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Use of Bifurcation Diagrams as Fingerprints of Chemical Mechanisms

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Various chemical reagents were fed continuously into a continuously stirred tank reactor to perturb the Belousov–Zhabotinskii system. The resulting bifurcation diagrams each contain multiple curves separating regions with different types of dynamical behavior. These very complex diagrams can be used as "fingerprints" of the perturbing chemical mechanism. Essentially the same bifurcation structures were observed under the addition of formaldehyde and sodium bromite, indicating the same mechanism. The effect of bromomalonic and hypobromous acids was also found to be nearly identical; the slight differences between their "fingerprints" is explained by the effect of bromine, which contaminates the HOBr. Finally, the effect of added bromide is shown in another bifurcation diagram.

Introduction

After the pioneering discoveries by Belousov, Zhabotinskii, and Noyes and his co-workers,[1-7] the Belousov–Zhabotinskii (BZ) reaction became an experimental workhorse not only for chemists but for nonlinear dynamicists as well. This is because the BZ reaction in a continuously fed stirred tank reactor (CSTR) is an excellent example of an open nonlinear dynamical system in chemistry. This system diplays a wide variety of interesting nonlinear phenomena such as multiple steady states, limit cycles, quasi-periodic and chaotic oscillations, and intermittency.[8-18] Perturbation experiments have revealed even more exotic chemical and dynamical behavior.[19-24] In spite of the extensive activity of chemists and nonlinear dynamicists in this field, there are still only few examples of the direct application of the methods of nonlinear dynamics in explaining or identifying particular steps of a chemical mechanism. In a recent paper[18] we studied the effect of trace impurities on a bifurcation structure in the BZ reaction. In the present work we show that by adding certain intermediates instead of contaminants in the feed stream we can produce similar, sometimes virtually identical, bifurcation diagrams. The similarity between bifurcation diagrams produced by two different feed-stream components (for example, by an impurity and by an intermediate) can be interpreted in chemical terms; namely, the similarity means that the two different components have a similar effect on the chemical mechanism. Thus bifurcation diagrams can be used as *fingerprints*: if they are identical for two components, it indicates that the chemical mechanism by which they affect the reaction is also the same for these components. In this work we present some illustrative examples of fingerprints.

Experimental Section

Materials. As we have shown in our previous paper,[18] it is crucial to use highly purified chemical components to obtain reproducible results for this system. Thus malonic acid and potassium bromate were purified as described previously.[18] Barium bromite ($Ba(BrO_2)_2$) was produced following Noszticzius et al.[25] There were some slight modifications in the recipe, however. The disproportionation of $Ba(BrO)_2$ was carried out at 0 °C, and the reaction time was increased from 2 to 6 h to get a better yield. Also, the product of the disproportionation (a mixture of wet crystals, mainly $BaBr_2$ and $Ba(BrO_2)_2$) was washed with distilled water (about 1 mL of H_2O/g of wet precipitate) before recrystallization to remove most of the contaminating bromide. Hypobromous acid (HOBr) was produced from $NaBrO_3$ solution with concentrated sulfuric acid, following Noszticzius et al.[26] The byproduct bromine, however, was removed in a different way, by bubbling air through the HOBr solution instead of shaking it with carbon tetrachloride.

Bromomalonic Acid Solution. In the present experiments we needed only a rather low concentration of bromomalonic acid in the malonic acid feed-stream solution. Thus we prepared a *mixture* of malonic and bromomalonic acid in the following way. Under the hood 0.31 mL (0.96 g or 6×10^{-3} mol) of liquid Br_2 was added dropwise from a separatory funnel to a continuously stirred 100-mL 1.5 M malonic acid solution. To keep any dibromomalonic acid production at a minimum, a great excess of malonic acid was used, and before adding each drop of bromine to the solution we waited until the yellow color due to the previous drop had faded. To remove the hydrogen bromide produced in the bromination reaction of malonic acid, the solution was titrated with 0.3 M $AgNO_3$ (about 20 mL) to the equilibrium point by using a bromide-selective electrode. The solution was filtered to remove the AgBr precipitate, and the precipitate was washed with about 20–30 mL of distilled water. The filtrate and the washing water were collected in a 200-mL volumetric flask. To neutralize the nitric acid produced from HBr and $AgNO_3$, about 20 mL of 0.3 M NaOH was added to the solution (the exact amount of 0.3 M NaOH needed was equal to the volume of the 0.3 M $AgNO_3$ solution used for titration). Then the solution was made up to 200 mL with distilled water. In this way a solution was produced with a malonic acid concentration of 0.75 M and a bromomalonic acid concentration of about 3×10^{-2} M. The exact concentration

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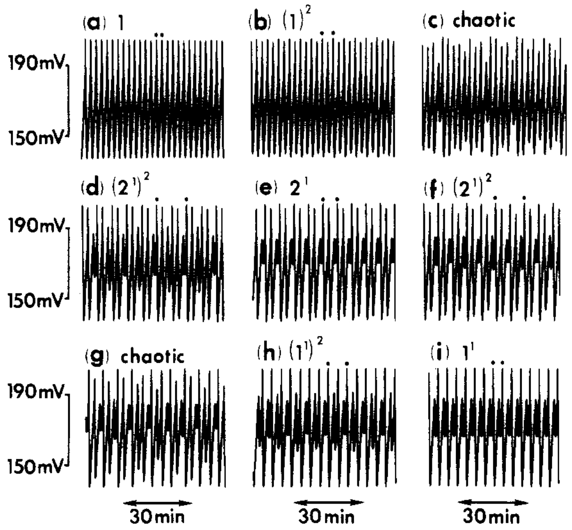

Figure 1. Time series for the bromide electrode potential observed for some of the states in a bifurcation sequence in the BZ reaction with pure malonic acid. For the periodic states the duration of a single period is the time between the dots above the time series. The values of the residence time t_r for the different states are shown on the abscissa in Figure 2a. The notation $(L^S)^R$, as in ref 29, indicates the number $L(S)$ of large (small) amplitude oscillations per period and the number of times R that the L^S motifs repeats in each period with only small variations in the amplitudes. Thus, for example, the $(2^1)^2$ state in Figure 1f has six oscillations in each period, which occur in the following order: two large, one small, two large, one small; this is a period-doubled period-three state—the wave forms for the successive period-three motifs are slightly different, as can be seen from the figure.

of the bromomalonic acid was calculated from the result of the titration.

All other chemicals were of reagent grade and were used without further purification.

Apparatus. The experimental setup was the same as that used previously to measure the effect of impurities in the malonic acid.[18] The bromide concentration was monitored by measuring the potential of a selective ion electrode with respect to a calomel reference electrode that was isolated from the reactor by means of a salt bridge filled with 0.2 M H_2SO_4. The feed-stream concentrations were as follows: (A) $[Ce^{3+}] = 2.5 \times 10^{-3}$ M, $[H_2SO_4] = 0.3$ or 0.6 M; (B) $[KBrO_3] = 0.3$ M, $[H_2SO_4] = 0.3$ or 0 M; (C) $[CH_2(COOH)_2] = 0.75$ M. Solutions A, B, and C were pumped into the reactor at equal rates; thus without reaction the reactor concentrations would have had the following values: $[Ce^{3+}]_0 = 8.33 \times 10^{-4}$ M, $[BrO_3^-]_0 = 0.1$ M, $[CH_2(COOH)_2]_0 = 0.25$ M, and $[H_2SO_4]_0 = 0.2$ M. With purified chemicals and no added perturbants the experimental results were the same, independently of whether the sulfuric acid was equally distributed in solutions A and B or it was only in solution A at twice the concentration. The solutions were freshly prepared every 3–4 days and were filtered through a membrane filter (Millipore cellulose nitrate; pore size 0.45 μm). The temperature was 28.0 ± 0.1 °C.

Results and Discussion

Dynamical States Observed with Pure Chemicals. The sequence of states observed with pure chemicals in the BZ reaction is illustrated in Figure 1, which shows time series of the potential of a bromide-selective electrode with respect to a calomel electrode. The figure shows only a few of the very large number of distinct states observed as the residence time t_r was varied. The observed sequence, which is part of the periodic–chaotic sequence observed by Roux and co-workers,[15,16,27,31] is entered (with increasing t_r) through a sequence of transitions in which the period of the initial state successively doubles; the time series before and after the first period doubling is shown in Figure 1, parts a and b, respectively. The dynamics is extraordinarily complex beyond the accumulation point that marks the end of the infinite period-doubling sequence, yet is has a universal character that can be understood in terms of one-dimensional maps.[15,16,28] Many distinct periodic states occur over small ranges in t_r.

The interpretation of the experiments in terms of one-dimensional maps suggests that with infinite resolution one would find an infinite number of these periodic states.[16,17,28,31] Figure 1e shows one of the periodic states, the period-three state, and Figure 1, parts d an f, shows the period-doubled period-three states that are observed at smaller and larger t_r, respectively. Note that although Figure 1, parts d and f, has the same symbolic motifs, the wave forms are not the same. The notation for the different motifs (symbol sequences) is described in the figure caption and in ref 29.

In addition to the periodic states, there are, according to the theory of one-dimensional maps, many values of t_r for which the behavior is intrinsically nonperiodic; this *chaotic* behavior, illustrated by the time series in Figure 1c,g, has been well confirmed by experiments; see the recent review by Argoul et al.[31] The complex bifurcation sequence illustrated in Figure 1 is extremely sensitive to the presence of certain feed-stream chemical components such as CH_2O, $NaBrO_2$, BrMA, HOBr, and Br^-. This striking effect is illustrated in Figures 2–4. In these figures only the periodic states that occur over a wide parameter range are explicitly indicated. The "chaotic" (black) regions presumably contain, in addition to chaotic states, an infinite number of periodic states that have large numbers of oscillations per period. However, high-period periodic states are in practice unobservable since the range in t_r over which they occur is extremely small; in fact, so small that in a typical one-dimensional map the probability of finding a periodic rather than chaotic state at an arbitrarily chosen point in the chaotic region is only about 0.1.

Experiments with Formaldehyde and Sodium Bromite. Results of experiments with formaldehyde and sodium bromite are depicted in Figure 2, parts a and b, respectively. Formaldehyde was chosen because (i) in previous experiments[18] we found that the bifurcation structure of the BZ reaction was rather sensitive to paraformaldehyde contamination in the malonic acid and (ii) the products of the acidic bromate–formaldehyde reaction, namely, bromous acid and formic acid, are known. Formaldehyde was added to the malonic acid solution[18] to avoid any reaction in the reservoir. Sodium bromite was chosen because in acidic medium it forms bromous acid, which is also formed in the formaldehyde–acidic bromate reaction. Bromous acid itself cannot be used because it is not a stable compound and disproportionates quickly[25,32] in acidic or in neutral solutions. Thus we introduced bromite to the reactor in the form of an alkaline sodium bromite solution. In the reactor bromous acid was formed very rapidly in reaction R1. The alkaline sodium bromite was added to the

$$NaBrO_2 + H^+ \rightarrow HBrO_2 + Na^+ \qquad (R1)$$

bromate reservoir. To avoid a disproportionation of bromite, 0.1 M NaOH concentration was established in the $KBrO_3$ solution, and all the sulfuric acid was added to the cerous reservoir. Also, a 0.1 M HNO_3 concentration was established in the cerous solution in addition to the 0.6 M sulfuric acid concentration to prevent any substantial change of the pH in the reactor. Separate experiments have shown that the simultaneous presence of 0.1 M NaOH in the bromate solution and 0.1 M HNO_3 in the cerous solution has no measurable effect on the bifurcation structure. We used nitric acid in the cerous solution instead of more sulfuric acid because any change in the sulfate concentration has a considerable effect on the bifurcation structure (see later).

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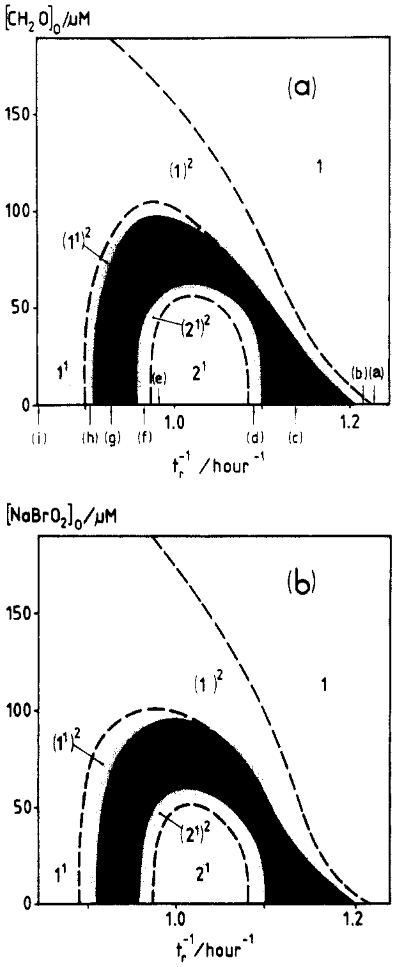

Figure 2. Effect of (a) formaldehyde and (b) $NaBrO_2$ on a bifurcation sequence in the BZ reaction. The figure should be viewed as schematic since the measurements were made with a fairly coarse mesh in concentration (steps of 20–30%) and t_r (steps of 2–5%). Only a few of the many periodic states are explicitly indicated; the notation is described in the caption for Figure 1. The white areas correspond to periodic states, while the black areas contain both chaotic and periodic states; see text. Dashes lines mark the beginning of period-double sequences. There is a continuous variation in wave form from the $(1)^2$ wave form, corresponding to the period doubling of the one-cycle, to the 1^1 wave form in the lower left region of the figures; there is no bifurcation marking this smooth variation with control parameters. The letters a–i on the abscissa in (a) correspond to the time series in Figure 1. Formaldehyde was mixed into the malonic acid feed stream and $NaBrO_2$ into an alkaline bromate feed stream; see text. $[CH_2O]_0$ and $[NaBrO_2]_0$ denote concentrations that would be established in the reactor if there were no chemical reactions.

The bifurcation diagrams in Figure 2 are the same within the experimental error. The chemical explanation is the following: Both $NaBrO_2$ and CH_2O generate $HBrO_2$ in the reactor. $NaBrO_2$ forms bromous acid in reaction R1 and formaldehyde does the same in reaction R2. (R1) is a fast diffusion-controlled reaction

$$CH_2O + H^+ + BrO_3^- \rightarrow HCOOH + HBrO_2 \qquad (R2)$$

which is complete within the time of mixing. (R2) is slower, but due to the high concentration of acidic bromate, on the time scale of the residence time it is fast enough to convert practically all CH_2O to formic and bromous acids. Thus equivalent amounts of $NaBrO_2$ and CH_2O will produce equivalent amounts of $HBrO_2$ in reactions R1 and R2, respectively. The product $HBrO_2$ is one of the autocatalytic intermediates of the BZ reaction that plays a crucial role in the mechanism.[1,2,33] The byproducts Na^+ in (R1) and HCOOH in (R2) are inert end products in the BZ system.[34,35]

In summary, both (R1) and (R2) produce the same autocatalytic intermediate of the BZ reaction: $HBrO_2$. Since bromous acid is a part of the positive feedback loop, a bromous acid source has a strong effect on the dynamics of the BZ reaction. This is reflected in the bifurcation diagrams of Figure 2. Since both $NaBrO_2$ and CH_2O form equivalent amounts of $HBrO_2$ in the reactor, they have identical bifurcation diagrams, the same *fingerprint*. This result is not obvious, though. For example, CH_2O could react in (R3) to form formic acid and HOBr, or in (R4)

$$CH_2O + HBrO_2 \rightarrow HCOOH + HOBr \qquad (R3)$$

$$CH_2O + HOBr \rightarrow HCOOH + H^+ + Br^- \qquad (R4)$$

to form formic acid and Br^-. If (R3) or (R4) were the dominant reaction in our system, CH_2O would be a *sink* instead of a *source* of $HBrO_2$, and the bifurcation diagram would be quite different. Especially in the case of (R4), not only would $HBrO_2$ be consumed, but also a control intermediate, Br^-, would be formed. In this way CH_2O would strengthen the *negative* feedback loop instead of the *positive* one. The near identity of the bifurcation diagrams for CH_2O and $NaBrO_2$ indicates that at the parameter values applied in our experiments, reaction R2 is dominant and the effect of (R3) and (R4) is negligible compared to (R2) in this case. Naturally it might happen that at other parameter values (for example, different sulfuric acid or bromate concentrations) (R2) would no longer be dominant. This fact too, however, would be reflected in the bifurcation diagrams; then $NaBrO_2$ and CH_2O would produce different fingerprints at those parameter values.

Experiments with Hypobromous and Bromomalonic Acids. The results of experiments with bromomalonic and hypobromous acids are shown in Figures 3, parts a and b, respectively. HOBr was added to the reservoir which contained acidic bromate ($[H_2SO_4]$ = 0.3 M) to slow down the disproportionation of hypobromous acid. In neutral solutions HOBr disproportionates rather quickly.[36] In the acidic medium of 0.3 M H_2SO_4 the disproportionation reaction is very slow. Nevertheless, the average length of one experiment, 8–12 h, is long enough for the appearance of some bromine as a product of the disproportionation of HOBr. The effect of that bromine will be discussed later. To keep such effects at a minimum, fresh, bromine-free HOBr–acidic bromate solutions were prepared every day. A mixture of malonic (MA) and bromomalonic (BrMA) acids was added to the malonic acid reservoir. Both HOBr and BrMA were chosen because they are important intermediates of the BZ reaction. Moreover, considering the high MA concentration in our system, it seemed reasonable to assume that HOBr will react rapidly in reaction (R5) to form bromomalonic acid.[37] Thus if (R5) is the dominant

$$MA + HOBr \rightarrow BrMA + H_2O \qquad (R5)$$

reaction of HOBr, we can expect similar or even the same bifurcation diagrams for HOBr and for BrMA. Figure 3 demonstrates that this is nearly the case; equivalent amounts of HOBr or BrMA yield rather similar *fingerprints*. The difference between the two fingerprints may be caused by the trace amount of bromine in the hypobromous acid. That Br_2 is being formed slowly in net process R6. The disproportionation reaction of HOBr takes place

$$5HOBr \rightarrow H^+ + BrO_3^- + 2Br_2 + 2H_2O \qquad (R6)$$

in the reservoir containing the HOBr–acidic bromate mixture. When Br_2 produced this way is introduced into the reactor, it reacts with the malonic acid there according to (R7). The important

$$Br_2 + MA \rightarrow BrMA + Br^- + H^+ \qquad (R7)$$

difference between (R5) and (R7) is that in (R5) the only reactive product is bromomalonic acid, while in (R7) a bromide ion is also formed. Bromide has a strong effect on the bifurcation structure even for concentrations that are 1 order of magnitude smaller than the effective concentrations of bromomalonic acid (see Figure 4).

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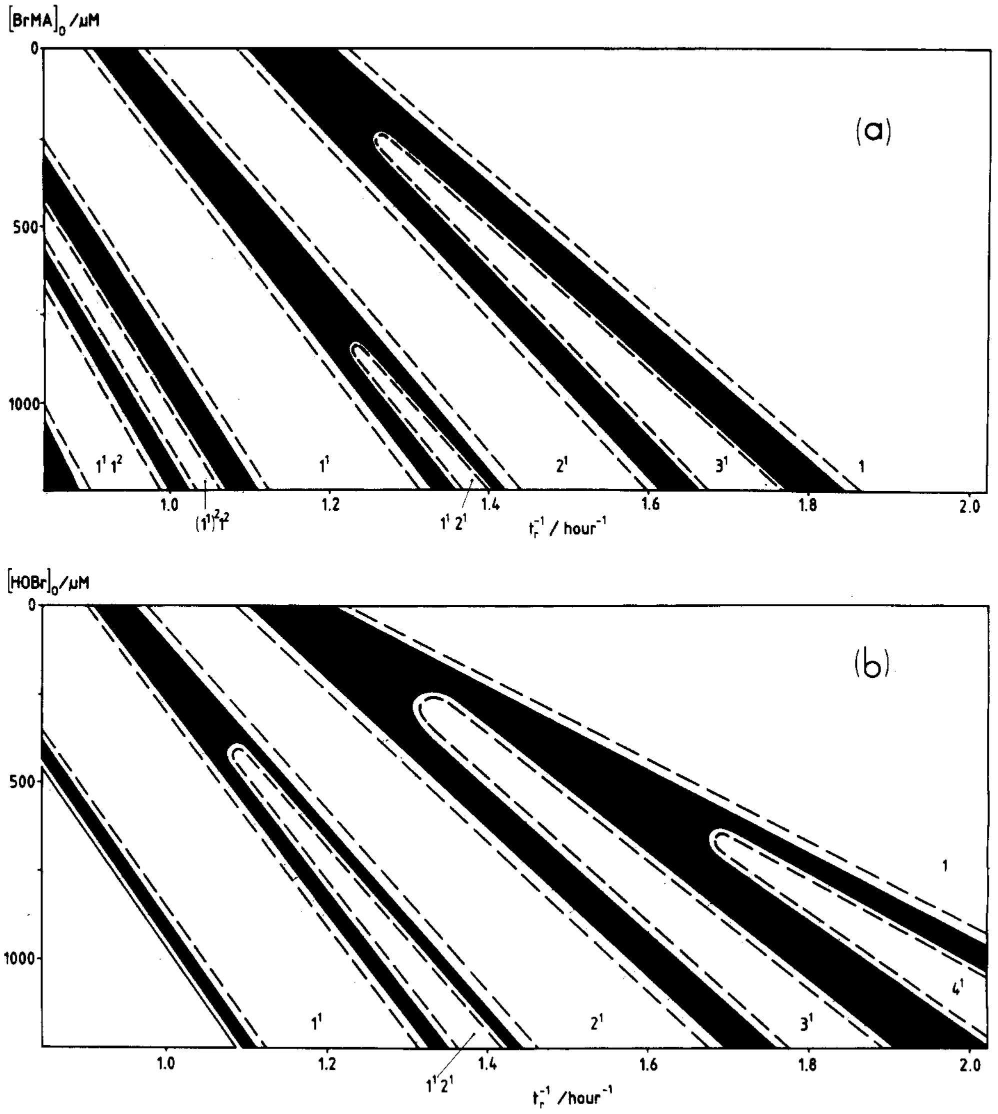

Figure 3. Effect of (a) bromomalonic acid and (b) HOBr on a bifurcation structure in the BZ reaction. The figure should be viewed as schematic since the measurements were made with a fairly coarse mesh in concentration (steps of 30–50%) and t_r (steps of 2–10%). Note that the direction of the concentration axis is opposite to that in Figure 2, but in both figures the direction of increasing complexity in the bifurcation structure is downward. Only a few of the many periodic states are explicitly indicated; the notation is described in the caption for Figure 1. The white areas correspond to periodic states, while the black areas contain both chaotic and periodic states; see text. Dashed lines mark the beginning of period-doubling sequences. Bromomalonic acid was mixed into the malonic acid feed stream and HOBr into the bromate. $[BrMA]_0$ and $[HBr]_0$ denote virtual reactor concentrations as in Figure 2.

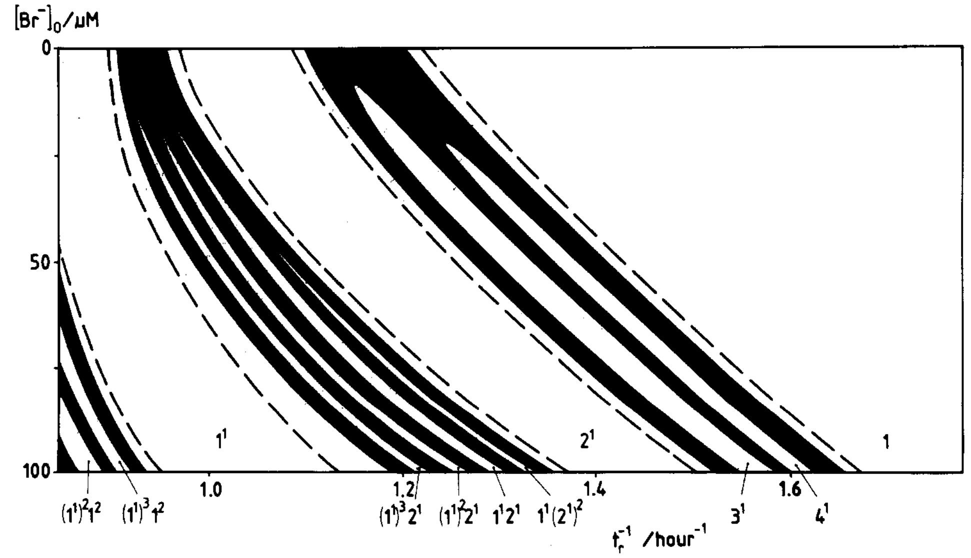

Figure 4. Effect of bromide on a bifurcation structure in the BZ reaction. Bromide was added to the malonic acid feedstream. Notation in this figure is the same as in Figure 3 except that dashed lines marking the beginning of the period-doubling sequence are omitted in the extremely narrow periodic peninsulas of the black chaotic sea.

Thus it is understandable that even a trace amount of bromine in the hypobromous acid can change the bifurcation structure considerably. If we could prevent somehow the disproportionation of HOBr during the experiments, the two fingerprints in Figure 3 might be identical. It is possible, however, that the indirect production of BrMA through bromine during the high bromide phase of the oscillations could also produce differences in the fingerprints. It is interesting that while $HBrO_2$, as a part of the positive feedback loop, decreases the complexity of the bifurcation structure, bromomalonic acid, which plays a role in the negative feedback loop,[33] increases it. Because of these opposite effects the concentration scales in Figures 2 and 3 are drawn in opposite directions. When drawn in this way, the complexity of the bifurcation structure decreases upward and increases downward in both figures.

Effect of Bromide and Sulfate Concentration on the Dynamics. The addition of bromide ions to the BZ reaction has an effect somewhat similar to the effect of adding bromomalonic acid; it increases the complexity of the bifurcation structure (see Figure 4). There are three important differences, however: (i) Bromide is roughly 10 times as effective as bromomalonic acid in changing the bifurcation structure. (ii) Bromide causes the appearance of many more periodic states: we observe numerous new peninsulas in the chaotic sea. (iii) The wave form of the oscillations is also different: the small oscillations within one motif are much smaller than in the cases depicted in Figure 1.

In the previous paragraphs we studied the effect of nearly all bromine-containing intermediates on the bifurcation structure. $HBrO_2$, HOBr, Br^-, and BrMA were studied; only Br_2 was not considered. Elementary bromine was not studied because it readily diffuses into the Plexiglass wall of the reactor and in this way it can cause memory effects.[38] Moreover, as we pointed out previously, bromine would react in the reactor to form bromide and bromomalonic acid. Thus its effect would be the same as a combination of bromide (Figure 4) and bromomalonic acid (Figure 3), at least as long as memory effects are negligible.

Finally, we want to mention the effect of sulfate on the bifurcation structure. This effect, which has not yet been studied systematically, was discovered accidentally in examining the possibility of using sodium malonate in our experiments instead of malonic acid. (Sodium malonate is usually available in a higher purity than malonic acid itself.) In this case $NaHSO_4$ would be produced in the reactor; therefore, we investigated the effect of $NaHSO_4$ on the bifurcation structure in a preliminary experiment. $NaHSO_4$ was added to the malonic acid solution at a concentration of 0.5 M (0.167 M in the reactor). The $NaHSO_4$ produced fundamental changes in the bifurcation structure and the nature of the oscillations. The amplitude of the oscillations increased by 50%, and much longer residence times (about 3 h instead of 1 h) were necessary to observe complex oscillations. The observed motifs were also very different; combinations of several large and several small oscillations (see, e.g., ref 35) appeared. Such motifs were not observed with lower sulfate concentration. The effect was caused mainly by the change in the sulfate concentration and not by the relatively small change in the pH. To prove that, we repeated the experiment using Na_2SO_4 instead of $NaHSO_4$, and the result was very similar. When $NaNO_3$ was added to the malonic acid solution in a concentration of 1.5 M (0.5 M in the reactor), the change in the dynamical state was negligible. Thus it was neither the pH nor the ionic strength of the solution that caused these changes but the sulfate concentration itself. Most probably these observations can be explained by the formation of different Ce^{4+}–sulfate complexes.[39]

Concluding Remarks

The bifurcation structures contain much more information than curves describing the dependence of an observable on a control parameter—these structures are a rich set of curves forming the boundaries of regimes with qualitatively different behavior. It would be a surprising coincidence if two perturbants that yielded the same bifurcation diagram corresponded to different chemical mechanisms.

Thus we believe that the term *fingerprint* provides a succinct and appropriate description of the bifurcation structures. Our earlier paper described a variety of organic perturbants that yielded quite different structures, and even in a case in which similar diagrams were produced (for example, by methanol and formaldehyde), the concentration scales were quite different. In contrast, for formaldehyde and sodium bromite the concentration scales as well as the shapes of the bifurcation structures are the same. This indicates that one molecule of $NaBrO_2$ is stoichiometrically equivalent to one molecule of CH_2O in the BZ reaction. Moreover, the well-known and accepted reactions R1 and R2 both produce the same amount of $HBrO_2$ (Na^+ and HCOOH are known to be inert products). Thus our conclusion that the mechanism of the perturbation is the same is supported by specific chemical arguments as well as the comparison of the bifurcation structures.

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Registry No. MA, 141-82-2; BrMA, 600-31-7; BrO_3^-, 15541-45-4; Ce, 7440-45-1; CH_2O, 50-00-0; BrO_2^-, 15477-77-7; HOBr, 13517-11-8; Br^-, 24959-67-9.

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