Transition Sequences of Oscillatory States of a Model Chemical System Showing Chaotic Oscillations

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The transition sequence from a complex oscillation or a combined complex oscillation to a chaotic oscillation of a three-variable model system of chemical reactions were studied through analyses of the bifurcation diagrams. Period-doubling sequences, discontinuous transitions between two different oscillation states, and intermittency-type pseudo-periodic oscillations were observed. A pseudo-periodic oscillation appears when a combined complex oscillation changes to a new oscillatory state under some transition conditions. By changing the conditions, the discontinuous transition becomes to occur, leading the hysteresis behavior of transition.

Aperiodic behavior (chaotic oscillation) in chemical reactions has been observed in the peroxidase-catalyzed oxidation of NADH,[1] the Belousov-Zhabotinskii (BZ) reaction,[2–11] and the chlorite–thiosulfate reaction.[12,13] Some periodic-chaotic sequences have been carefully examined for the BZ reaction and the chlorite oscillators carried out in a continuous flow stirred tank reactor (CSTR).

A chemical reaction model which exhibits chaotic oscillations was first proposed by Rössler[14] in 1976. The Rössler model is a chemical system with three variables and its chaotic behavior has been fully investigated through numerical calculations. The Oregonator[15] is the most well-known model for the BZ reaction and, however, any attempt to find out chaotic oscillations for the three-variable Oregonator has not yet succeeded. Turner et al. modified the original Oregonator to make up a new model having four variables and showed the appearance of chaotic oscillations.[7] On the other hand, Tomita and Tsuda proved for a three-variable model of the BZ reaction to show chaotic oscillations by introducing flow terms.[17]

Some routes from periodic oscillations to chaotic oscillations have been uncovered; period doubling,[16] intermittency,[18] and quasi-periodicity[19] are typical examples. The intermittency,[8,10] and the quasi-periodicity[20] have been experimentally observed in the BZ reaction. The period-doubling sequence from the oscillating state with a single amplitude to the chaotic state was found experimentally in the BZ reaction by Simoyi et al.[9] and numerically in the modified Oregonator by Ringland and Turner.[21] But the route from a complex oscillation or a combined complex oscillation to a chaotic oscillation is not yet examined.

The BZ reaction is the most well-known experimental system which exhibits chaotic oscillations. Swinney et al. examined in detail the transition sequence using CSTR and found a staircase relationship by plotting the Firing number F against the residence time of the flow reactor as a control parameter. The BZ reaction in CSTR shows complicated oscillations made of L cycles of large amplitude oscillations and S cycles of small amplitude oscillations and the Firing number of the oscillation is defined as $F=L/(L+S)$.

In our preceeding paper,[22] a three-variable model chemical system was studied and its bifurcation structures from a complex oscillation to a chaotic or a combined complex oscillation have been reported. When the transition sequence was displayed by the relationship of the firing number F with a control parameter, according to the way of Swinney et al., the resulting staircase behavior of F is very similar to the staircase diagram observed experimentally in the BZ reaction. This result strongly suggests a similarity of the mathematical structure between the BZ reaction and the present model. Thus, it is expected that the detailed analyses of the present model give us a more detailed prospect of the transition sequence in the BZ reaction.

In this paper, the model chemical system of three variables was studied through numerical calculation and period-doubling sequences from complex or combined complex oscillations to chaotic oscillations was demonstrated. Here, the terms, "complex oscillation" and "combined complex oscillation", are defined as follows.[22] A complex oscillation is an oscillatory state combining of one large amplitude oscillation and $n-1$ small amplitude oscillations. The symbol $\pi(n)$ is used to note this complex oscillation. The term of combined complex oscillation is used for a combination of two or more complex oscillations and the symbol $\pi(m)\pi(n)$ is for a combined complex oscillation consisting of complex oscillations $\pi(m)$ and $\pi(n)$. Now, the detailed structure of transition sequence of the model chemical system will be investigated by using a bifurcation diagram, which is made by plotting the peak height of each pulse in a periodic or an aperiodic state on a two-dimensional phase plane. There appear a period-doubling sequence, a discontinuous transition between a combined complex oscillation and a pseudo-periodic oscillation, and an intermittency-type pseudo-periodic oscillation. The term of "pseudo-periodic oscillation" is hereafter used when we can not determine whether the oscillation is chaotic or not. A discontinuous change implies usually a hysteresis correlation and coexistence of two different oscillatory states. This phenomenon, which is called birhythmicity, has been found in the experimental[23] and the computational works.[24] However, this is the first paper reporting the birhythmicity between a combined complex oscillation and a pseudo-periodic oscillation.

Chemical Oscillation Model

In the present investigations, the system consisting of the following chemical reactions is considered. This model system has been proposed in a previous paper.[22]

$$\mathrm{P + Z \xrightarrow{k_1} E + Z}, \quad \text{(R1)}$$

$$\mathrm{E + X \xrightarrow{k_2} R + X}, \quad \text{(R2)}$$

$$\mathrm{A + 2X + E \underset{k_4}{\overset{k_3}{\rightleftarrows}} 3X + E}, \quad \text{(R3)}$$

$$\mathrm{B + X \underset{k_6}{\overset{k_5}{\rightleftarrows}} C}, \quad \text{(R4)}$$

$$\mathrm{Q \xrightarrow{k_7} Z}, \quad \text{(R5)}$$

$$\mathrm{Z + X \xrightarrow{k_8} D + X}, \quad \text{(R6)}$$

where A, B, P, and Q are reactants, C, D, and R are products and E, X, and Z are intermediates. Then, three differential equations concerning the concentrations of E, X, and Z will describe the time behavior of the system;

$$\frac{dE}{dt} = k_1PZ - k_2EX, \quad (1)$$

$$\frac{dX}{dt} = k_3AEX^2 - k_4EX^3 - k_5BX + k_6C, \quad (2)$$

$$\frac{dZ}{dt} = k_7Q - k_8XZ. \quad (3)$$

The following values are substituted in respective parameters and the equations are solved numerically by the aid of FACOM M380 (Fujitsu). These values were selected to afford a chaotic behavior of oscillations. The value of P is selected as a variable for the calculation. A=1.3, B=5.0, C=5.3, Q=1.0, 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, and k_8=0.4.

Results and Discussion

Period-Doubling Sequence. By solving Eqs. 1—3 numerically, complex oscillations, combined complex oscillations and chaotic oscillations were confirmed to appear in a range $1.08 \leqq P \leqq 1.31$, and the global profile of the transition sequence has been reported in a preceding paper.[22] Some characteristics of transition sequences were studied by the aid of bifurcation diagrams, which are made by plotting the peak value of X of every pulse in an oscillatory state. The bifurcation diagram shown in Fig. 1 is obtained on increasing the value of P stepwise from 1.250 to 1.262. In solving Eqs. 1—3 numerically for each P value, the final values of E, X, and Z in a preceeding step with a given value of P were used for the initial values of the calculation for the next step of P.

Figure 1 shows the transition sequence from the complex oscillation $\pi(2)$ to the combined complex oscillation $\pi(2)\pi(1)$, passing through the combined complex oscillations $[\pi(2)]^2\pi(1)$ and $[\pi(2)]^3\pi(1)$. The notation $[\pi(m)]^i[\pi(n)]^j$ means a combined complex

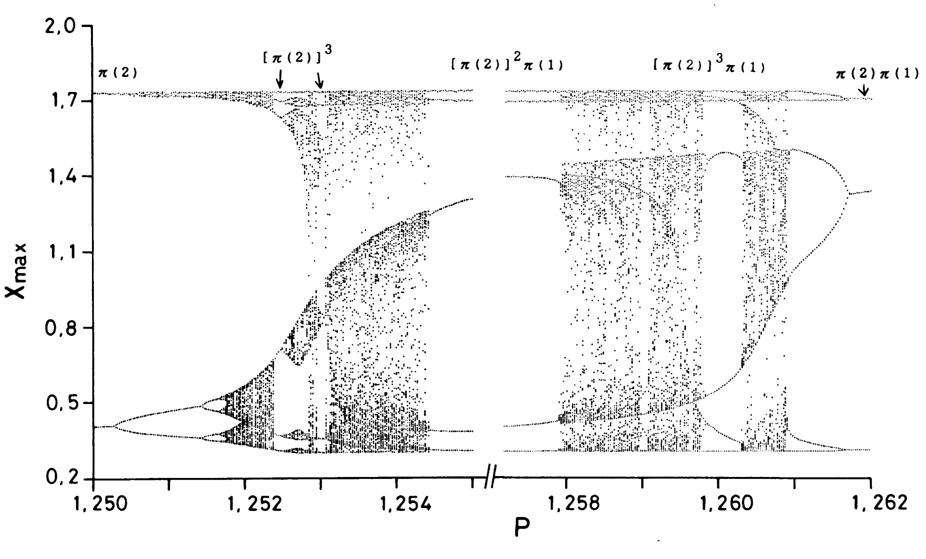

Fig. 1. A bifurcation diagram displaying from $\pi(2)$ to $\pi(2)\pi(1)$. The regimes of respective oscillations are noted.

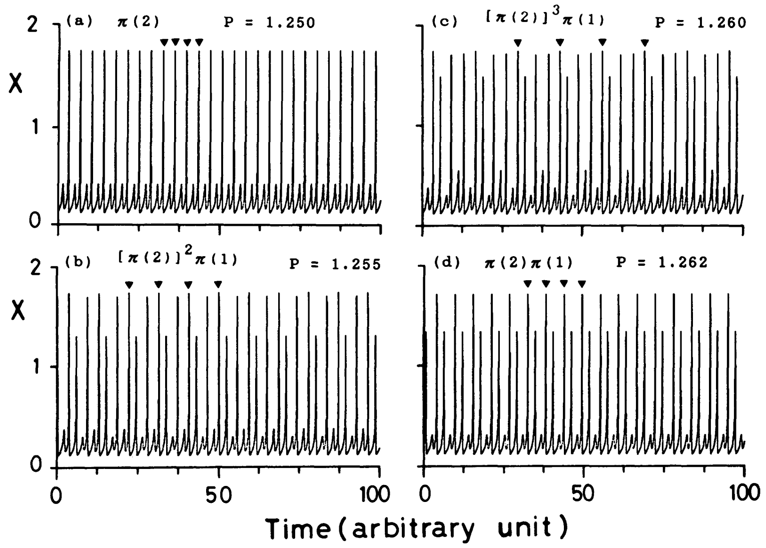

Fig. 2. Representative periodic oscillations designated in Fig. 1. Marks above the oscillations show the period.

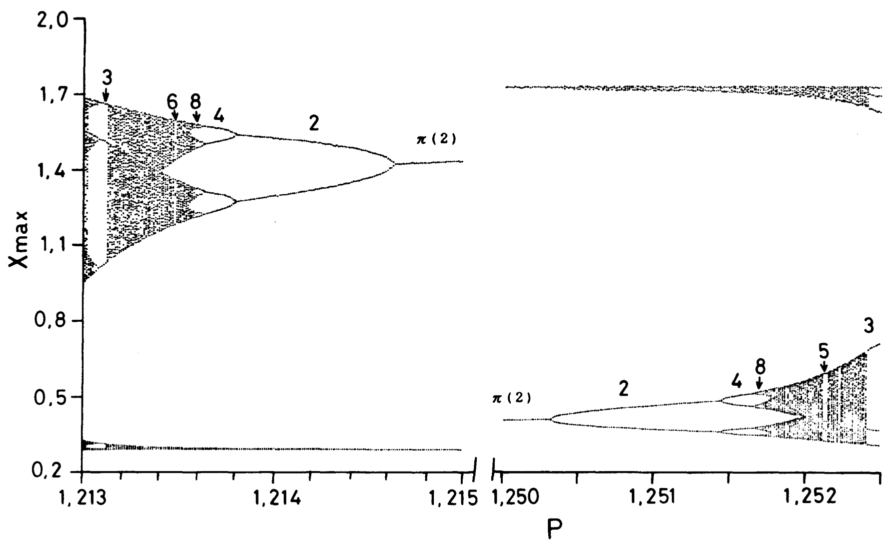

Fig. 3. Period-doubling sequences of the complex oscillation $\pi(2)$ for increasing and decreasing P. The 2^n-cycle oscillations of $\pi(2)$ are marked with n. Windows of 6, 5, and 3-cycle oscillations can be seen.

oscillation consisting of i-cycle $\pi(m)$ and j-cycle $\pi(n)$.[22] The oscillation behavior of $\pi(2)$, $[\pi(2)]^2\pi(1)$, $[\pi(2)]^3\pi(1)$, and $\pi(2)\pi(1)$ are shown in Fig. 2. As shown in the preceding paper,[22] the number F defined as $F=L/(L+S)$ according to Maselko and Swinney,[25] where S and L are respectively the numbers of small and large amplitude oscillations per period, is staircase-like increasing function against P, when only the conspicuous oscillations with large regimes on P are selected. In detail, however, the values of F for the oscillations $\pi(2)$, $[\pi(2)]^2\pi(1)$, $[\pi(2)]^3\pi(1)$, and $\pi(2)\pi(1)$ with an increase of P are 1/2, 3/5, 4/7, and 2/3, respectively, and this order is not an increasing order. That is, this series of oscillations is out of the rule of staircase-like increasing function of F. Similar trends are occasionally seen in the fine structures of the bifurcation diagram of the present model. Experimentally such a trend has never been observed but probably could be found by a careful experiment.

A period-doubling sequence is clearly seen in Fig. 1. The complex oscillation $\pi(2)$ appears at $P=1.250$. As P increases, $\pi(2)$ becomes unstable and diverges to the 2-cycle oscillation of $\pi(2)$ (i.e. $[\pi(2)]^2$). The right hand figure of Fig. 3 displays an enlarged view of this region. With a further increase in P, $[\pi(2)]^2$ develops to the 4-cycle oscillation of $\pi(2)$ (i.e. $[\pi(2)]^4$), followed by the higher order 2-cycle oscillations. The range of P of 2^n-cycle oscillation of $\pi(2)$ becomes steeply narrower as n increases, and finally a chaotic oscillation appears. According to Li and Yorke,[26] a chaotic oscillation resulting from the sequence of infinitely high order 2-cycle oscillations is a typical example of the chaotic oscillations. The chaotic oscillations are shown as a diffuse and vertical distribution of dots in the diagram. The bifurcation diagram shown in Fig. 3 is partly broken by "windows" of 6-cycle and 5-cycle oscillations of $\pi(2)$ and is very similar to that of May's system with a typical period-doubling bifurcation.[27]

Feigenbaum[17] showed that an asymptotic limit of the ratio $(P_n-P_{n-1})/(P_{n+1}-P_n)$, where P_n is the parameter value at which the n^{th} doubling bifurcation begins, is a universal number called Feigenbaum's constant, i.e., $\delta=4.6692\cdots$. The values of P_n in the present model are: $P_1=1.250332$, $P_2=1.251452$, $P_3=1.2516700$, $P_4=1.2517154$, and $P_5=1.2517252$. The P_n with $n\geqq 6$ could not be determined. From these values, the ratio $(P_4-P_3)/(P_5-P_4)=4.6\pm 0.1$, being fairly in agreement with Feigenbaum's constant.

The bifurcation diagram in the region from $P=1.213$ to 1.215 is shown in the left hand of Fig. 3, where the similar period-doubling bifurcation takes place in a decreasing direction of P. Thus, it was concluded that the complex oscillation $\pi(2)$ changes to a chaotic oscillation through the period-doubling bifurcation with both the increasing and the decreasing directions of P.

For the cases of $\pi(n)$ ($n=1$, 3, 4, 5, and 6), the period-doubling sequences were always observed, so that we can conclude that a complex oscillation diverges to another oscillatory state through a period-doubling sequence. The period-doubling sequence of $\pi(1)$ is clearly seen in Fig. 4.

Intermittency-Type Pseudo-Periodic Oscillation. As the value of P increases up to 1.255, the complex oscillation $\pi(2)$ changes to the combined complex oscillation $[\pi(2)]^2\pi(1)$, where the F value changes from 1/2 to 3/5. That is, the mixing of $\pi(2)$ with $\pi(1)$ should take place after the period-doubling sequence of $\pi(2)$. Similarly, when the combined complex oscillation $[\pi(2)]^2\pi(1)$ changes to the following oscillatory state having a different value of F with an increase in P, the mixing of some oscillatory component into $[\pi(2)]^2\pi(1)$ would take place, resulting in a change in the F value. The bifurcation diagram of Fig. 5 shows a sudden transition at about $P=1.257886$, where $[\pi(2)]^2\pi(1)$ enters into a new oscillatory state. The sudden change in the distribution of dots should be noticed and the period-doubling sequence is not observed in this case. The oscillations before and after the transition are also shown in Fig. 5. After the transition the regular oscillation $[\pi(2)]^2\pi(1)$ is occasionally disturbed by two or three repetitions of irregular oscillation. The irregular oscillation happens to appear intermittently. This type of oscillation is called hereafter as "intermittency-type pseudo-periodic oscillation", because we can not definitely determine whether it is chaotic or not.

Figure 1 shows many transitions which seem to be discontinuous. Some of them were investigated in detail and found to be the transitions with intermittency-type pseudo-periodic oscillations. We can say that this type of transition occurs when a combined complex oscillation changes to a new oscillatory state

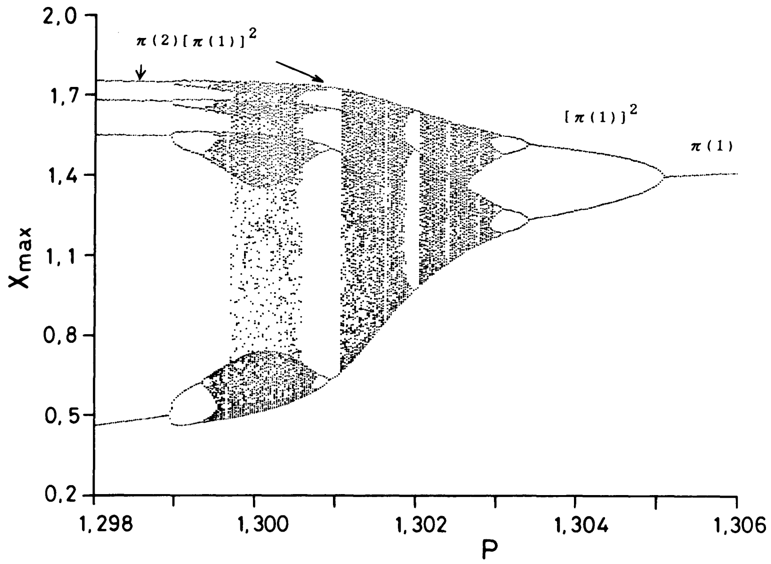

Fig. 4. A bifurcation diagram displaying from $\pi(2)[\pi(1)]^2$ to $\pi(1)$ with the period-doubling sequence of $\pi(1)$.

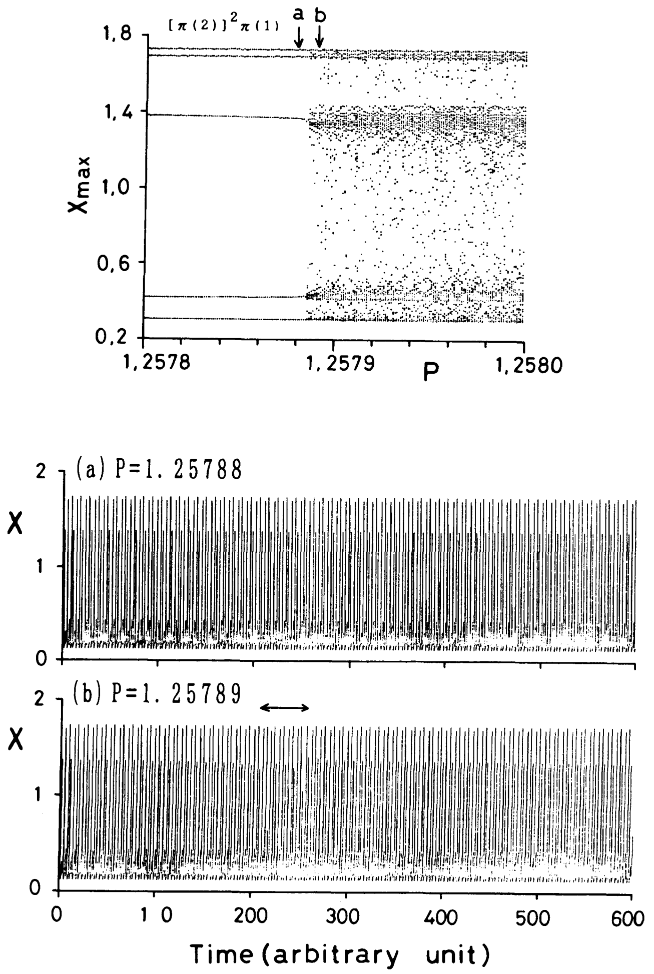

Fig. 5. A bifurcation diagram showing a sudden transition from $[\pi(2)]^2\pi(1)$ to a new oscillatory state and oscillatory behaviors before and after the sudden transition. (a) $P=1.25788$ and (b) $P=1.25789$. The bar in (b) indicates the region where $[\pi(2)]^2\pi(1)$ is disturbed.

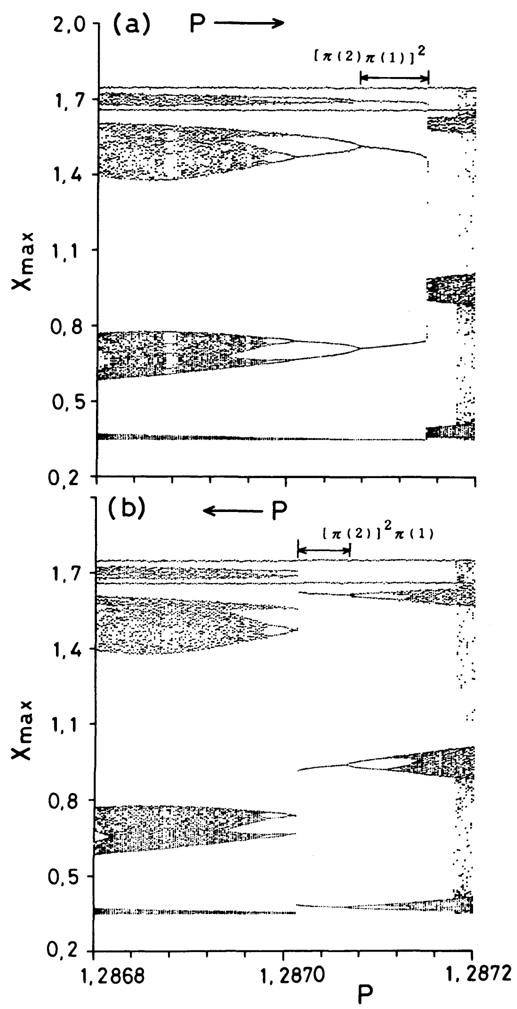

Fig. 6. Dependence of the bifurcation diagram on the direction of change in P. (a) P is increasing, and (b) P is decreasing.

with a different F value. Now we face a question whether the intermittency-type pseudo-periodic oscillation occurs always in a transition state from an oscillatory state to another with a change in F. The answer is that it is not always true. A different type of transition behavior will be shown in the next section.

Birhythmicity. A discontinuous change is observed at about $P=1.28714$ in a sequence of the combined complex oscillations $\pi(2)\pi(1)$. At this point, the birhythmicity appears and one of two different oscillations is realized depending on the initial conditions of calculation. This result suggests strongly the existence of hysteresis behavior of oscillations as for the changing direction of P. Figure 6 displays the dependence of the bifurcation diagram on the changing direction of P. The transition is discontinuous and hysteresis behavior is clearly shown. Interestingly, the F values of the coexisting oscillations, $[\pi(2)\pi(1)]^2$ and $[\pi(2)]^2\pi(1)$, are different one another and the correlation of F vs. P shows also hysteresis. The transition from $[\pi(2)\pi(1)]^2$ to $[\pi(2)]^2\pi(1)$ occurs at $P=1.287148$ as P increases, and the reverse transition does at $P=1.287012$ as P decreases, without showing any intermittency-type pseudo-periodic oscillations.

The hysteresis behavior could be related to a casp-type catastrophy with a folded phase plane in a three dimensional phase space. Thus, an interpretation of birhythmicity is undertaken with a three-dimensional profile. Figure 7 shows bifurcation diagrams at the discontinuous transition with various values of A. When $A=1.286$, $[\pi(2)\pi(1)]^2$ changes to $[\pi(2)]^2\pi(1)$, passing through a sudden transition. In this case no hysteresis is observed. When the value of A increases further, the region of pseudo-periodic oscillations becomes narrower and finally disappears, as shown in Fig. 10(b). When the value of A increases further, hysteresis behavior begins to appear.

On the basis of these computations, a schematic profile of the folded phase plane leading these bifurcation diagrams would be drawn as shown in Fig.

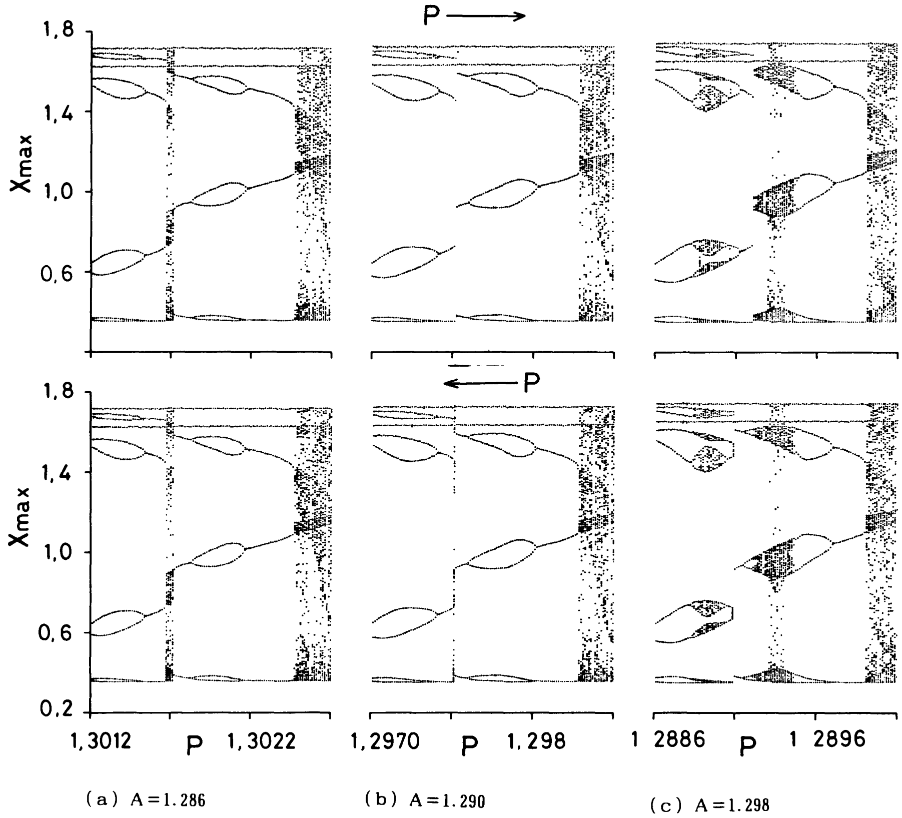

Fig. 7. Bifurcation diagrams with various values of A. In case (a), a sudden transition takes place and no hysteresis is observed. In case (b), the region of intermittecy-type pseudo-periodic oscillation almost disappeared, but no hysteresis is observed. In case (c), a transition accompanied by hysteresis is observed.

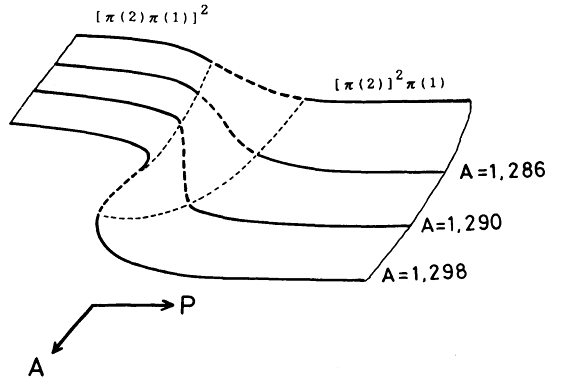

Fig. 8. A phase portrait with a casp catastrophy inferred from the bifurcation diagrams in Fig. 7. The dashed part of each line shows the region of an intermittency-type pseudo-periodic oscillation. The perpendicular coordinate is used to figure the respective states of oscillation.

8. The transition region from $[\pi(2)\pi(1)]^2$ to $[\pi(2)]^2\pi(1)$ is shown by dotted lines. As the value of A increases, the transition region becomes concaved more steeply and finally folded completely between the oscillatory states of $[\pi(2)\pi(1)]^2$ and $[\pi(2)]^2\pi(1)$. Under the latter conditions, the transition between the two combined complex oscillations takes place without showing any pseudo-periodic oscillation, and the birhythmicity is caused by the hysteresis nature of a folded phase plane.

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