between successive "dip-ins" varied between 22 and 72 s. The velocity of very large circular waves, for which curvature effects can be neglected, was measured at a distance of 3–11 mm away from the initiation point as a function of this period of time.

Results

The immersing test with silver-coated glass capillaries, which we used to determine the smallest diameter necessary for wave expansion, shows that the initiation of waves is an all-or-none reaction. Fig. 2 shows that with increasing electrode radius there exists a small range around $R_{\text{crit}} \approx 16$ μm , where the electrodes become capable of initiating waves. Note that to this real electrode diameter the thickness δ of the diffusion layer of the silver ions, which are responsible for the initiation of the waves, should be added (δ is roughly estimated to be on the order of 5 μm).

Fig. 3 describes our experimental results for the relationship between normal velocity and curvature. The data are well

FIG. 2. Wave initiation as a function of the electrode radius. A, no waves were initiated; B, waves were initiated.

represented by a regression line, as expected from Eq. 2. The slope, which corresponds to the diffusion coefficient D , is $(1.903 \pm 0.084) \times 10^{-5}$ cm^2/s . The intersect with the velocity axis yields a value $c = 82.5 \pm 1.7$ $\mu\text{m}/\text{s}$. The values for c and D are in agreement with the results previously obtained in the case of negative curvature (13). In that case, the propagation of wave fronts was measured in the cusp-like areas of colliding circular waves, initiated by immersing a pair of silver wires (diameter, 100 μm) into the BZ solution. The (negative) curvatures were determined in the vertices of hyperbolas fitted to selected isoconcentration levels. A direct comparison of these two independent procedures to verify Eq. 2 is given in Fig. 4. The slopes of the two experiments are slightly broken at the ordinate because of minor experimental differences (e.g., small temperature shifts, aging of the solution).

As a further result of the evaluation of the positively curved fronts, we obtained an estimation of the critical radius by extrapolation to the intersect with the curvature axis. The value for R_{crit} is 23.1 ± 1.0 μm .

The results for the dispersion relation are presented in Fig. 5. The velocity of the first, the second, and up to the fifth wave is plotted as a function of the initiation period (see legend). While the velocity of the first wave obviously does not depend on this period, all subsequent waves slow down with increasing frequency. For any given frequency, the velocity of the successive wave fronts decreases until it reaches a lower limit (for the fourth and any following waves). The higher the frequency the larger this effect. The velocity values used in this graph were obtained from data measured at a room temperature of 25°C. Small changes of this temperature value occurring during the course of the measurement were subsequently extrapolated to $t = 25^\circ\text{C}$. This was done on the basis of the Arrhenius relationship by using the activation energy for wave propagation ($E_a = 34.9$ $\text{kJ}\cdot\text{mol}^{-1}$) given in ref. 14. The velocity of the first oxidizing

FIG. 3. Relation between curvature K and normal velocity N as determined from measurements of the dependence of radius R on time (see example in *Inset*) of outward propagating circular waves. Open and solid circles represent two series of measurements.

FIG. 4. Relation between curvature K and normal velocity N based on values of diffusion coefficient D and the plane wave velocity c obtained in the case of negative curvature from figure 3 in ref. 13 and in the case of positive curvature from Fig. 3 of this paper.

front is always $\approx 125 \mu\text{m/s}$. For the smallest initiation period of 22 s, the decrease of the velocity amounts to 61%.

Discussion

As the most important finding, the capillary tests show that in the prepared reaction system there exists a "critical radius" with macroscopic dimension, which is necessary to initiate a chemical wave. Thus, the reaction volume of the initiation in an excitable medium is found to follow an all-or-none rule. In Eq. 2, the critical radius corresponds to $N = 0$. By inserting the values measured for negative and positive curvature for D and c ($D = 1.996$ resp $1.903 \times 10^{-5} \text{ cm}^2/\text{s}$; $c = 95$ resp $82 \mu\text{m/s}$; see Fig. 4), the critical radius is numerically estimated to be 21 resp 23 μm . Both this estimate for R_{crit} and the result of the direct capillary test given above agree remarkably well with the value predicted in ref. 6.

FIG. 5. Dispersion of the velocity of successive plane waves as a function of initiation period. $\bullet$, First; $\times$, second; Δ , third; $\circ$, fourth; ∇ , fifth; and $\square$, sixth wave; $\blacksquare$, data for spiral waves.

The measurements of the effect of positive curvature show proportionality between the normal velocity and the curvature of the outward propagating wave fronts within the experimental inaccuracies. Keener and Tyson (6) obtained a linear relationship under the assumption that the diffusion coefficients of both reaction components u and v (see Eq. 1) are equal, which is justified when considering the sizes of the reactants involved. Under this assumption, the linear relationship is not in controversy with the nonlinear relation between velocity and curvature predicted by Zykov (8, 9) for systems in which only one of the reaction components is able to diffuse. It could be of great interest to measure the velocity-curvature dependence in a gel system in which the catalyst ferroin is bound to the polymer network so that diffusion of this component cannot take place. Then a nonlinear relationship, resulting from the interaction of the two species with different diffusive behavior, should be observed.

The issue of the critical radius is indirectly related to the controversial discussion about the heterogeneous or homogeneous nucleation theories. According to Tyson and Fife (15), the origin of a wave pattern in excitable media is a heterogeneity (for example, an "autocatalytic" particle or a thermal stimulus), which leads the kinetics locally to oscillatory behavior. On the other hand, the Brussels group (16) shows that in oscillatory medium a local internal molecular fluctuation, which can lead to a local frequency shift to frequencies higher than that of the bulk solution, can act like a stimulus. Both in excitable and oscillatory media, the homogeneous or heterogeneous stimulus changes only the local kinetic behavior, which builds up concentration gradients. For the radial propagation of this local perturbation sufficiently large gradients in u (the autocatalytic species) in an extended area* are necessary so that diffusion can take place. Our experiments, performed in an excitable medium, support the approach that in such a system a macroscopic stimulus is necessary for wave initiation. The detailed condition for wave initiation in oscillatory medium needs to be further investigated.

Besides the curvature-velocity effect, the dispersion of the velocity is important for the understanding of the dynamic behavior of spatial pattern, especially for the formation of spiral-shaped waves. A typical feature of the dispersion relation is a decrease of velocity by an increase in the frequency of wave initiation because waves are propagating in the wake of the previous wave, so the relaxation of the medium is not complete, the concentration gradients do not have their final steepness, and, consequently, the velocity is smaller. The velocity reduction for small initiation periods is, in our case, in the same range as measured by Pagola *et al.* (17) (60%) in the case of an oscillatory medium (18). For sufficiently small frequencies, there is enough time for the medium to recover full excitability before the next wave train travels through the medium with nearly maximum speed of the medium. However, because of aging effects, the solution never reaches its final speed, which is reflected by the velocity for periods > 50 s, which are always lower than that of the first wave (Fig. 5).†

*Since the term critical radius is used in different meanings—e.g., in connection with broken ends (8, 9)—it should be pointed out that in the case of a circular region of excitation critical radius means the radius that is necessary to build up such a critical, sufficiently large area, as noted above.

†It should be pointed out that, because of the lower velocities of successive wave fronts, the distance between wave fronts increases with time or with increasing distance from the initiation point. For this reason, any following wave front sees a concentration distribution that corresponds to a wave train initiated with larger periods, so that the wave speeds up with time. This effect is larger the more the velocities of successive wave fronts differ from each other; for the third and the following waves, this effect is only minor, because the front velocities are similar.

Spiral waves in the BZ system rotate with a characteristic maximal frequency, which corresponds to the minimal period of successive wave fronts that can be realized by the system. The data for the rotation period (17.3 s) and the corresponding propagation velocity (76 $\mu\text{m/s}$) for spiral waves (■ in Fig. 5) measured in the same solution agree well with the dispersion relation.

The results of the study presented here clearly relate the macroscopic criteria of pattern formation to the underlying chemical reaction mechanism. They stress the essential relationship between the critical concentration and gradients of the autocatalytic species and the macroscopic minimal initiation volume.

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