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Temperature gradients traveling with chemical waves

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Local thermal inhomogeneities traveling with oxidation wave fronts are measured in an excitable liquid layer of Belousov-Zhabotinsky reagent. Measurements are carried out with an infrared thermopile detector and a pyroelectric film. An exothermic reaction occurring in these excitation fronts generates a local temperature rise of 50 mK. This result allows one to exclude that temperature changes act constructively in the mechanism of convection processes induced by chemical waves and yields a clear indication that the driving forces have to be produced by local concentration changes alone. [S1063-651X(96)08805-8]

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I. INTRODUCTION

Propagating waves of chemical excitation in the Belousov-Zhabotinsky (BZ) reaction are a well established example of patterns forming in a system far from equilibrium, which in many cases can be described successfully by a cooperation of reaction and diffusion [1]. A shallow liquid layer remains excitable until a local disturbance generates a spreading circular wave. In its wake the medium remains in the refractory state until it becomes excitable again. In recent years these experiments have been mostly run in a gel to suppress fluid motion and to ensure that diffusion is the only transport mechanism.

Nevertheless, hydrodynamic flow in a BZ solution is of great current interest in itself, as it exhibits an example for the competition between the transport mechanisms of diffusion and convection as well as a linkage between hydrodynamic and chemical pattern formation [2–7]. Miike and coworkers observed convective patterns traveling with waves in a shallow layer of liquid solution [2,3]. If the chemical wavelength is large, each wave carries a pair of convection rolls with a pronounced downward flow at the site of the front. A weak upward flow is distributed over a broad zone far away from the wave. At the surface this generates a flow against the direction of wave propagation in front of the wave and in the direction of propagation behind the wave. This convection is strongly connected to the wave geometry and independent of evaporative surface cooling [2].

Yet the driving force for this chemically induced convection still remains unclear as, on the one hand, gradients in density (Bénard-type convection) [5–8] and, on the other hand, local changes in surface tension (Marangoni-type convection) may give rise to the fluid motion [8–10]. Both are changed by the chemical composition itself as well as by thermal gradients resulting from an exothermic reaction step arising in the front [5,8]. Some other, well known systems forming exothermic propagating fronts, e.g., the nitric acid–iron (II) reaction [11] and the chlorate-sulfite reaction [12], show convection caused by thermal gradients. Therefore the local temperature distribution over the wave pattern is an important factor that in the BZ reaction has not been measured yet.

Temperature measurements in a spatially homogeneous, continuously stirred oscillating Belousov-Zhabotinsky reaction have been reported by several workers [13–19]. Körös, Orbán, and Nagy found the total reaction to be exothermic with almost all the heat released during the autocatalytic reaction step, leading to a stepwise increasing temperature. The amount of heat was determined to about 200–300 J/l per oscillation, depending on the initial concentrations and the type of catalyst used [16]. For a typical ferroin system this corresponds to a temperature rise of 50 mK per oscillation.

In this work we present local measurements of such temperature changes in a spatially extended solution layer. Here heat diffusion and also convection may smooth the induced temperature gradients, and heat exchange with the surrounding is also present. The measurements are carried out with a thermopile infrared (IR) detector placed over the surface of the solution. We add measurements of the time derivative dT/dt of the temperature using a pyroelectric detector with an improved spatial resolution.

II. EXPERIMENT

Solutions are prepared with the following initial concentrations: 300 mM $NaBrO_3$, 100 mM malonic acid, 46 mM NaBr, 200 mM H_2SO_4, and 3.5 mM ferroin serving as a catalyst and indicator. With this preparation and by careful cleaning of the reaction container the spontaneous formation of waves in the bulk and at the boundaries of the reaction vessel is suppressed. Single waves with a period of about 10 min are initiated by a silver wire (diameter of 0.5 mm) dipped into the solution for a few seconds. From the point of initiation (see Fig. 1) a wave takes 285 s to reach the center of the measured area (time instants indicated by arrows in the measurements; see figures below). All experiments are carried out at an ambient temperature of 25±1 °C.

Direct measurements of the temperature are carried out at the surface of the liquid layer in the following way: 5 ml of the solution is filled into a petri dish supplied with a cover that leaves an air gap of 6 mm above the surface and minimizes evaporation. A small thermopile IR sensor (IPHT Jena, Germany) is attached in the middle of the cover at a distance of 5 mm to the sample surface. It thus receives a

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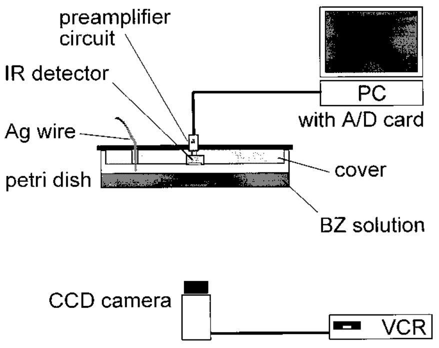

FIG. 1. Experimental setup for measurements of T. The signal from the thermopile IR detector is preamplified and recorded with a PC. The sample is observed from below with a CCD camera and a time-lapse VCR. The diameter of the measuring area is 6 mm; the distance from the sample surface to the detector is 5 mm.

signal from a circular area with a diameter of about 6 mm (Fig. 1). This detector converts thermal IR radiation into voltage by a series of 72 thermocouples with the detector case providing the reference temperature. Thus, for a sufficient thermostating of the case, the whole detector is inserted into the dish cover of copper. The output voltage of the sensor is boosted, low-pass filtered (time constant of 1.0 s), and recorded with a personal computer (PC) via a Keithley DAS1201 analog to digital converter card. In order to correlate the temperature changes with the propagating fronts, the petri dish is observed from below with a charge coupled device (CCD) camera (Hamamatsu C3077) connected to a time-lapse videotape recorder (SONY).

The presented method contains an uncertainty of up to 60 s in assigning a specific phase of the passing wave to the temperature signal because of the spatial extension of the observed area. Thus we carried out additional measurements with a setup using a pyroelectric polyvinylidene (PVDF) film below the sample (Fig. 2). It provides a signal proportional to dT/dt [20,21]. For our purpose 1 ml of the solution is filled into a container equipped with a bottom of a 2-μm Mylar sheet (a chemically very inert polycarbonate). Below this foil a (1×1)-mm^2 stripe of 18-μm-thick pyroelectric PVDF with metalized faces is fixed in the middle of the container [Fig. 2(b)]. The pyroelectric coefficient of this PVDF is 22×10^{-12} C/mm^2 K. The current arising from the pyroelectric effect with the onset of temperature changes is measured over the PVDF faces with a picoampere meter (Keithley 6512). The output signal is filtered (1.0 s) and recorded digitally as above. Again, the propagating fronts are observed with a CCD camera for comparison with the detector signal. In this measurement, a wave takes 270 s to reach the measuring site from the point of initiation.

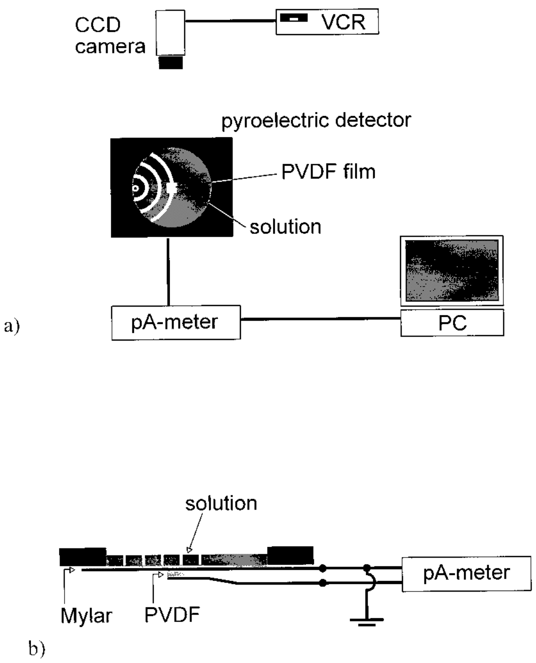

FIG. 2. Experimental setup for measurements of dT/dt. (a) Schematic view of the total setup. The PVDF film $(1\times1\ \text{mm}^2)$ is placed below the center of the reaction vessel (diameter of 37 mm). The pyroelectric current is measured with a picoampere meter. Data recording and observation of waves are as in Fig. 1. (b) Attachment of PVDF film (side view). The film (9 μm) is fixed below the Mylar foil (2 μm) serving as the bottom of the vessel. The pyroelectric current is picked up with electrodes from the PVDF faces.

III. RESULTS

A. Measurements of temperature *T*

Figure 3 shows a typical time trace of a measurement of the local temperature in an excitable Belousov-Zhabotinsky preparation (curve a). The temperature rises steeply when a wave approaches the center of the sensor field and decreases smoothly afterward. The temperature rise amounts to 40–60 mK.

In all experiments a drift is superposed on the signal. To examine whether this drift is independent of the reaction, we performed measurements of the same solution, except that no catalyst was added and thus no oscillations could occur. This yields a temperature course as shown in curve b. The reactive sample [Fig. 3(a)] is distinctly shifted towards higher ΔT values with respect to the nonreactive one [Fig. 3(b)]. The drift, however, is present in both cases and is obviously

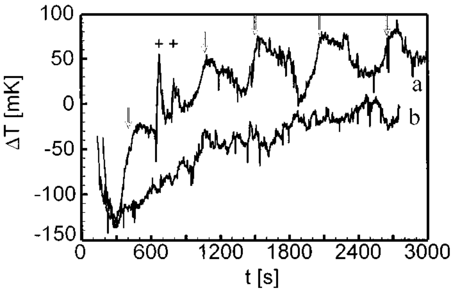

FIG. 3. Measurement of ΔT. Curve a: excitable preparation. Arrows indicate moments when the wave is at the center of the sensor field; pluses indicate the occurrence of external disturbances. Curve b: unexcitable preparation (BZ reaction without catalyst). The zero point is arbitrarily chosen.

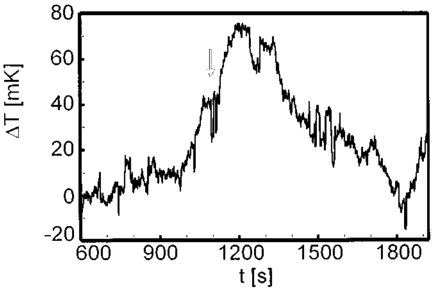

FIG. 4. Measurement of ΔT in a single wave. The temporal distance to the preceding wave is 14 min.

due to the establishment of a thermal and evaporative equilibrium in the space above the surface after filling the dish.

To show the time relation between the temperature and the wave in detail, Fig. 4 depicts a part from a measurement where fronts are initiated with an extremely large time interval of 14 min. In this case, the wave propagates into totally recovered medium and any temperature changes caused by the preceding wave have vanished. The rise starts about 200 s before the wave passes through the measuring site. The maximum is reached about 60 s afterward. Again, the temperature rises by 60 mK.

In the case of waves that follow each other at a short distance of less than 10 mm, the temperature rises appear smaller the closer the fronts follow. However, this result should be quantified in more detail with a detector of superior spatial resolution to be developed in future experiments.

B. Measurements of the rate of temperature change dT/dt

Figure 5 exhibits a typical measurement obtained with the pyroelectric detector, yielding a signal proportional to dT/dt. The signal is distorted by a long-term drift that makes any transformation of the whole measurement into temperature or rate of temperature change futile. Thus, in the graph the current obtained from the PVDF film is shown without further evaluation. Nevertheless, the signal shows a characteristic response to a passing wave: Each passage leads to a peak in the signal representing the moment of steepest increase in temperature. This occurs about 20 s before the front reaches the measuring site. The peak height is equivalent to a temperature change of at most 0.4 mK/s. In analogy to the direct temperature method, we also observed that the rise in temperature decreases with decreasing wavelength between subsequent waves.

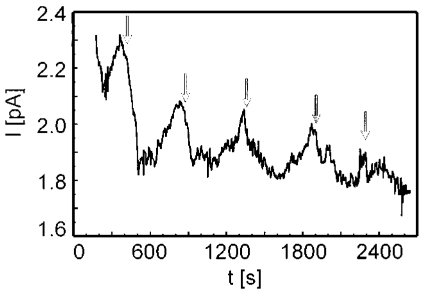

FIG. 5. Measurement of the pyroelectric current (proportional to dT/dt) obtained from an excitable preparation of the BZ reaction. The scale is not converted to dT/dt or T because of offset and drift. Arrows indicate that the wave crosses the center of the PVDF film.

IV. DISCUSSION

The following results were obtained in good agreement for both techniques. An isolated propagating wave produces a marked increase in the local temperature, causing a temperature gradient moving with the wave. For the given BZ solution, the pyroelectric measurement yielded a maximum gradient 20 s before the wave reaches the measuring point, i.e., at a distance of 2 mm in front of the wave (with respect to the propagation speed of approximately 100 μm/s). About 60 s after passage, i.e., at a distance of 6 mm behind the front (with respect to the system uncertainty), the temperature change reaches its maximum, as found with the thermopile detector. The increase amounts to 40–60 mK and corroborates that the reaction taking place in the front is truly exothermic. Even the amount of increase is in accordance with the results obtained by Körös, Orbán, and Nagy [15,16]. The observed decrease following the front contrasts with the stepwise rising temperature in the homogeneous case and is a consequence of the thermal openness of the petri dish compared with the calorimeter used in [15,16]. The decreasing temperature change in the case of a close distance of waves could indicate that temperature diffusion smoothes the gradients or it gives a hint to a dependence of the temperature rise on the extent of recovery present when the site becomes excited anew.

From these results we can draw an important conclusion about the mechanism of chemically driven convection: Temperature changes cannot have any supporting effect on the onset of convection—neither via gradients in density nor in surface tension. This exclusion of the influence of temperature changes can be understood from the following argument.

If the flow were driven alone by buoyancy forces caused by thermal gradients, it should be descending in the local temperature minimum [5,22]. As mentioned above, the fluid actually is descending close to the site of the wave. Our investigations yielded a local temperature maximum shortly behind the front, contradicting the supposition. Thus temperature gradients cannot cause a Bénard-type convection with the observed properties.

On the other hand, a Marangoni-type flow is directed towards a local maximum of the surface tension σ [8,22]. In a homogeneous batch experiment of the ferroin-catalyzed BZ reaction a maximum value of σ was found during the oxidation of the catalyst [10], which makes a maximum at an oxidized front in an unstirred shallow solution likely. This would be consistent with the flow pattern at the surface. Local changes in the surface tension with a passing wave were indeed detected recently [23]. The surface tension of nearly all aqueous solutions, however, decreases with rising temperature; unpublished measurements also confirmed this for BZ solutions [23]. This result means that the temperature maximum at the site of the front can only generate a minimum in σ. The observed thermal gradients, consequently, cannot support a Marangoni-type convection in this system either. Therefore, concentration gradients affecting the local density and/or surface tension remain the only driving force for the observed convection.

The thermal changes should be taken into account, nevertheless, for a thinkable multicomponent convection, driven by surface tension [24] as well as buoyancy [5], providing a component that counteracts the effect of concentration gradients. Furthermore, to reach a more accurate clarification of the convective mechanism, a thorough study of the local changes in surface tension and density moving with the waves is necessary and should be compared with precise numerical investigations.

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