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Intermittencies and Related Phenomena in the Oxidation of Formaldehyde at a Constant Current

Hiroshi Okamoto,* Naoki Tanaka, and Masayoshi Naito

Advanced Research Laboratory, Hitachi, Ltd., Hatoyama, Saitama 350-03, Japan

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In the galvanostatic oxidation of formaldehyde on Pt at 43 °C, we have found type III intermittency (in the Pomeau−Manneville classification) as well as type I intermittency. Potential oscillation patterns change with time, and type I intermittency is usually observed after a periodic oscillation in a sequence of periodic oscillations, which appear in decreasing order of their periods and are interposed between chaotic states. At a comparatively low current density (e.g., 0.23 mA cm^{-2} or less for a 1 mol dm^{-3} formaldehyde solution) in a solution with a formaldehyde concentration of 1 mol dm^{-3} or more, we observe type III intermittency before a periodic oscillation in the sequence. Under other conditions we observe a type-III-like intermittent pattern followed by a reverse period-doubling cascade. We confirm the characteristics of type III intermittency with a period-*k* laminar flow by the shape of *k*th and (2*k*)th return maps, by the relation between a laminar duration and the time from the period-*k* pattern, and by the relation between a maximal Lyapunov exponent and that same time. Here we regard time as a parameter related to some surface states. We also observe that type I and type III intermittencies coexist. We sometimes observe a randomly alternating sequence of period-(n+1) and period-*n* patterns without any intermittencies. When the sequence of periodic oscillations appear in increasing order of their periods, the order in which type I and type III intermittencies appear is also reversed.

Introduction

Chemical oscillations show diverse phenomena, such as periodic oscillations,[1−3] chaotic oscillations,[4] spikes,[5] and intermittencies,[6] that appear because of the nonlinearity of the chemical reaction systems. Consequently, their analysis is explicitly or implicitly based on nonlinear dynamics. We have been studying nonlinear behavior in the galvanostatic, constant current, oxidation of formic acid and formaldehyde,[7−12] and recently we clarified the chaotic behavior in the oxidation of formaldehyde.[11,12] To identify aperiodic potential patterns as manifestations of chaos and to discuss a temporal change in potential oscillation patterns, we mainly used a first return map, which shows the relation between one potential minimum and the next.

Since then we have found not only type I intermittency according to Pomeau−Manneville classification[13] but also type III intermittency. To confirm the presence of these intermittencies, we have plotted a *k*th return map, showing the relation between one potential minimum and the *k*th potential minimum after that. Type I intermittency is the intermittency seen after a tangent bifurcation, and this intermittency in formaldehyde oxidation was found by Schell et al.[14] We, however, are the first to find type III intermittency in the same reaction, although Bassett and Hudson[15] found it in the electrodissolution of copper and Dubois et al.[16] in the Rayleigh−Bénard convection. We have also found a type-III-like intermittency which is subharmonic but is observed between chaos and a reverse period-doubling cascade. We have also observed two new phenomena: the coexistence of the type-I and type-III intermittencies and a randomly alternating sequence of neighboring periodic patterns without intermittencies.

Theories and models of intermittencies have recently attracted much attention as deterministic substitutes for stochastic theory in research on ion channels[17] and receptors[18] in biological cells as well as in research on packet traffic[19,20] in communication systems. This common interest suggests that intermittencies play important roles in nature and engineering. We have investigated the intermittencies and newly found phenomena in various ways, for example, by using high-order return maps and Lyapunov exponents, although we have not been able to explain them in terms of reaction mechanisms or by computer simulation yet. This paper describes the three intermittencies and the new phenomena that were found in formaldehyde oxidation.

Experimental Section

We measured current and potential with a conventional three-electrode cell at 43 °C. The reference electrode was a reversible hydrogen electrode (rhe), the counter electrode was a platinum wire, and the working electrode was a platinum net with a purity of 4 N (99.99%) and a true surface area of 2.6 cm^2. The pretreatment of the working electrode and the preparation of electrolytic solutions (0.5 mol dm^{-3} sulfuric acid and various concentrations of formaldehyde) were described in previous papers.[11,12] We acquired the time sequence of potential or current values with a Hewlett-Packard data acquisition/control unit (3852A or 75000) while simultaneously recording it with X−T and X−Y recorders. We sampled the data to 5.5 significant figures at a sampling interval of 3 ms or longer. The number of sampled data values was usually 10 000 and the number of minimum peaks in the potential oscillation for a return map was between 200 and 500.

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Results

Type I Intermittency. We showed in previous papers[11,12] that during oscillation the oscillation pattern changed with time due to the change in some surface states. Hence, we regard time as a convenient system parameter, even though it probably subsumes two or more system parameters.[12] The pattern change was such that after a period-doubling bifurcation an alternating periodic and chaotic sequence appeared in descending order; that is, the oscillation period of the periodic oscillations interposed between chaotic states decreased monotonically. A sequence in the reverse order was also observed, but here we focus first on the descending-order sequence.

To conveniently analyze oscillation patterns, we often use a return map (also called a Lorenz map or a one-dimensional Poincaré map) in which we plot one potential minimum as the abscissa and plot the *p*th potential minimum after that as the ordinate. For $p = 1, 2, ...$ the maps are called first, second, ... return maps. For chaotic patterns, we expect that the *p*th return map would tend to obscure a structure with increasing *p*, because chaos is sensitive to initial values and small differences in the initial values, caused by either noise or experimental error, exponentially expand. For periodic oscillations, on the other hand, such a tendency in the *p*th return map is expected to be absent.

Experimental data gathered during formaldehyde oxidation confirmed these expectations (Figure 1). For a chaotic oscillation pattern the first through fourth return maps show a clear structure, the sixth return map begins to scatter, and the eighth does not show a structure. For a period-3 pattern, though, each of the return maps from the first to the twelfth gives three discrete dots. As shown below, however, even if the oscillation is chaotic the *p*th return map with a large *p* sometimes provides useful information, especially for one kind of chaos: intermittencies.

As shown in Figure 2(a1, a2), we observed type I intermittency in the oscillation after a period-3 pattern. We can see that the period-3 pattern is randomly destroyed and reformed many times: for example, the large peak appearing every three peaks declines monotonically, shows no periodicity, and after an unpredictable time again shows periodicity. In the Pomeau−Manneville classification,[13] this type of oscillation pattern is called type I intermittency. The intermittency was observed after a tangent bifurcation following the period-3 pattern. As shown in Figure 2(a4), the third return map clearly shows the situation just after the bifurcation, and this map is similar to that found by Schell at al.[14] The intermittent pattern was followed by a pattern which showed no continuing periodicity.

As shown in Figure 2(b1, c1), we also observed type I intermittency after period-4 and period-5 patterns. Their fourth or fifth return maps ((b3, c3)) show the situations just after tangent bifurcations, but they tend to increasingly scatter with an increase in the oscillation period of the periodic patterns just before bifurcations.

As described in a previous paper,[12] in the descending-order sequence we observed mixed-mode oscillation after a chaotic pattern with small amplitudes following a period-doubling cascade except when that chaotic pattern was followed by a period-3 pattern. A mixed-mode oscillation pattern is, as shown in Figure 3a, a type of oscillation pattern in which both small-amplitude and large-amplitude chaotic oscillations are interspersed. Its first return map (b) already exhibits a little scatter and its fourth map (d) no longer shows a structure. Mixed-mode oscillation thus leads to the map blurring more easily than does chaotic oscillation without distinct large and small amplitudes, probably because a clear expression of mixed-mode oscillation would require the use of a two-dimensional or higher dimensional map.[12]

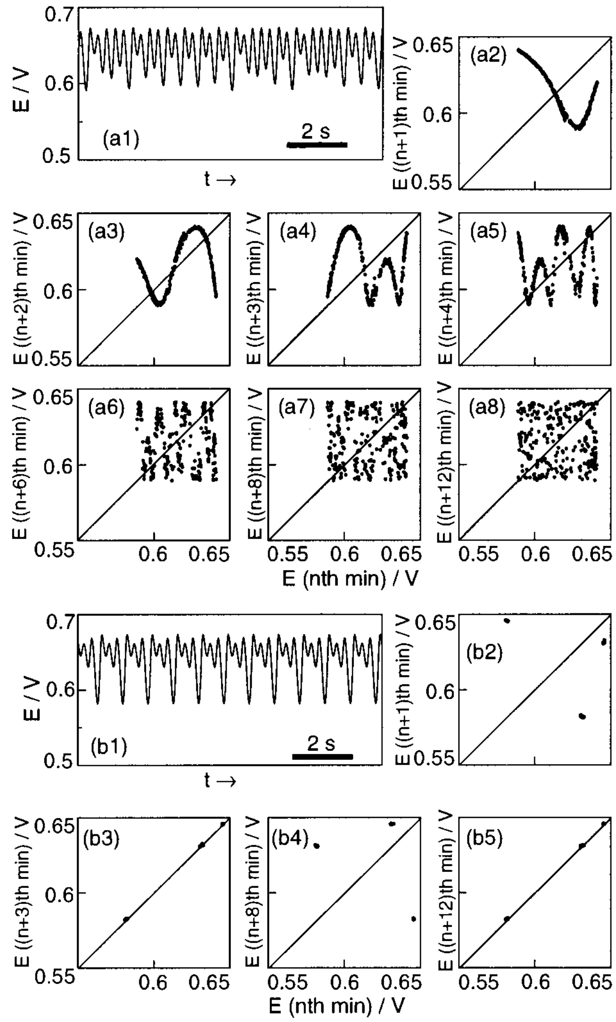

Figure 1. Chaotic and periodic oscillation patterns and their return maps for 1 mol dm^{-3} formaldehyde oxidation at 0.9 mA. (a1) a chaotic potential oscillation pattern; (a2−a8) its 1st, 2nd, 3rd, 4th, 6th, 8th, and 12th return maps. (b1) a period-3 potential oscillation pattern; (b2−b5) its 1st, 3rd, 8th, and 12th return maps.

Type III Intermittency. Although we observed type I intermittency after periodic oscillations, we observed type III intermittency before periodic oscillations at a low current (e.g., 0.6 mA or less) in a solution with a formaldehyde concentration of 1 mol dm^{-3} or more. As indicated in Figure 4b, at a low current type III intermittency appeared before a periodic pattern, which was followed by type I intermittency. The ensuing oscillation pattern will be described later. As shown in Figure 5(a1, a2), before a period-3 pattern, the large oscillation peak present every three peaks alternately grows and declines, shows no periodicity, and after an unpredictable time shows periodicity again. In the Pomeau−Manneville classification,[13] this type of intermittency with subharmonic oscillations is called type III intermittency.

As partly shown in Figure 6(a1, a2), for type III intermittency with a period-*k* laminar flow, the *k*th return map shows normals to the diagonal line at *k* cross points, and the (2*k*)th return map shows cubic curves tangent to the diagonal line at *k* cross points.[21] Here the laminar flow means a periodic part of intermittent oscillation. Incidentally, as partly shown in Figure

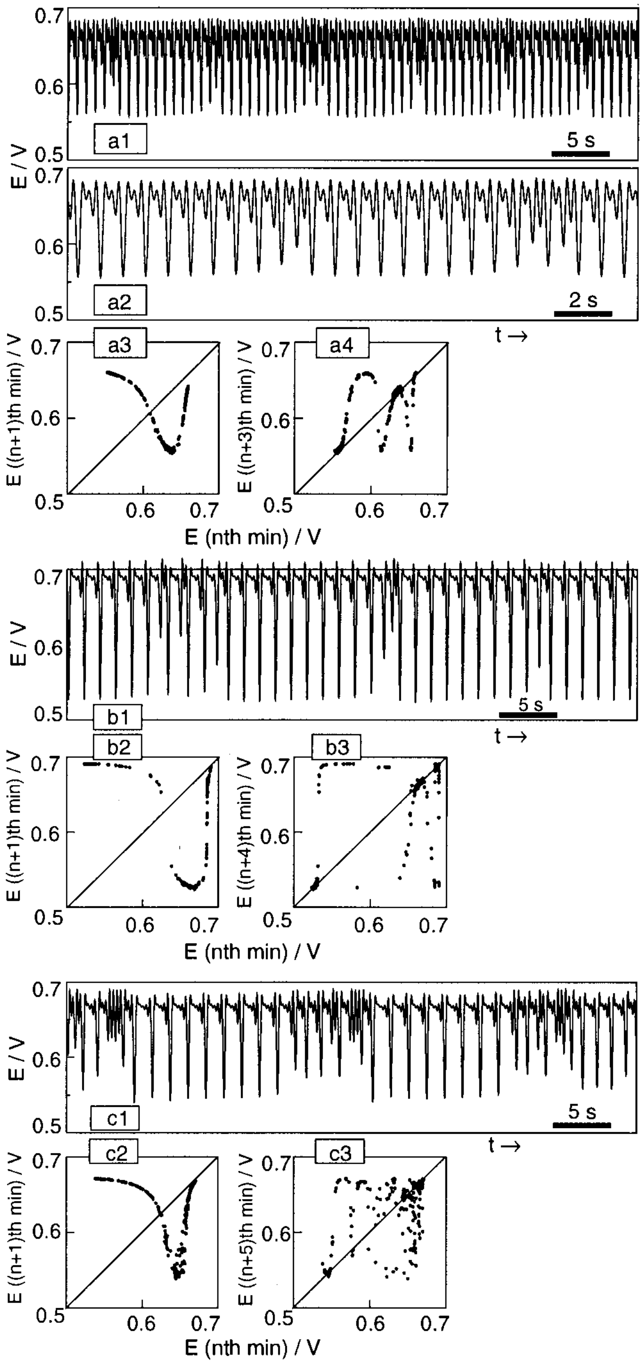

Figure 2. Type I intermittencies observed in the oxidation of 1 mol dm^{-3} formaldehyde. (a1) an intermittent potential oscillation pattern shown after a period-3 pattern at 0.9 mA, (a2) an enlarged version of a1, (a3 and a4) its first and third return maps. (b1) a potential oscillation pattern observed after a period-4 pattern at 0.6 mA, (b2 and b3) its first and fourth return maps. (c1) a potential oscillation pattern observed after a period-5 pattern at 0.65 mA, (c2 and c3) its first and fifth return maps.

6b, for type I intermittency with a period-k laminar flow, the kth map shows k quadratic curves asymptotic to the diagonal line.

The oscillation patterns shown in Figure 5(a1, a2) provide normals to the diagonal line at three points in the third return map (a4) and cubic curves tangent to the diagonal line at three points in the sixth return map (a5). As time passed, the duration of the laminar flow increased and finally the oscillation was stabilized directly to the period-3 pattern (c1). This change in

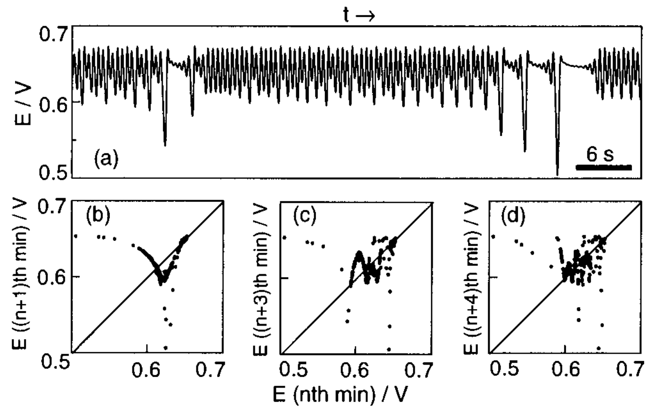

Figure 3. A mixed-mode oscillation pattern (a) and its return maps (b−d). The pattern was obtained from the oxidation of 1 mol dm^{-3} formaldehyde at 0.5 mA.

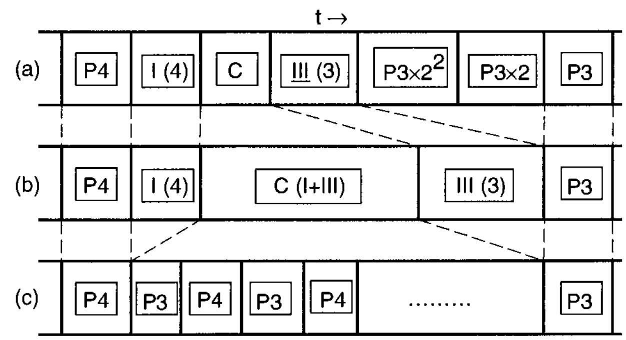

Figure 4. Sequence of appearance of intermittencies, chaos, and periodic oscillations: (a) at comparatively high currents (e.g., 1−0.65 mA for a 1 mol dm^{-3} formaldehyde solution), (b) at comparatively low currents (0.6−0.4 mA for a 1 mol dm^{-3} formaldehyde solution), (c) at very low currents (expected). Pn: periodic oscillation with n periods, I (n): type I intermittency with a period-n laminar flow, III (n): type III intermittency with a period-n laminar flow, III (n): type-III-like intermittency with a period-n laminar flow, C: chaos without any continuing periodicities, C(I+III): coexistence of type I and type III intermittencies.

oscillation patterns indicates that return maps change directly to the one composed of three discrete points, as shown in Figure 5(c2−c4).

Figure 7 shows another example of type III intermittency obtained at a low current (0.55 mA). Here the laminar flow is period-4. The fourth return map (a3) reveals normals and the eighth return map (a4) reveals cubic curves tangent to the diagonal line at the cross points. We should note here that even the eighth return map shows a clear structure, whereas the eighth return map for a chaotic pattern without any continuing periodicities does not (Figure 1(a7)). Then the oscillation pattern changed directly to a period-4 one (b1−b4). We did not observe period III intermittency with a period-2 laminar flow because it would have taken a very long time (more than 10 h) before the intermittency appeared.

Type-III-like Intermittency. Although we observed type III intermittency at a low current in concentrated formaldehyde solutions, under other conditions (which are more usual) we observed type-III-like intermittency before periodic patterns. As shown in Figure 8(a1), the oscillation pattern before a period-3 pattern showed subharmonic intermittency. This intermittency, however, is not genuine type III intermittency for the following two reasons. The first is that the third return map (a3) does not show normals to the diagonal line at three cross points. More clearly the sixth return map (a4) does not give tangents but cross lines with a finite angle to the diagonal line, though this is shown

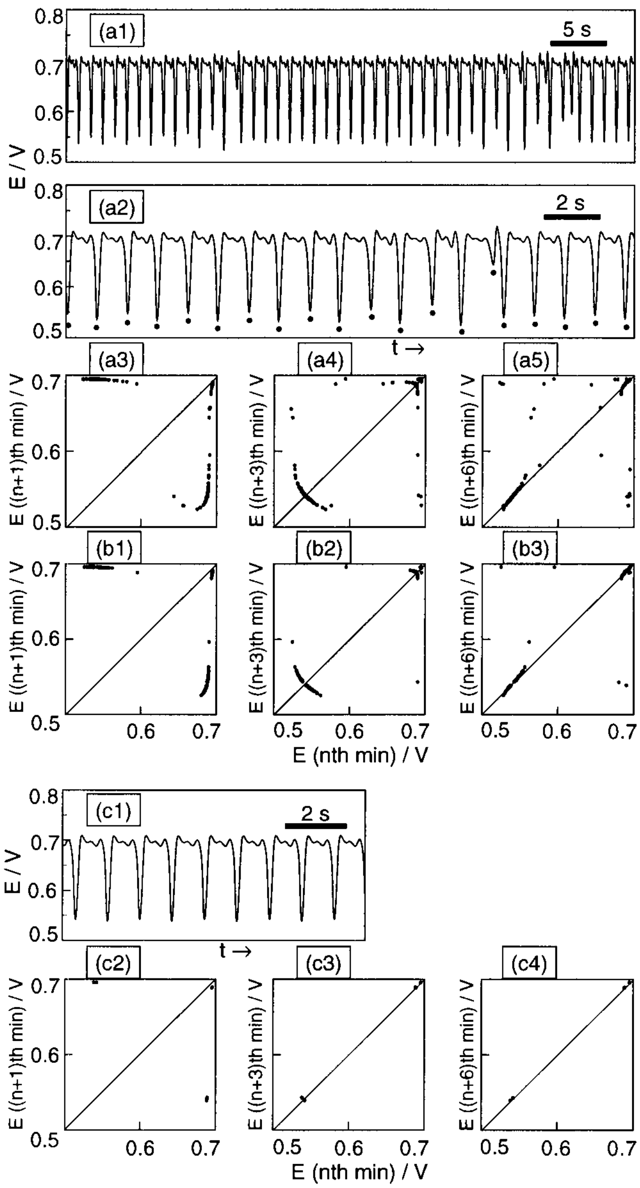

Figure 5. Type III intermittency observed before a period-3 pattern in the oxidation of 1 mol dm^{-3} formaldehyde at 0.6 mA. (a1 and a2) a type-III intermittent oscillation pattern and an enlarged version of that pattern, dots in (a2) indicating the large peaks appearing every three peaks; (a3−a5) its first, third, and sixth return maps. (b1−b3) the first, third, and sixth return maps for the pattern just before a period-3 pattern. (c1−c4) the period-3 pattern and its first, third, and sixth return maps.

only at one cross part at the smallest E of the three. The second is that the oscillation pattern changed through period-3 $\times$ 2^2 and period-3 $\times$ 2 patterns (c1) to the period-3 pattern. Because intermittency with a period-k laminar flow is a phenomenon appearing near periodic oscillation with k periods but not with $k \times 2$ periods or others, such a reverse period-doubling cascade should be absent near the intermittency. These are the reasons that the pattern shown in Figure 8(a1) cannot be a genuine type-III-intermittent one. We call this type of intermittency type-III-like intermittency.

Here we look at changes in the return maps when the oscillation pattern changed from the one shown in Figure 8(a1) to the period-3 $\times$ 2 pattern (c1). Although the oscillation pattern remained similar to the one shown in (a1), its maps (b1−b3) first became fragmentary. And the sixth return map (b3) shows two crossing points (u and w) on both sides of one fixed point

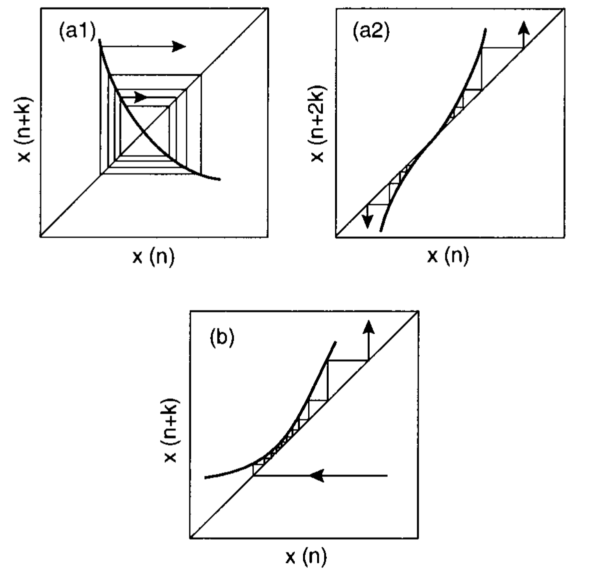

Figure 6. A sketch explaining (a1) and (a2) type III intermittency in Pomeau-Manneville classification, and (b) type I intermittency. The neighborhood of one of the k fixed points is shown for intermittency with a period-k laminar flow.

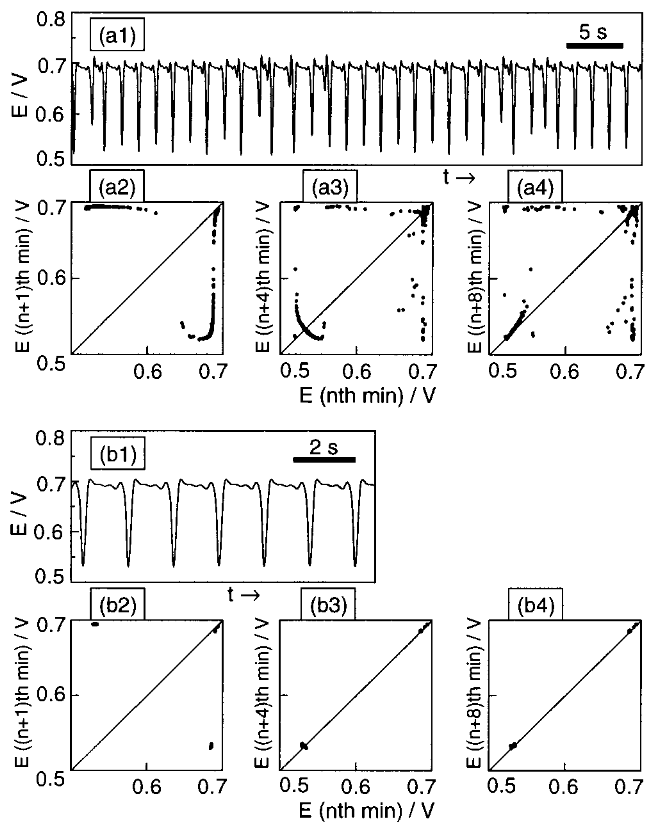

Figure 7. Type III intermittency observed before a period-4 pattern in the oxidation of 1 mol dm^{-3} formaldehyde at 0.55 mA. (a1−a4) a type-III intermittent oscillation pattern and its first, fourth, and eighth return maps; (b1−b4) a period-4 pattern and its first, fourth, and eighth return maps.

in the third return map (v) more clearly than does the sixth return map (a4) for the oscillation pattern shown in (a1). As time passes, these six (=2 $\times$ 3) crossing points remain, while the other map points gradually disappear, leaving in the sixth return map only the points on the diagonal line (c4), corresponding to the period-3 $\times$ 2 pattern. If the 12th return map were plotted, 12 (= 2^2 $\times$ 3) crossing points would appear and remain in the

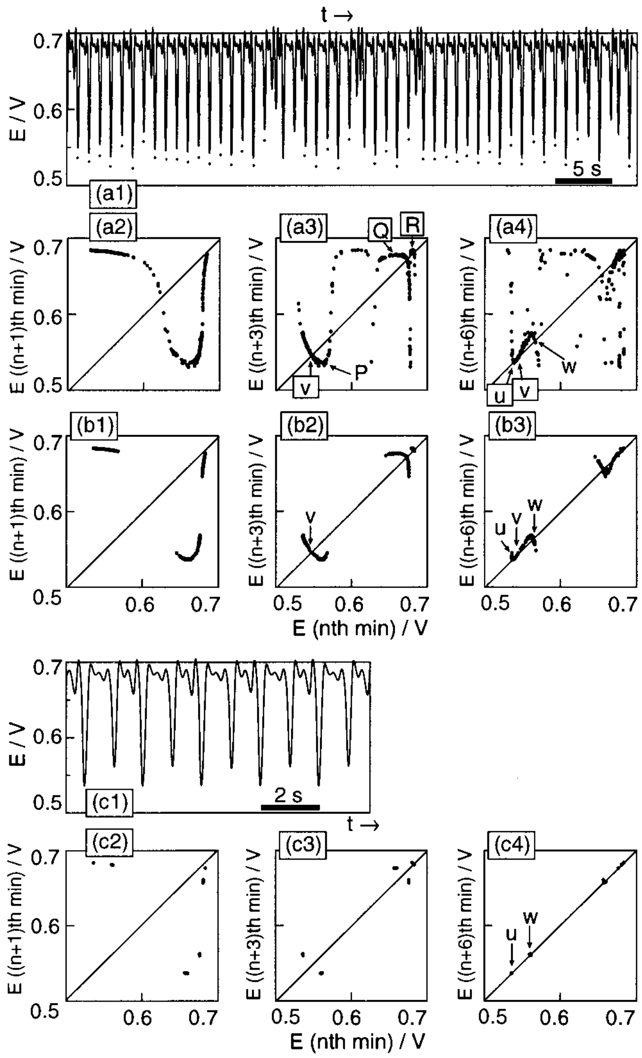

Figure 8. A type-III-like intermittent oscillation pattern observed before a period-3 pattern in the oxidation of 1 mol dm^{-3} formaldehyde at 0.65 mA. (a1) a type-III-like intermittent pattern, dots indicating the large peaks appearing every three peaks; (a2−a4) its first, third, and sixth return maps. (b1−b3) the first, third, and sixth return maps for the pattern just before a period-3 × 2 pattern. (c1−c4) the period-3 × 2 pattern and its first, third, and sixth return maps. The crossing point *v* is one of the three fixed points in the third return map, and in the sixth return map *u* and *w* are the crossing points on each side of *v*. *P* (minimum point), *Q* (maximum point), and *R* (maximum point) are the symbols for comparing the map changes for the reaction system with those for the logistic system.

same way as above to result in a map corresponding to the period-3 × 2^2 pattern before the appearance of the period-3 × 2 pattern. We did not plot such a high-order map because it would certainly have been blurred.

As shown in Figure 9(a1), a type-III-like intermittent pattern was easily observed before a period-2^2 pattern and sometimes before a period-2^3 pattern. This is in contrast to the fact that we did not observe a type-III-intermittent pattern with the period-2 laminar flow. Although the second return map (a3) shows normals and the fourth return map (a4) shows tangents to the diagonal line at two points, the manner of crossing in the latter does not seem to be cubicly tangent. Furthermore, the fourth return maps (a4, b3, c4) clearly show that as time passes the four (=2 × 2) crossing points on both sides of the fixed points in the second return map become more clearly shown and tend to remain, while the other map points gradually disappear. The pattern shown in a1 is, therefore, a type-III-like intermittent pattern. Incidentally, although the oscillation pattern (c1) looks like a period-2^2 pattern, it is not that pattern because traces of subharmonicity are present and maps are fragmentary (c2−c4).

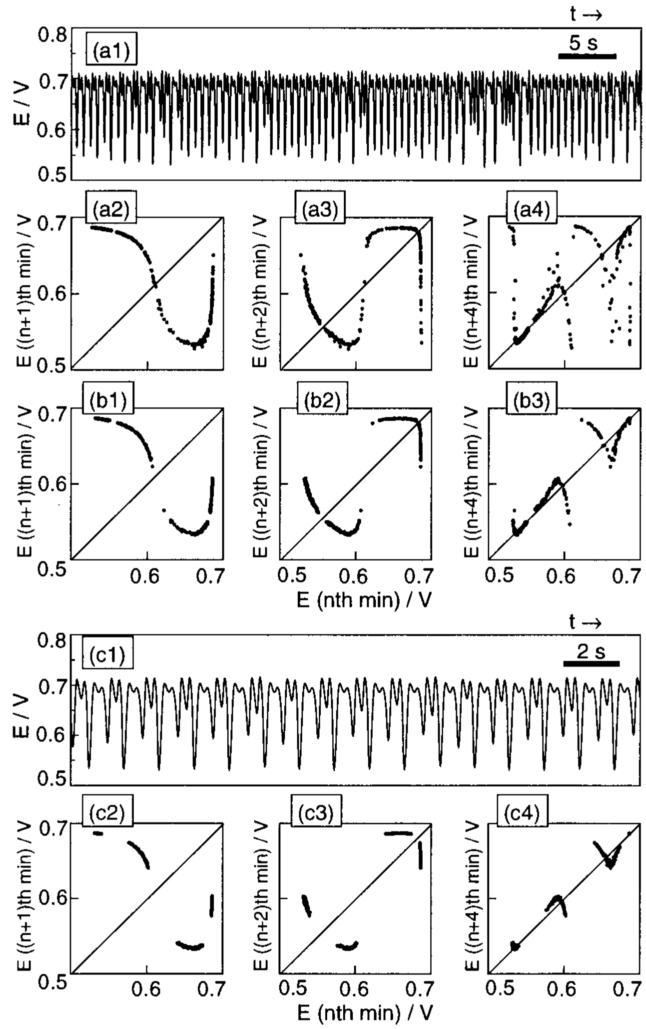

Figure 9. A type-III-like intermittent oscillation pattern observed before a period-2^2 pattern in the oxidation of 1 mol dm^{-3} formaldehyde at 0.75 mA. (a1) a type-III-like intermittent pattern; (a2−a4) its first, second, and fourth return maps. (b1−b3) the first, second, and fourth return maps for the pattern a little before a period-2^2 pattern. (c1) a pattern just before the period-2^2 pattern; (c2−c4) its first, second, and fourth return maps.

Because type-III-like intermittent patterns changed to type-III-intermittent patterns with decreasing current, the difference between the two intermittencies was not clear. Furthermore, the difference was more unclear because it took a very long time to observe type III intermittency because the applied current had to be very low. Consequently, it is difficult to determine the conditions for the appearance of III intermittency. We can, however, broadly state conditions such that the formaldehyde concentration must be at least 1 mol dm^{-3} and that the applied current must be very low (0.6 mA or lower for 1 mol dm^{-3}). This is because we observed type III intermittency in solutions containing 1, 3, or 10 mol dm^{-3} formaldehyde but not in solutions containing 0.3, 0.1, or 0.03 mol dm^{-3} formaldehyde (where only type-III-like intermittent patterns were observed).

Intermittency-Related Phenomena. As shown in Figure 10, we observed that type I and type III intermittencies coexisted at a low current. After a period-4 pattern, potential oscillation first showed type I intermittency with a period-4 laminar flow

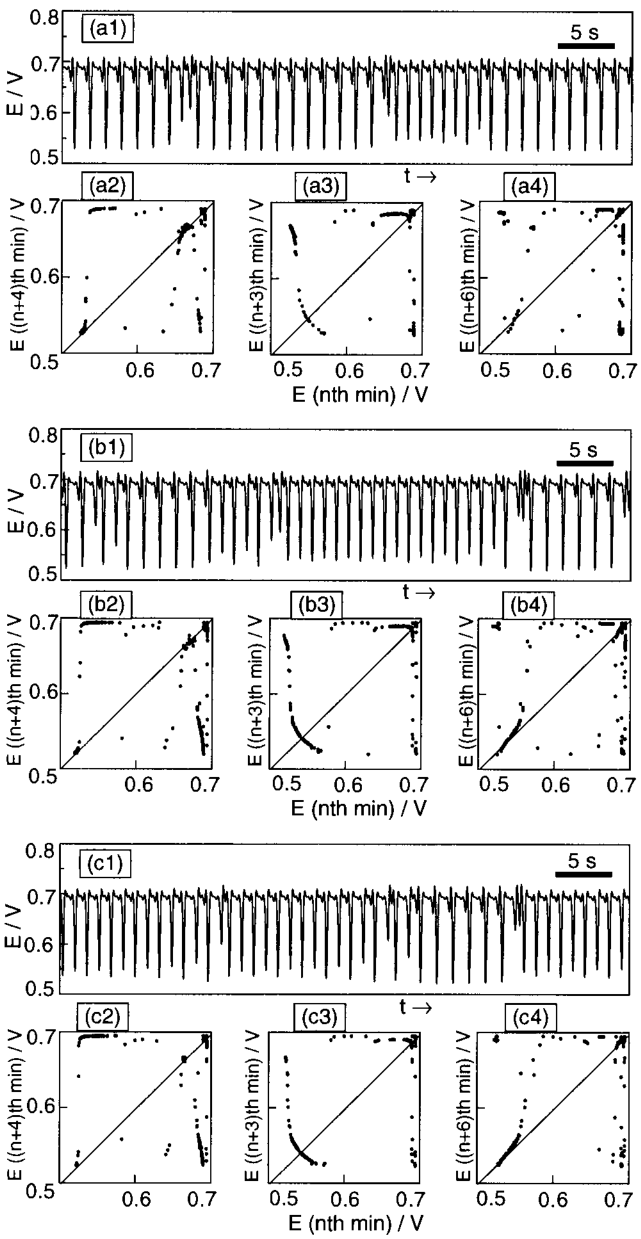

Figure 10. Coexistence of type I and type III intermittencies in the oxidation of 1 mol dm^{-3} formaldehyde at 0.6 mA. (a1) an oscillation pattern a little after a period-4 pattern; (a2−a4) its fourth, third, and sixth return maps. (b1) an oscillation pattern observed halfway between the period-4 and period-3 patterns; (b2−b4) its fourth, third, and sixth return maps. (c1) an oscillation pattern a little before the period-3 pattern; (c2−c4) its fourth, third, and sixth return maps.

together with a little type-III-like intermittency with a period-3 laminar flow (a1−a4). As time passed, we observed the coexistence of type I and type III intermittencies (b1−b4). That is, the fourth return map shows quadratic curves asymptotic to the diagonal line at the same time that the third map shows normals and the sixth map shows cubic curves tangent to the diagonal line. As shown in c1−c4, the coexistence continued during the oscillation a little before a period-3 pattern, although type I intermittency decreased. Then the oscillation changed directly to the period-3 pattern. We almost always observed such a coexistence when the oscillation showed type III intermittency, and the coexistence is indicated by C(I+III) in Figure 4b.

Here we compare the order in which chaotic, intermittent, and periodic patterns appear in the case of type III intermittency

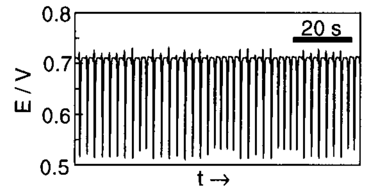

Figure 11. Randomly alternating period-4 and period-3 patterns without intermittencies (obtained in the oxidation of 0.1 mol dm^{-3} formaldehyde and 0.1 mol dm^{-3} methanol at 0.7 mA).

and in the case of type-III-like intermittency. We explain, as an example, the appearance order during the change from a period-4 pattern to a period-3 pattern. As shown in Figure 4a, when type-III-like intermittency is observed, the period-4 pattern is followed by type I intermittency with a period-4 laminar flow. Then a chaotic pattern without any continuing periodicity appears and is followed by type-III-like intermittency with a period-3 laminar flow, which is in turn followed by a reverse period-doubling cascade that results in the period-3 pattern.

As shown in Figure 4b, when type III intermittency is observed (usually at a current lower than that in the case above), there is no reverse period-doubling cascade, type-III-like intermittency changes to type III intermittency, and the chaotic state without any continuing periodicities becomes a state in which type I and type III intermittencies coexist. Then we may expect, as shown in Figure 4c, that, with further decreasing current, all the transient phenomena, intermittencies and period-doubling cascades, will disappear. Instead a randomly alternating sequence of period-4 and period-3 patterns will appear.

We observed such a pattern in a solution of 1 mol dm^{-3}, but at a high current: 1.5 mA, at which an alternating periodic and chaotic sequence in reverse order was observed (described later). Unfortunately, since we could not obtain a fine pattern when using the computer acquisition, Figure 11 shows a similar pattern obtained from the oxidation of 0.1 mol dm^{-3} formaldehyde and 0.1 mol dm^{-3} methanol at 0.7 mA. It shows randomly alternating period-4 and period-3 patterns, which if the time scale is compressed look like a vertically striped pattern with stripes of two lengths. We could not, however, determine the conditions for the appearance of such patterns, because we did not observe them at low currents and we sometimes did observe them at high currents. Incidentally, we sometimes observed that one periodic pattern changed abruptly once and for all to the next periodic pattern. Since such a once-and-for-all change is like one stepwise change in the striped pattern, we think these phenomena are related.

Intermittencies in the Ascending-Order Sequence. At a current too high for the occurrence of an alternating periodic and chaotic sequence in descending order, and in a solution of 0.3 mol dm^{-3} formaldehyde or more, we observed the sequence in reverse order.[12] For the reverse-order sequence, we found type I intermittency before a periodic pattern and found type III intermittency after the periodic pattern. This order of the intermittency appearance is reversed from that observed for the sequence in descending order, which this paper has dealt with up to now.

As shown in Figure 12, after a period-doubling cascade, a chaotic pattern (a1) gives a third return map (a2) like that shown in Figure 1(a4). The ensuing pattern (b1) a little before a period-3 pattern shows type I intermittency with a period-3 laminar flow and provides the third return map (b2) indicating the characteristics of type-I intermittency. After the period-3 pattern (c), the oscillation pattern (d1) shows type III intermittency with a period-3 laminar flow and gives the third return

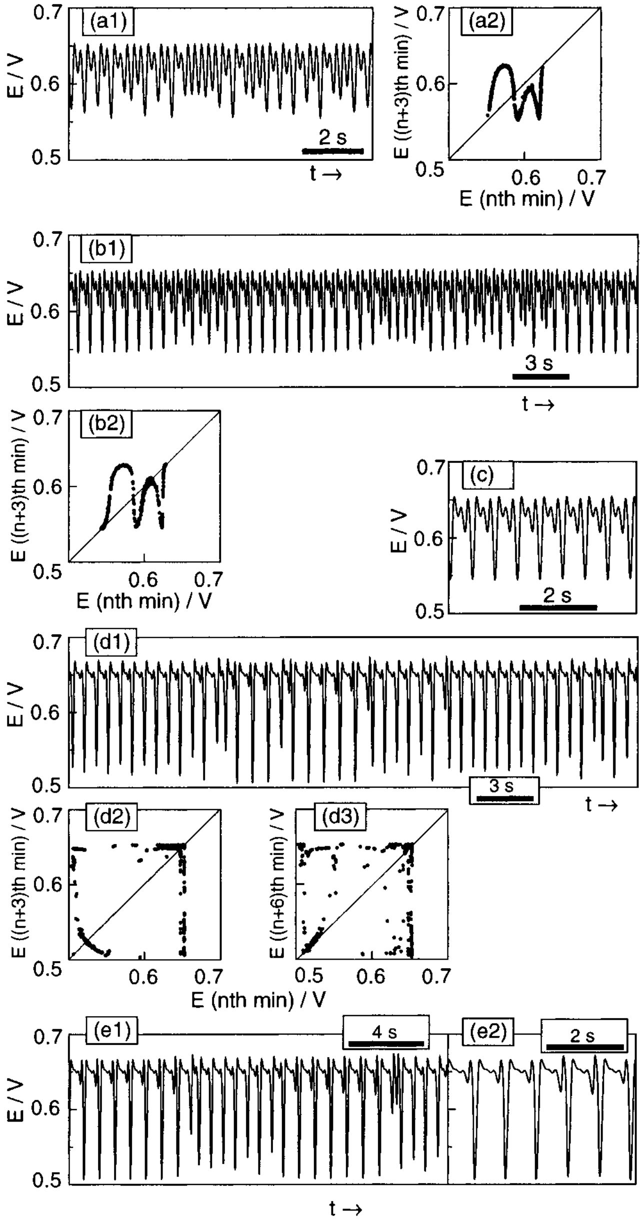

Figure 12. Alternating periodic and chaotic sequence in ascending order and intermittencies obtained from the oxidation of 1 mol dm^{-3} formaldehyde at 1.2 mA. (a1) a chaotic pattern after a period-doubling cascade, (a2) its return map. (b1) an oscillation pattern a little before a period-3 pattern, (b2) its third return map. (c) the period-3 pattern. (d1) an oscillation pattern observed halfway between the period-3 and period-4 patterns; (d2 and d3) its third and sixth return maps. (e1) an oscillation pattern a little before the period-4 pattern; (e2) an enlarged part of a period-4-like pattern.

map (d2) normals and the sixth return map (d3) cubic curves tangent to the diagonal line. In the pattern we can recognize a little type I intermittency with a period-4 laminar flow, and this intermittency increases (e1, e2) till a period-4 pattern is directly stabilized.

Discussion

Consider now a series of third return maps for the oscillation from before the period-3 pattern to the period-2^2 pattern in the descending-order sequence obtained from the oxidation of 1 mol dm^{-3} formaldehyde at 0.9 mA. The maps are shown in Figure 13(a1−a6) (some of them are the same as maps shown in previous figures). We can see a systematic change in the third

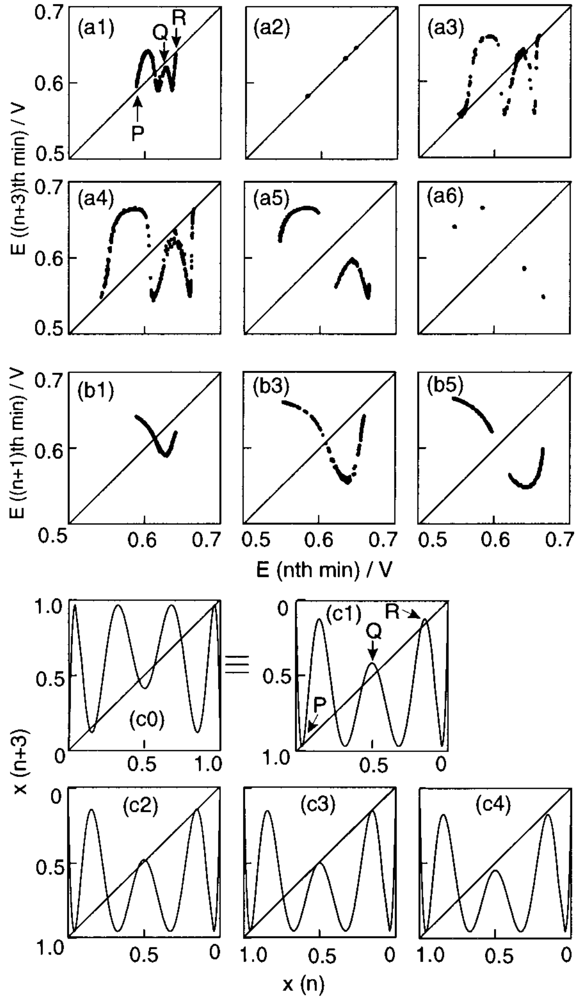

Figure 13. Temporal change in the return maps for oscillations before and after a period-3 pattern during the oxidation of 1 mol dm^{-3} formaldehyde at 0.9 mA, and a comparison with the change in the third return maps for the logistic difference equation, $x(n+1) = Ax(n)\{1 - x(n)\}$. (a1 and b1): for the oscillation pattern before a period-3 pattern (the same as Figure 1(a4, a2)). (a2): for the period-3 pattern (the same as Figure 1(b3)). (a3 and b3): for the pattern just after the period-3 pattern (the same as Figure 2(a4, a3)). (a4): for the pattern observed halfway between the period-3 and period-2^2 patterns. (a5 and b5): for the pattern just before the period-2^2 pattern. (a6): for the period-2^2 pattern. The rest of the return maps are the ones calculated using the logistic equation with (c0 and c1) $A = 3.87$ (chaos), (c2) $A = 3.84$ (a period-3 pattern), (c3) $A = 3.83$ (type I intermittency), and (c4) $A = 3.81$ (another chaos). *P*, *Q*, and *R* in a1 and c1: see legends in Figure 8.

return maps in such a way that the left-end minimum (*P* in a1), the central maximum (*Q*), and the right-end maximum (*R*) first approach to touch the diagonal line (a2), when the period-3 pattern appears, and then withdraw from the diagonal line (a3−a5), displaying the characteristics of type I intermittency (a3). As shown in b1, b3, and b5, however, the first return map seems to change monotonically in the meantime. Hence, for this pattern change, the third return map provides more information than the first one.

Because the first return map is continuous and continuously differentiable with one extremum and the oscillation shows a period-doubling cascade, this reminds us of the logistic map, though the logistic map has a maximum and the map for the reaction has a minimum. Upon the decrease of parameter *A* in the logistic difference equation:

$$x(n+1) = Ax(n)\{1 - x(n)\} \quad (1)$$

near the appearance of the period-3 pattern, the third map changes as shown in c1−c4. This map is depicted upside down and right-side left to allow an easier comparison with the map for the reaction. The map changes in such a way that *P*, defined above, monotonically goes up, and *Q* and *R* monotonically go down as the oscillation changes from chaotic (c1) through period-3 (c2) and type-I-intermittent (c3) to another chaotic (c4). This change in the logistic map is different from that in the map for the reaction, where *P*, *Q*, and *R* change their directions before and after the period-3 pattern.

To see if the nonmonotonic change in the map is a characteristic of the reaction, we compare the third return maps for the oscillations before the period-3 pattern obtained at 0.9 mA and at 0.65 mA. At 0.65 mA we observed, after a period-doubling cascade, an alternating periodic and chaotic sequence in descending order beginning with a period-5 pattern. Before the period-3 pattern we observed a pattern shown in Figure 8(a1), the third return map (a3) of which is similar to the logistic one shown in Figure 13(c1). That is, *P* is lower than the diagonal line and *Q* and *R* are higher than the diagonal line. After the period-3 pattern the oscillation patterns give third return maps that change in a very similar way to the change shown in Figure 13(a3−a5). Such a monotonic change in the return maps was observed in several other runs for oscillations not just after the period-doubling cascade. Thus we can conclude that the map change for the reaction system is similar to that for the logistic system for oscillations before and after the period-3 pattern, except just after the period-doubling cascade. We also obtained an indication that the same conclusion holds for oscillations before and after the period-4 or period-5 pattern, though the map points were substantially scattered.

With regard to type I and type III intermittencies, we can evaluate the degree to which the experimental results agree with those predicted theoretically,[21] by measuring the laminar duration and by calculating the maximal Lyapunov exponent as a function of the time from the end or the beginning of periodic oscillation. As mentioned earlier, here we regard time as a convenient system parameter related to some surface states, although it has the following disadvantage. That is, the parameter time is not such a parameter as *A* in the logistic difference eq 1 and, strictly speaking, it is not an appropriate parameter but one that probably subsumes two or more system parameters.[12]

Theory predicts the limit values as the parameter of the bifurcation approaches zero, when periodic oscillation is achieved. For experimental measurements, on the other hand, we regard time *t* as the tentative parameter of the bifurcation. Furthermore, we cannot determine the origin of *t* because for the beginning or the end of periodic oscillation it is not always the origin. We tentatively define *t* as α plus the time from the beginning or the end of a periodic pattern. The value α is determined through trial and error so that we can plot points as near a straight line as possible. Consequently, we should not expect a strict comparison. Although there is another quantity to be compared with the theoretical prediction, a histogram for the laminar duration at a fixed system parameter, we could not obtain such a quantity because the system parameter, time, always changed.

Figure 14a shows, for type III intermittency, the relation between *t* (with $\alpha = 100$ s) and *t*(lam), the laminar duration averaged over a time interval of 100 s. Part of the oscillation pattern we calculated with is shown in Figure 5(a1). Although the plotted points scatter, we draw a straight line by the least-squares method and the slope of this line is −0.96. Since the value expected theoretically is −1.0, this agreement is excellent. Although the same theoretical slope is also expected for type B intermittency[22,23] (i.e., on−off intermittency[24]), the observed intermittent pattern cannot be the on−off one because the on−off intermittent pattern does not show subharmonics.

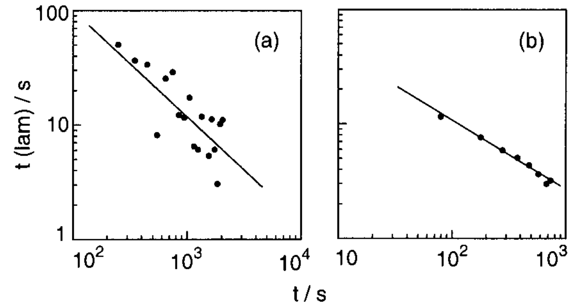

Figure 14. The laminar duration averaged over a time interval of 100 s, *t*(lam), related to *t*, α plus the time from the end or the beginning of periodic oscillations: (a) for type III intermittency before a period-3 pattern with $\alpha = 100$ s, c.f. Figure 5(a1); (b) for type I intermittency after the period-3 pattern with $\alpha = 30$ s, c.f. Figure 2(a1).

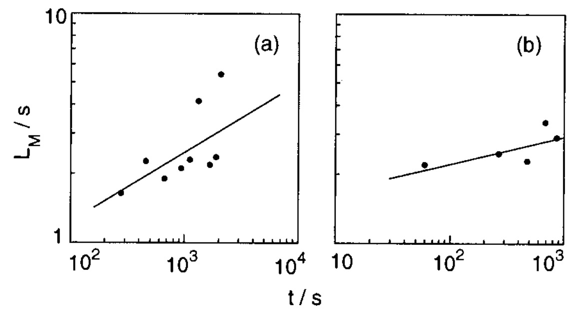

Figure 15. The maximal Lyapunov exponents L_M related to the *t* defined for Figure 14: (a) for type III intermittency before a period-3 pattern, (b) for type I intermittency after the period-3 pattern.

As shown in Figure 14b, for type I intermittency, a similar relation between *t* (with $\alpha = 30$ s) and *t*(lam) gives a straight line with a slope of −0.60. Part of the oscillation pattern we calculated with is shown in Figure 2(a1). This slope is near the theoretical one, −0.5. We think the agreement between the experimental and theoretical values is very good despite the use of the tentative parameter.

The maximal Lyapunov exponents L_M were calculated using the method of Sano and Sawada[25] with the embedding dimension 5. Figure 15a shows, for type III intermittency, the relation between L_M and the *t* defined previously for Figure 14a. Although the plotted points scatter very much, we can use the least-squares method to draw a straight line with a slope of 0.36. Since the value expected theoretically is 1.0, the agreement is not good. As shown in Figure 15(b), for type I intermittency, a similar relation between L_M and the *t* defined previously for Figure 14b gives a line with a slope of 0.12, whereas the value expected theoretically is 0.5. Although the agreement between the experimental and theoretical slopes themselves is not good, the ratio of the slope for type I intermittency to that for type III intermittency, about 0.33, is near the one predicted theoretically, 0.5. Considering the scattering of data points and the use of the tentative parameter, we think the agreement in the L_M slope ratio is also good enough to conclude that the experimental results agree with theory.

Summary

We showed the presence of type I and type III intermittencies (in Pomeau−Manneville classification) in the galvanostatic oxidation of formaldehyde on Pt at 43 °C. When we observed an alternating periodic and chaotic sequence in descending order after a period-doubling cascade, we observed type I intermittency after each periodic oscillation in the sequence. When we compared the *k*th return maps for the experimental oscillations with those for the logistic difference equation before and after the period-*k* oscillation, we found they changed in a similar way except just after the period-doubling cascade. We also found that mixed-mode oscillation blurred the return map more easily than did chaotic oscillation without distinct large and small amplitudes.

At a comparatively low current density (0.6 mA per 2.6 cm^2 or less) in a solution with a formaldehyde concentration of 1 mol dm^{-3} or more, we observed a type-III-intermittent pattern before periodic oscillation in the descending-order sequence. Under other conditions, we observed a type-III-like intermittent pattern followed by a reverse period-doubling cascade before each periodic oscillation in the sequence. We showed four pieces of evidence of type III intermittency with a period-*k* laminar flow: (1) the *k*th return map exhibited normals and the (2*k*)th return map displayed cubic curves tangent to the diagonal line, (2) the oscillation pattern changed directly to the period-*k* pattern, (3) the slope of a plot of the logarithm of the laminar duration vs the logarithm of the time from near the beginning of the period-*k* pattern was near the theoretical slope, and (4) the ratio of the slope of a plot of the logarithm of the maximal Lyapunov exponent vs the logarithm of the time from near the end of the period-*k* pattern for type I intermittency to the corresponding slope for type III intermittency was near the theoretical value. Here we regarded time as the tentative system parameter related to some surface states.

We observed that type I and type III intermittencies coexisted at a low current. We sometimes observed a randomly alternating sequence of period-(n+1) and period-n patterns ($n = 2$, 3, ...) without intermittencies, though we could not determine the conditions for its occurrence. In the sequence in ascending order we found respectively type I intermittency before a periodic pattern and type III intermittency after the pattern; the order the intermittencies appeared was reversed to that for the sequence in descending order.

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