PHYSICAL REVIEW A VOLUME 40, NUMBER 11 DECEMBER 1, 1989

Transition sequence and birhythmicity in a chemical oscillation model showing chaos

Makoto Morita,* Kazutoshi Iwamoto, and Manabu Senō
Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan
(Received 7 August 1989)

Using a chemical oscillation model, a transition sequence in a chaotic region was studied in detail, and its fine structure in the vicinity of a critical point where a simple oscillation with a small amplitude becomes unstable and diverges to a new oscillatory state was reported. Neither a combined complex oscillation nor a chaotic oscillation appears between the two complex oscillations in this region, contrary to other cases reported already. Moreover, coexistence of a complex oscillation and a simple oscillation with a small amplitude was found to appear.

I. INTRODUCTION

One of the most active subjects in the field of nonequilibrium thermodynamics is the investigation of the transition sequence in a chaotic region,[1,2] and the period doubling sequence,[3–5] the discontinuous transition[6] and the intermittency[7,8] have been reported. Especially the period doubling sequence has been intensively studied and is called a U sequence (or universal sequence) because of its system-independent properties.[9] The Belousov-Zhabotinskii (BZ) reaction is the most well-known experimental system which exhibits chaotic oscillations,[10–12] and the period-doubling sequences[13] and intermittency[7,8] have been observed. Moreover, some periodic states formed from combinations of large- and small-amplitude oscillations appear. Swinney *et al* carried out a detailed examination on the BZ reaction in a continuous-flow stirred tank reactor (CSTR) and revealed a staircase relationship by plotting a ratio W of the number of small-amplitude oscillations to the total number of oscillations per period.[14] As the control parameter, the flow rate of chemicals was used.

In our previous paper,[15] a three-variable model chemical system was studied and its bifurcation structures from a complex oscillation to a chaotic or a combined complex oscillations have been reported. A whole profile of the transitions from a simple oscillation with a small amplitude to a simple oscillation with a large amplitude was figured in the F-P phase plane, according to the way of Swinney *et al.*[14] The resulting staircase function of F versus P is very similar to the F-P diagram observed for the BZ reaction and this result strongly suggests a similarity of mathematical structures between the BZ reaction and the present model.

Here, the terms, "complex oscillation," "combined complex oscillation," "pseudoperiodic oscillation," and "simple oscillation" are defined as follows. A complex oscillation is an oscillatory state formed of one large-amplitude oscillation and $(n-1)$ small-amplitude oscillations, for which the symbol $\pi(n)$ is used hereafter. A combined complex oscillation means a combination of two or more complex oscillations and the symbol $\pi(m)\pi(n)$ is used for the combined complex oscillation formed of complex oscillations $\pi(m)$ and $\pi(n)$. The term of pseudoperiodic oscillation is used for a long-period oscillation for which it is hard to determine definitely whether it is chaotic or not. A simple oscillation is the oscillation with a single amplitude. There are two kinds of single oscillations; one is a large amplitude oscillation and the other is a small amplitude one. The complicated oscillatory behaviors in which we are concerned appear between these simple oscillations.

The transition sequence starting from the simple oscillation with a large amplitude is the period-doubling one, where no special behavior is found to appear.[15] A similar period-doubling sequence has been observed in the experiment of the BZ reaction.[13] However, the transition sequence starting from the simple oscillation with a small amplitude is quite a novel one, on which we will report in this paper.

II. CHEMICAL OSCILLATION MODEL

In the present investigation, the system consisting of the following chemical reactions[6] is considered:

$$P+Z\xrightarrow{k_1}E+Z\ , \tag{1}$$

$$E+X\xrightarrow{k_2}R+X\ , \tag{2}$$

$$A+2X+E\underset{k_4}{\overset{k_3}{\rightleftarrows}}3X+E\ , \tag{3}$$

$$B+X\underset{k_6}{\overset{k_5}{\rightleftarrows}}C\ , \tag{4}$$

$$Q\xrightarrow{k_7}Z\ , \tag{5}$$

$$Z+X\xrightarrow{k_8}D+X\ , \tag{6}$$

where A, B, P, and Q are reactants, C, D, and R are products, and E, X, and Z are intermediates. In order to sustain the system far from equilibrium, the concentrations of the reactants and the products are assumed to be constant.

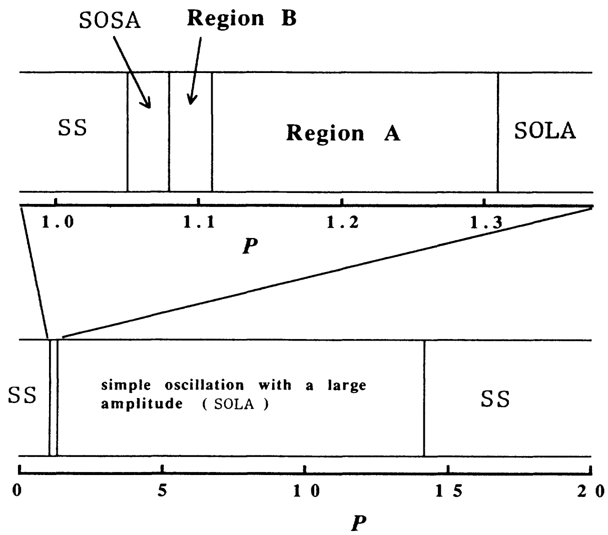

FIG. 1. The phase diagram of the periodic states in the region between two stable steady-state regions. The stable steady-state regions are shown by SS, and the region shown by SOSA is of the simple oscillation with a small amplitude. In Region A, complex oscillations, combined complex oscillations, and chaotic oscillations appear in sequence by a change of P. In Region B, coexistence of complex oscillations and simple oscillation with a small amplitude is observed.

III. KINETIC EQUATIONS

The kinetic equations tracing the concentration changes of the intermediates E, X, and Z are given by the following differential equations:

$$\frac{dE}{dt}=k_1PZ-k_2EX\ , \tag{7}$$

$$\frac{dX}{dt}=k_3AEX^2-k_4EX^3-k_5BX+k_6C\ , \tag{8}$$

$$\frac{dZ}{dt}=k_7Q-k_8XZ\ . \tag{9}$$

The following values were selected for the respective parameters and all the calculations were executed for respective P values, if not specially mentioned: $k_1=1.0$, $k_2=5.0$, $k_3=100.0$, $k_4=50.0$, $k_5=10.0$, $k_6=1.0$, $k_7=0.1$, $k_8=0.4$, $A=1.3$, $B=5.0$, $C=5.3$, and $Q=1.0$.

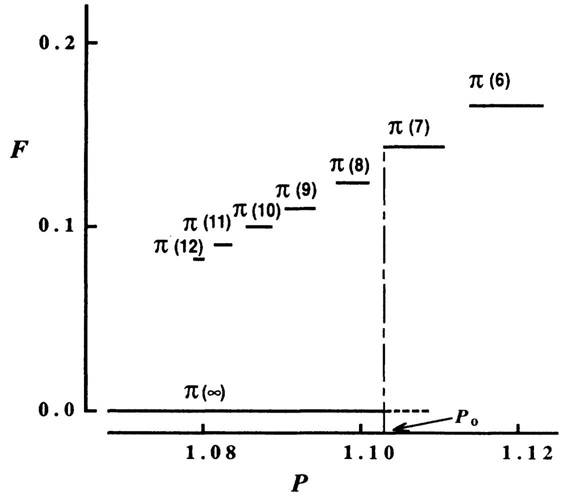

FIG. 3. A staircase function of F vs P near the transition point from $\pi(\infty)$ to the complex oscillations. Coexistence of complex oscillations and $\pi(\infty)$ is shown. As P increases beyond over P_0, $\pi(\infty)$ becomes unstable and period doubling begins. $P_0=1.1036$.

IV. RESULTS AND DISCUSSION

According to the standard linearized stability analysis, Eqs. (7)–(9) have one unstable steady state in a region of P from 1.05 to 14.2, and one or multiple oscillatory states appear for the respective P values in this region. Simple oscillations, complex oscillations, combined complex oscillations, and chaotic oscillations were found to appear. A phase diagram of the present model system is shown in Fig. 1. In Region A and Region B, there appear complex oscillations, combined complex oscillations, and chaotic oscillations in sequence by changing P continuously, and the staircase relationships of the Firing number F (Ref.

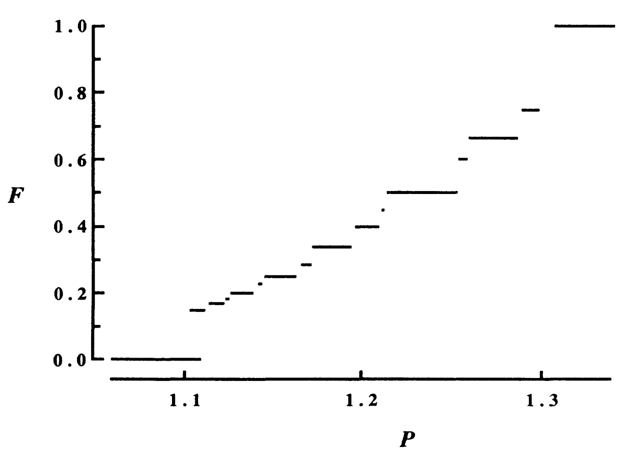

FIG. 2. The staircase relation formed by plotting the ratio F of the number of large amplitude oscillations to the total number of oscillations for each periodic state of P.

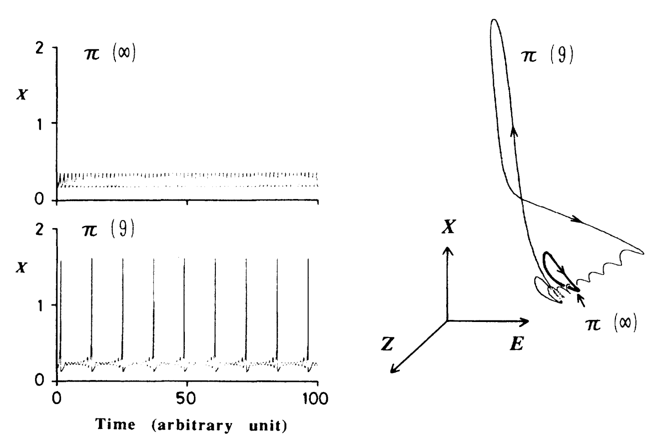

FIG. 4. Oscillatory states and their three-dimensional views at $P=1.093$. Both the oscillatory states $\pi(\infty)$ and $\pi(9)$ are coexisting.

16) was reported already (Fig. 2). Swinney *et al.*[14] carried out the BZ reaction in the CSTR and plotted the ratio W against the flow rate of the chemicals, showing a staircase relation. The staircase in the BZ reaction is very similar to that of the present model system, suggesting a general structure in the system containing complex-combined complex-chaotic oscillation sequences. Under these circumstances, we push analyses of the present model system because we can get much knowledge about the transition sequence of periodic states in the BZ reaction by means of computer simulations with ease, compared to the experimental study on the actual system which is usually accompanied by time-consuming experiments. Moreover, changes of experimental conditions often necessitate the modification of the size or shape of the reaction cell or so on, but in the model system this can be attained easily by changing parameter values.

The detailed structure in Region B is quite different from that of Region A, that is, coexistence of complex oscillation and simple oscillation is characteristic in this region. Figure 3 illustrates the stepwise increasing function of F in the near region of the transition from a simple oscillation with a small amplitude to a complex oscillatory state. $F=0$ and $\pi(\infty)$ corresponds to the simple oscillation with a small amplitude. Within our calculations, $n=12$ was the largest in the $\pi(n)$ oscillation to appear. According to the previous work,[6,15] there should appear combined complex oscillations or chaotic oscillations between the two neighboring complex oscillations, $\pi(n)$ and $\pi(n-1)$. However, no such combined complex oscillation nor chaotic oscillation appears in these regions, only the simple oscillation $\pi(\infty)$ appears. To our knowledge, this kind of transition sequences has never been reported. We will describe some peculiar behaviors found in this transition sequence.

Figure 3 also shows the coexistence of $\pi(\infty)$ and $\pi(n)$ where $n=7$, 8, 9, 10, 11, and 12. Although no finite staircase structure between $\pi(7)$ and $\pi(6)$ is shown in Fig. 3, a combined complex oscillation and a pseudoperiodic oscillation appear in this region as usual. Both of the oscillations, $\pi(n)$ and $\pi(\infty)$, were confirmed to be asymptotically stable by respective calculations. Figure 4 shows which of the coexisting oscillations, $\pi(\infty)$ and $\pi(9)$, is

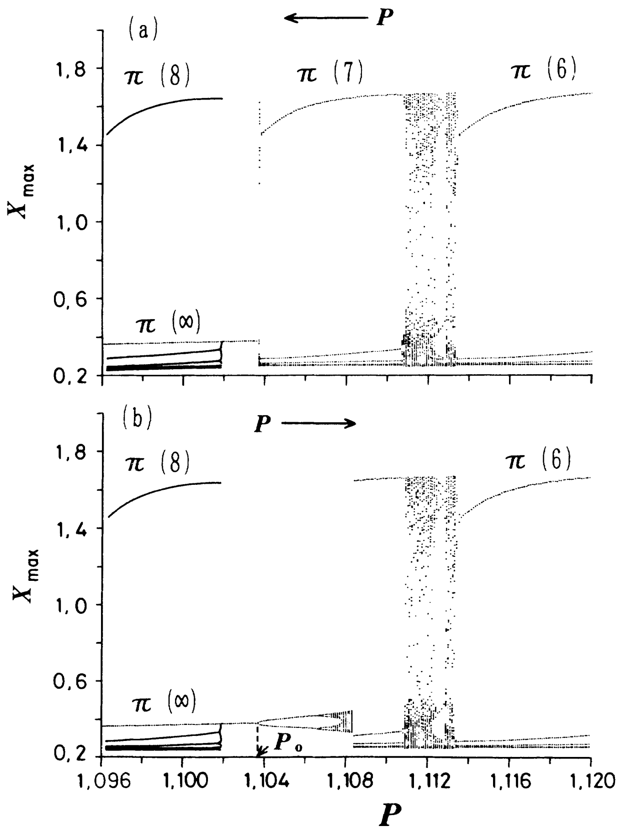

FIG. 5. Dependence of the bifurcation diagram on the changing direction of P. Arrows in the figure show the changing direction of P. $\pi(8)$ is also shown.

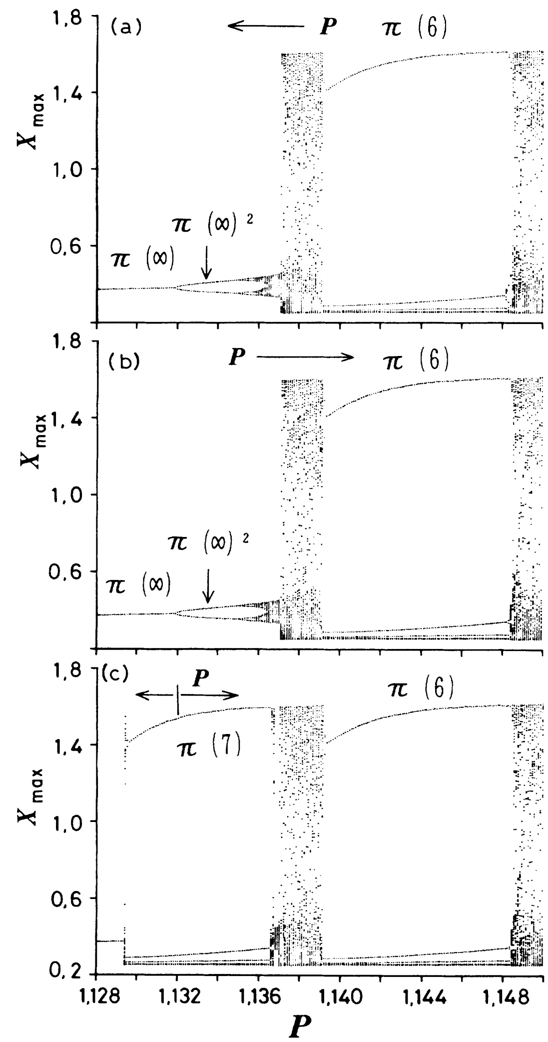

FIG. 6. Dependence of the bifurcation diagram on the changing direction of P at $A=1.275$. No hysteresis is observed. When the same calculation was started from $P=1.132$ to the increasing and decreasing directions of P, $\pi(7)$ appears initially, as shown in (c). In case (c), $\pi(7)$ does not last to the bifurcated oscillatory region continuously but changes to the high-order cyclic state of $\pi(\infty)$ discontinuously with the increasing P.

realized depending on the initial conditions. In the right-hand side of Fig. 4, three-dimensional profiles of the respective oscillations are shown. One orbital passes very near the other orbital and even a very small deviation on one of the orbitals could cause the transfer to the other. At the same time, spreading of one orbital by a bifurcation sequence causes an interaction between the respective trajectories, resulting in the falling into the more stable state. This would be the reason why only $\pi(\infty)$ appears in the region between two complex oscillations.

In Fig. 5 the bifurcation diagrams near the crucial points, where the simple oscillations $\pi(6)$, $\pi(7)$, and $\pi(8)$ become unstable, are shown. In case (b) with an increasing P value, $\pi(\infty)$ begins to bifurcate to $\pi(\infty)^2$ at P_0 and develops to higher-order cyclic states with a further increase in P. The region where the trajectory of a higher-order cyclic state of $\pi(\infty)$ runs spreads wider in the course of the period-doubling bifurcation and finally begins to overlap with the trajectory of $\pi(7)$. In this case, $\pi(7)$ is more stable than the high-order cyclic state of $\pi(\infty)$ and switching to $\pi(7)$ takes place.

On the other hand, when P decreases from the region of stable $\pi(7)$, the $\pi(7)$ oscillation continues steadily to P_0 and finally begins to bifurcate to the high-order cyclic states to interact with $\pi(\infty)$, resulting in the transit to the simple oscillation. That is, $\pi(\infty)$ is more stable than $\pi(7)$ in this region. This is also true in the cases of other oscillations $\pi(n)$ ($n=8$–12). On increasing or decreasing P beyond over the critical point where $\pi(n)$ becomes unstable, $\pi(n)$ begins to bifurcate to the higher-order cyclic states and transfers to $\pi(\infty)$.

In Figs. 1 and 5, the bifurcation point P_0 of $\pi(\infty)$ seems to coincide with the starting point of the $\pi(7)$ region. Detailed calculations support this coincidence within an error of 0.0001 of P. However, this is not always true but is an accidental coincidence. Because, when one of the parameters, for an example A, is changed, P_0 does not agree with the starting point of $\pi(7)$, as shown in Fig. 6.

As clearly shown in Fig. 5 ($A=1.3$), the bifurcation behavior between $\pi(\infty)$ and $\pi(7)$ is of a hysteresis nature and depends on the changing direction of P. When the bifurcation is studied in the case of $A=1.275$, the hysteresis behavior disappears and a continuous transition between $\pi(6)$ and $\pi(\infty)$ is observed, as shown in Fig. 6(a) and 6(b), passing through a very complicated oscillation region. The main difference from the case of Fig. 5 is that the two oscillations, $\pi(\infty)$ and $\pi(7)$ in Fig. 6, collide after diverging to the pseudoperiodic oscillations and, therefore, each oscillatory state holds a certain part of the other trajectory in common, because both the oscillatory states are pseudoperiodic and have various modes of oscillation in part. Therefore, the continuous change happens through the common oscillatory parts.

As mentioned already, only $\pi(\infty)$ is the stable oscillation between two complex oscillations and any trajectories will relax to $\pi(\infty)$ sooner or later independently of the initial state. When the relation behavior was studied in detail, a peculiar result was obtained. Figure 7 shows some traces of the relaxation. A complex oscillation appears at an early stage of relaxation and continues for relatively a long period, and then it suddenly falls into $\pi(\infty)$ after a few repetitions of irregular oscillations. The characteristic point of this relaxation is that the relaxation time to $\pi(\infty)$ changes irregularly, contrary to the usual relaxation processes, by a regular change in the initial value of X_0. Only a small difference in X_0 by 0.0001 induces noteworthy differences in the duration time, and prediction of the duration time is practically impossible. This is considered to be owing to the essential nature of the chaotic oscillatory system in which a very small difference in the initial state rapidly increases during the excursion along the chaotic trajectory. The same behavior is observed in the region between $\pi(n+1)$ and $\pi(n)$, where $n=7$, 8, 9, 10, and 11, respectively.

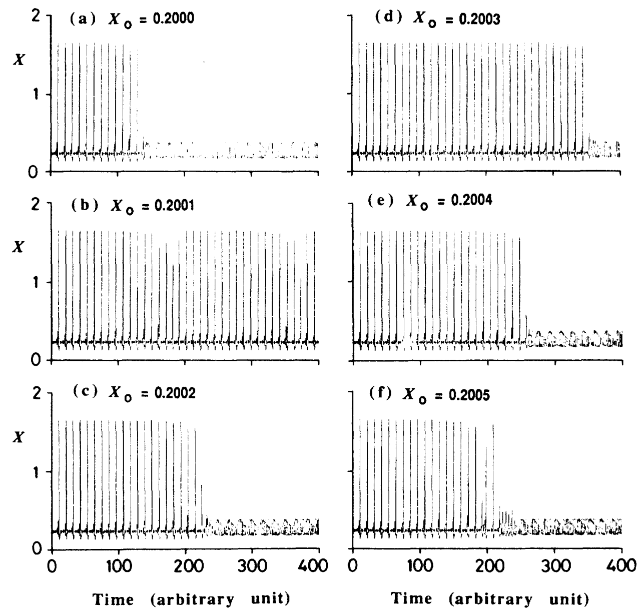

FIG. 7. Dependence of duration of complex oscillations before falling into $\pi(\infty)$ $P=1.102$. E_0 and Z_0 values at the initial states are the same and only X_0 is changed in calculations. The numbers in the figure is the values of X_0 used for calculations. $E_0=1.0$ and $Z_0=1.0$.

Although $\pi(\infty)$ is not chaotic, some irregularity is observed in the relaxation process. The final state $\pi(\infty)$ is probably surrounded by a region of pseudoperiodic oscillation and the system has to pass though the region during relaxation before falling into the final state. This seems to be feasible because a long relaxation time and an irregular oscillation were often observed in our investigation when other oscillatory states were studied. These facts suggest the difficulty of the experiment on chaotic oscillations, because a long-period experiment is necessary to determine whether the concerned oscillation is in the final state or on the relaxation process.

V. CONCLUSION

A transition sequence was found in the model system of nonlinear chemical reaction and its detailed behavior was described. Although the present chemical system is a special one and does not have a definite correlation with any real systems, its fundamental structure is closely related to the BZ reaction in a mathematical meaning. Therefore, it is expected that the similar transition sequence will be found by a careful experiment on the BZ reaction.

*Permanent address: Mitsubishi Kasei Company, Midori-ku, Yokohama, Kanagawa, 227 Japan.

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[16] The ratio F of each periodic state is defined as $F = L/(L+S)$, where L is the number of large-amplitude oscillations and S is the number of small-amplitude oscillations per period. The ratio W defined by Swinney *et al.* (Ref. 14) is given by $W = S/(L+S)$ in our notation.