Transition between Fronts and Spiral Waves in a Bistable Surface Reaction

M. Bär, S. Nettesheim, H. H. Rotermund, M. Eiswirth, and G. Ertl
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany
(Received 12 May 1994)

The transition between wave fronts and spiral waves in the CO oxidation on a Pt(110) surface has been investigated by means of photoemission electron microscopy and treated theoretically by simulations with a reaction-diffusion model under bistable conditions. Periodic external forcing of spirals near the transition to front behavior led to a complex pattern best characterized as a pulsating spiral-front hybrid, thus confirming the bistable nature of the underlying reaction kinetics.

PACS numbers: 82.20.Mj, 82.65.Jv

Pattern formation under nonequilibrium conditions has been an important field of research in areas ranging from hydrodynamics and nonlinear optics to morphogenesis and biological rhythms [1]. In chemical systems the interplay between reaction and diffusion produces a large variety of spatial structures including traveling waves [2] and stationary Turing-type structures [3]. Most pattern-forming reactions are discussed in terms of the activator-inhibitor concept: A fast autocatalytic species (activator) produces a second substance (inhibitor) on a slow time scale, which in turn consumes the activator, thus introducing a negative feedback. If the diffusion of the inhibitor dominates, stationary structures may be formed, and, if the activator diffusion prevails, traveling waves can be expected. The particular type of wave pattern depends strongly on the local dynamics of the system under consideration. Oscillatory and excitable conditions produce pulse waves, target patterns, and rotating spirals [4]. One-component bistable media (i.e., media without an inhibitor species) can only give rise to wave fronts of the most stable state [4(a)]. A two-component bistable system is more complex: If the new inhibitory species diffuses faster than the activator, interaction of fronts may lead to formation of complicated, labyrinthine patterns [5]. In this Letter we present an example of a bistable chemical reaction with dominating activator diffusion. In this case, both states may become unstable with respect to front propagation. Such a behavior is called front multiplicity or dynamic bistability [6]. Recent theoretical studies predict also the possibility of persistent structures like pulses and wave trains [7] under these conditions. The latter are qualitatively different from excitable conditions studied earlier [8].

Generally, in excitable media only one (stable) steady state exists and fronts cannot form. Although spiral waves can be obtained under both bistable and excitable conditions, they behave quite differently, as is shown below.

Experimentally, the coexistence of different fronts was observed in the CO oxidation on Pt(110) by means of photoemission electron microscopy (PEEM) [8]. The aim of the present Letter is to show that the formation of pulses and spirals under conditions of dynamic bistability depends strongly on the interaction of wave fronts. The second goal is to demonstrate the behavior of spirals in the bistable regime under periodic perturbations of the external parameter. Then the spiral center starts to drift similarly to experiments under excitable conditions [8], but the overall pattern changes dramatically and is now best characterized as a pulsating spiral-front hybrid revealing the underlying bistable kinetics of the reaction. The experimental findings can be reproduced nicely with a reaction-diffusion model.

The experiments were carried out with a Pt(110) single crystal in an ultrahigh vacuum (UHV) chamber equipped with a photoemission electron microscope (PEEM), which provides a spatial resolution of 0.2 μm and a time resolution of 20 ms [9]. External control parameters are given by the partial pressures of CO and oxygen, p_{CO} and p_{O_2}, and by the temperature T. The reaction proceeds via the Langmuir-Hinshelwood mechanism [10] and interacts with the surface structure by lifting of the 1×2 reconstruction at sufficiently high surface coverages of CO [11]. It can be modeled by a two-component reaction-diffusion system, describing the dynamics of the CO/O coverage u and the surface structure w [11,12]. The spatial coupling in the reaction is provided by the CO surface diffusion. This model, described in detail in Ref. [12], reads in dimensionless units

$$\frac{du}{dt} = -\frac{1}{\varepsilon} u(u-1)\left(u - \frac{w+b}{a}\right) + \nabla^2 u, \tag{1a}$$

$$\frac{dw}{dt} = f(u) - w, \tag{1b}$$

with

$$f(u) = \begin{cases} 0, & u < 0.6, \\ 1 - 31.25(u - 0.4)(u-1)^2, & 0.6 \le u \le 1, \\ 1, & u > 1. \end{cases} \tag{1c}$$

 0031-9007/95/74(7)/1246(4)$06.00

The special form of $f(u)$ is taken from the experimental dependence of the surface structure w on the CO coverage u [10]. Note that $u = 0$ ($u = 1$) here corresponds to a CO coverage of 0.95 monolayers (ML) (0.2 ML) and w simply gives the degree of the 1×2 reconstruction of the surface. One space (time) unit in Eqs. (1) is of the order of magnitude 1 μm (1 s) for the conditions of the experiments presented below. The physical parameters T, p_{CO}, and p_{O_2} can be mapped into a, b, and ε. ε represents the ratio of the time scales of the surface reaction and the structural transformation [12]. The value of a determines whether the system is excitable ($a < 1$) or bistable ($a > 1$); it mainly depends on the rate of CO desorption (and hence temperature). b expresses whether CO or oxygen prevails on the surface; it becomes smaller (larger) for increasing p_{CO} (p_{O_2}, T). For details of the parameter mapping, see [12]. The quantities a and ε change only slowly in the bistable regime of the parameter space; therefore we assume them to be constant ($a = 1.8$, $\varepsilon = 0.025$). The parameter b is very sensitive to changes of temperature or partial pressures and will be used here as the bifurcation parameter. A temperature decrease of 1 K corresponds in Eqs. (1) to a decrease of 0.12 in b for an absolute crystal temperature around 470 K. If one leaves aside the details of the specific reaction, Eqs. (1) represent an activator-inhibitor system, where the coverage (surface structure) can be identified with the activator (inhibitor) species. Therefore the phenomena described here are expected for a large class of systems.

For fixed partial pressures $p_{CO} = 5.6 \times 10^{-5}$ mbar and $p_{O_2} = 4.0 \times 10^{-5}$ mbar, the following scenario was found in the experiments. At high temperatures, above 485 K, the platinum surface was covered predominantly with oxygen. Upon the lowering of T, CO fronts appeared, indicating a transition to dynamic bistability, since at the same time CO-covered regions can return to the O-covered state via oxygen fronts. These oxygen fronts are always faster then the CO fronts, so that they are able to catch up with any preceding CO front. In this case, the CO-covered spot vanishes and the fronts annihilate each other (cf. Fig. 1). For temperatures around 465 K the velocities of CO and O fronts become comparable and the interaction between fronts is altered. In a narrow temperature region pulselike CO-covered areas coexist with propagating fronts. Further decrease of T leads to the emergence of spiral waves. This transition can be found in a wide range of temperatures and CO partial pressures at fixed oxygen supply. It can be reproduced with simulations of Eq. (1) in one spatial dimension by changing the parameter b (note that low b values

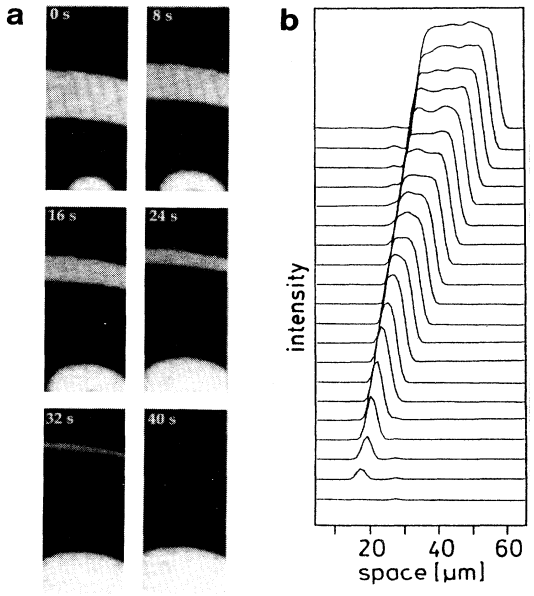

FIG. 1. Annihilation of wave fronts as observed experimentally with PEEM; the black oxygen front catches up with the white CO front. (a) Original PEEM images; the height of one picture is 80 μm. (b) Intensity profiles of the interacting fronts drawn from images as in (a); time difference between two lines is 2 s.

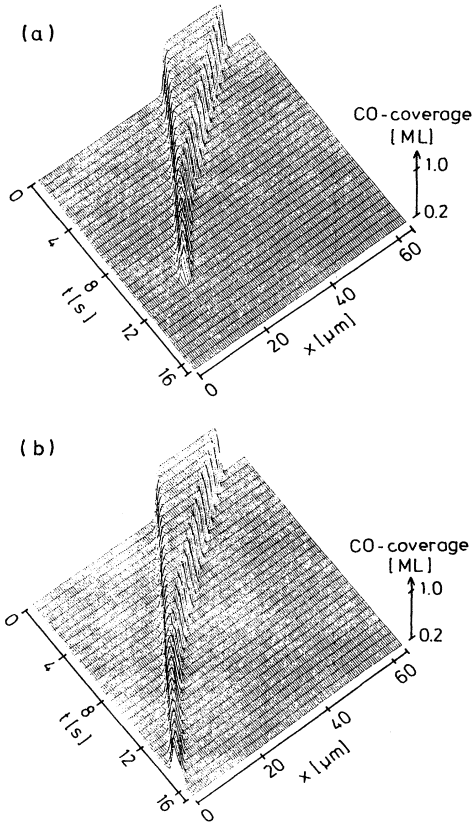

FIG. 2. Interaction of waves in a one-dimensional simulation of Eqs. (1) with $a = 1.8$ and $\varepsilon = 0.025$. (a) Annihilation of fronts ($b = 0.384$). (b) Formation of a stable pulse ($b = 0.386$).

correspond to high temperatures and vice versa). Below a critical value $b_{c,1} = 0.385$, fronts annihilate each other; above $b_{c,1}$, the faster oxygen wave slows down and forms a stable CO pulse with the slower CO front (cf. Fig. 2).

If the model calculations are extended to two dimensions, another transition in the pattern-forming properties of the system is observed: Above $b_{c,2} = 0.425$, spiral waves can be formed by suitable perturbations of the wave fronts (pulses). As in excitable media [13], under conditions of dynamic bistability the possibility of pulse waves in one dimension is a necessary prerequisite but does not guarantee formation of rotating spirals in two dimensions. The main difference compared to an excitable medium is that spiral waves coexist with wave fronts. However, since spirals represent a periodic wave source, they annihilate any wave fronts. Consequently, the coexistence between spirals and wave fronts is rarely observed under constant external conditions. Nonetheless, this particular feature of spirals under bistable conditions became visible, if periodic perturbations were applied to the external parameters.

In the next experiment, at a constant temperature of $T = 463$ K and partial pressures as described above, a spiral wave with a rotation period of 7 s developed. Then a periodic forcing of the temperature with an amplitude of 0.5 K and a period of 10 s was applied. The resulting behavior is displayed in Fig. 3. Upon increase of the temperature the white spiral arm first retracts and a dark oxygen-covered region develops in the spiral center. Subsequent lowering of the temperature makes the white arm curl again into the black central region, thus initiating a white CO front which forms a small dark arm with the original white spiral arm. As the temperature rises again, the newly formed black arm moves into the white region and causes a black front. This cycle continues and produces a complex pattern which replaces the original spiral and looks like a mixture between pure spiral and front patterns (cf. Fig. 4). This dynamic behavior is reproduced in the model equations (1) by choosing a periodic perturbation in b via

$$b(t) = b_0[1 + \delta b \sin(\omega t)]. \quad (2)$$

Since the experiments were carried out close to the critical temperature value ($T = 464$ K) for spiral waves, we chose $b_0 = 0.46$ close to $b_{c,2} = 0.425$. There, the spirals have a period of 6.5 s. The relative amplitude $\delta b = 15\%$, corresponding to an absolute amplitude of 0.0675, and a period $\tau = 2\pi/\omega = 9.9$ s are used here to mimic the experimental conditions (see above). The perturbation was again applied after a stable spiral had formed. The dynamics of the pattern after the application of the perturbation is shown in Fig. 5. Again retraction of the black (white) arm and subsequent initiation of the corresponding front dominates the picture and leads to a spiral-front hybrid. Thus the periodic perturbation reveals the bistable nature of the spiral by showing that the spiral tip is able to create wave fronts in a large domain in the spiral center. Perturbations near (or beyond) the existence boundary of spirals are favorable since there spiral periods and core sizes become very large.

Quite recently, a new technique has been developed which allows the study of pattern formation in separated areas of the catalyst by use of photolithography [14]. From three separate domains, one was homogeneously covered with CO and one with oxygen, while in the third one spiral waves appeared for similar parameter values as shown above [14(b)]. This provides additional proof that the experimental observations of spirals close to the transition to wave fronts are obtained under locally bistable conditions. Altogether, we showed that experimental observations in the CO oxidation are consistent with calculations in a realistic reaction-diffusion model under bistable conditions. The transition to spiral wave behavior is closely linked with a change in the interaction

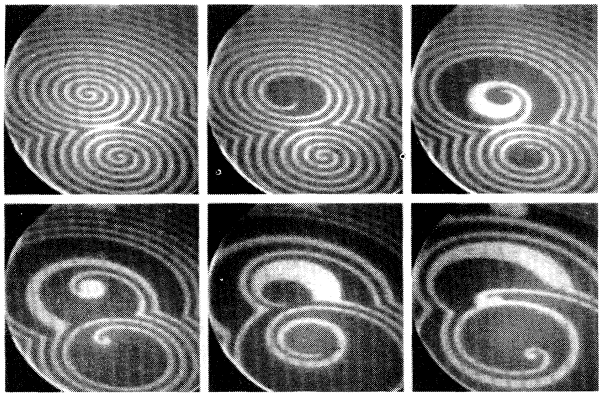

FIG. 3. Sequence of PEEM images at $p_{CO} = 5.6 \times 10^{-5}$ mbar, $p_{O_2} = 4.0 \times 10^{-4}$ mbar, and $T = 463$ K after a periodic forcing of the catalyst temperature with an amplitude of 0.5 K and a period of 10 s has been applied at the time of the first frame. The time difference between two slides is 15 s; the picture size is 173×173 μm^2.

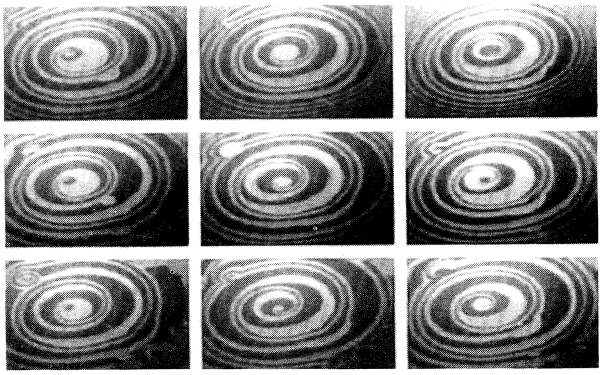

FIG. 4. PEEM images of a stable spiral-front hybrid 5 min after the periodic forcing started. The picture size is 160×256 μm^2 and the time difference between the pictures is 10 s.

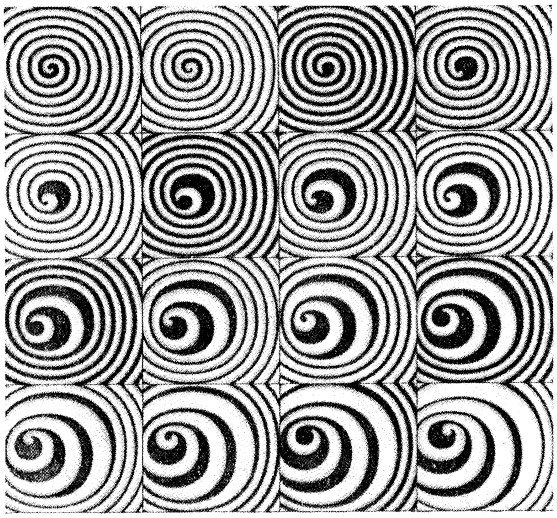

FIG. 5. Numerical simulation of a spiral-front hybrid with Eqs. (1) and (2). The parameters are $a = 1.8$, $\varepsilon = 0.025$, and $b_0 = 0.46$. The relative amplitude of the forcing δb is 15% and the period 9.9 s. The time difference between two pictures is 4.8 s, the picture size 130×130 μm^2, and 512×512 grid points were used.

of wave fronts. It was demonstrated that a periodic perturbation creates a novel type of pattern, which stems from the coexistence of spirals and wave fronts. This effect clearly distinguishes spirals in bistable from those in excitable media.

The authors thank A. S. Mikhailov for useful suggestions and stimulating discussions.

[1] M. C. Cross and P. C. Hohenberg, Rev. Mod. Phys. **65**, 851 (1993).
[2] J. Ross, S. C. Müller, and C. Vidal, Science **240**, 460 (1988).
[3] A. M. Turing, Philos. Trans. R. Soc. London B **237**, 37 (1952); V. Castets, E. Dulos, J. Boissonade, and P. d. Kepper, Phys. Rev. Lett. **64**, 2953 (1990); Q. Ouyang and H. L. Swinney, Nature (London) **352**, 610 (1991).
[4] (a) A. S. Mikhailov, *Foundations of Synergetics I* (Springer, Berlin, 1990); (b) E. Meron, Phys. Rep. **218**, 1 (1992).
[5] K. J. Lee, W. D. McCormick, Q. Ouyang, and H. L. Swinney, Science **261**, 192 (1993); A. Hagberg and E. Meron, Phys. Rev. Lett. **72**, 2494 (1994).
[6] P. Ortoleva and J. Ross, J. Chem. Phys. **63**, 3398 (1975); C. Zülicke, A. S. Mikhailov, and L. Schimansky-Geier, Physica (Amsterdam) **163A**, 559 (1990).
[7] A. Hagberg and E. Meron, Phys. Rev. E **48**, 705 (1993); S. Koga, Prog. Theor. Phys. **90**, 1361 (1993).
[8] S. Nettesheim, A. von Oertzen, H. H. Rotermund, and G. Ertl, J. Chem. Phys. **98**, 9977 (1993).
[9] W. Engel, M. E. Kordesch, H. H. Rotermund, S. Kubala, and A. von Oertzen, Ultramicroscopy **36**, 148 (1991).
[10] G. Ertl, Science **254**, 1750 (1991).
[11] K. Krischer, M. Eiswirth, and G. Ertl, J. Chem. Phys. **96**, 9161 (1992).
[12] M. Bär, N. Gottschalk, M. Eiswirth, and G. Ertl, J. Chem Phys. **100**, 1202 (1994).
[13] A. T. Winfree, Chaos **1**, 303 (1991).
[14] (a) M. D. Graham, I. G. Kevrekidis, K. Asakura, J. Lauterbach, K. Krischer, H. H. Rotermund, and G. Ertl, Science **264**, 80 (1994); (b) J. Lauterbach, Ph.D. thesis, Freie Universität Berlin, 1994.

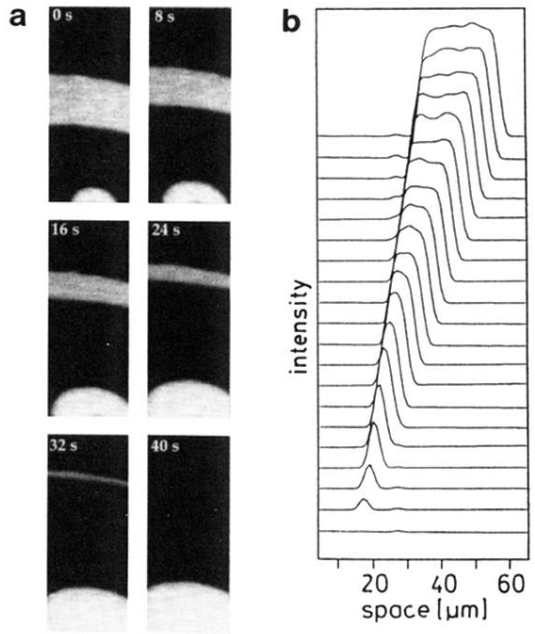

FIG. 1. Annihilation of wave fronts as observed experimentally with PEEM; the black oxygen front catches up with the white CO front. (a) Original PEEM images; the height of one picture is 80 μm. (b) Intensity profiles of the interacting fronts drawn from images as in (a); time difference between two lines is 2 s.

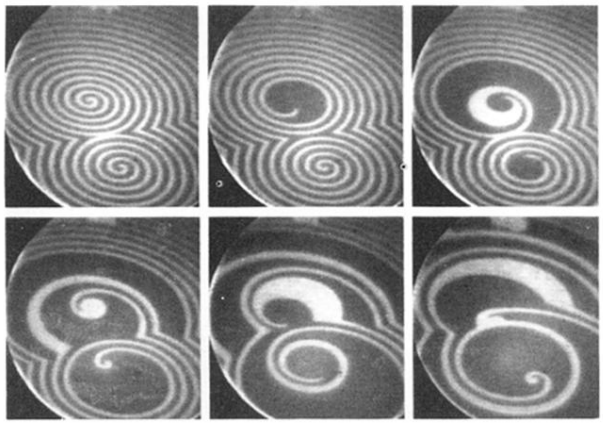

FIG. 3. Sequence of PEEM images at $p_{CO} = 5.6 \times 10^{-5}$ mbar, $p_{O_2} = 4.0 \times 10^{-4}$ mbar, and $T = 463$ K after a periodic forcing of the catalyst temperature with an amplitude of 0.5 K and a period of 10 s has been applied at the time of the first frame. The time difference between two slides is 15 s; the picture size is 173×173 μm^2.

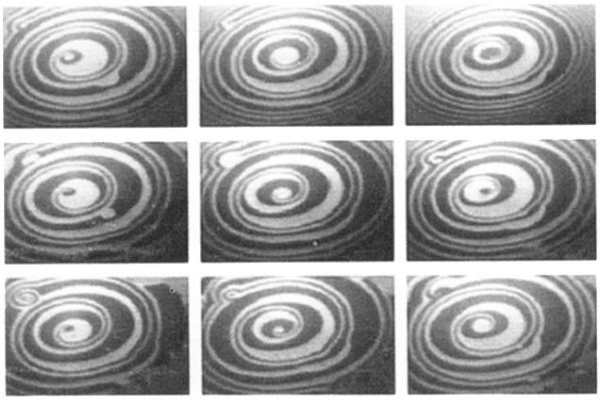

FIG. 4. PEEM images of a stable spiral-front hybrid 5 min after the periodic forcing started. The picture size is $160 \times 256\ \mu m^2$ and the time difference between the pictures is 10 s.

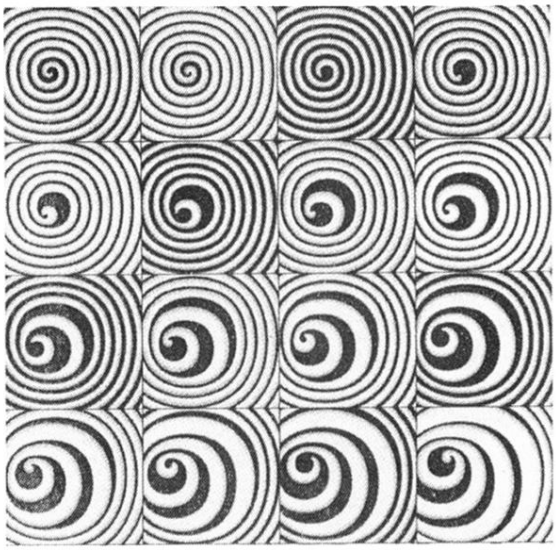

FIG. 5. Numerical simulation of a spiral-front hybrid with Eqs. (1) and (2). The parameters are $a = 1.8$, $\varepsilon = 0.025$, and $b_0 = 0.46$. The relative amplitude of the forcing δb is 15% and the period 9.9 s. The time difference between two pictures is 4.8 s, the picture size 130×130 μm^2, and 512×512 grid points were used.