

# Period of homogeneous oscillations in the ferroin-catalyzed Zhabotinskii system

M-L. Smoes

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109  
(Received 27 July 1978)

This work is primarily an experimental investigation of the ferroin-catalyzed Zhabotinskii system [malonic acid (MA), sulfuric acid, sodium bromate, traces of bromide ions, and ferroin]. We measure the transmittance as a function of time at 546 nm. The emphasis is placed on the properties of the period of homogeneous oscillations. It is found that  $T$  depends on the initial concentrations of reactants:  $T(s) = C [\text{BrO}_3^-]_0^{-1.6} [\text{H}_2\text{SO}_4]_0^{-2.7} [\text{MA}]_0^{-0.27} \text{ s (mol dm}^{-3}\text{)}^{4.57}$ . The period is not perfectly constant. We investigate the conditions which favor irregularities: Low concentrations of  $\text{BrO}_3^-$ ,  $\text{H}_2\text{SO}_4$ , or MA; high concentrations of catalyst or reaction products. The irregularities in the period of homogeneous oscillations are of direct interest for our understanding of the formation of waves in the distributed system. Also, we find bifurcations in which a transition from steady state to full-blown oscillations is observed. Such bifurcations may be due to an unstable limit cycle or to a saddle-node transition. We discuss the saddle-node case in terms of the Bautin model. Finally, two steady states are observed. One of them has not been reported previously: In this state, the catalyst is mostly oxidized (blue). The oxidized steady state occurs at low  $[\text{MA}]_0$ . Under the same conditions of low  $[\text{MA}]_0$ , the distributed system exhibits both oxidizing (blue) and reducing (red) waves. This interesting new observation shows how much the ferroin-catalyzed Zhabotinskii system is still underinvestigated.

## I. INTRODUCTION

Oscillations in a mixture of citric acid, bromate, and cerium ions were reported by Belousov in 1959.<sup>1</sup> Zhabotinskii<sup>2</sup> has further investigated these oscillations and demonstrated their occurrence in a number of variations of the basic chemical system involved. Several recent reviews<sup>3-5</sup> discuss in some detail the various possible reactants. For the sake of clarity, we define Zhabotinskii oscillations as the periodic or quasiperiodic changes in concentrations which occur in appropriate mixtures of malonic acid (MA), sulfuric acid ( $\text{H}_2\text{SO}_4$ ), bromate ions ( $\text{BrO}_3^-$ ), and any appropriate catalyst (cerium or manganese ions or ferroin, the tris-1,10-phenanthroline iron complex ions, for instance). In the particular case of the cerium-catalyzed Zhabotinskii reaction, Noyes and Field<sup>6</sup> and several other groups<sup>7-9</sup> have investigated the chemical mechanism. Some real progress has been made towards the understanding of the complex kinetics involved. In contrast, only scant work has been done on the kinetics of the ferroin-catalyzed oscillations.<sup>7,8,10</sup> This is unfortunate since most experimental studies of the Zhabotinskii waves are made on the ferroin-catalyzed system.<sup>11-15</sup> The present work tries to answer some simple questions concerning the period of the ferroin-catalyzed Zhabotinskii oscillations in the case of homogeneous conditions. These questions are important for our understanding of the corresponding chemical waves in the distributed system.

The period of oscillations is related to the chemical mechanism through the rate equations. Therefore, a study of the period as a function of temperature and initial concentrations of reactants should provide a relatively simple test<sup>55</sup> of the validity of a proposed mechanism. It could also be used in order to build a less detailed model for the oscillations. This method has been used by Zhabotinskii and his collaborators in the case of cerium-catalyzed oscillations.<sup>16,17</sup> Since then, the period of homogeneous oscillations has not attracted much attention. The available results show an Arrhe-

nus dependence on temperature for the frequency. The activation energy varies with the catalyst.<sup>18-20</sup> Both cerium- and manganese-catalyzed oscillations have been analyzed in terms of initial concentrations by Rastogi and his collaborators.<sup>18,21</sup> For ferroin-catalyzed oscillations, an earlier report from us<sup>22</sup> compares the experimental period with the period of an exactly soluble model for chemical oscillations, the Bautin system.<sup>23-25</sup> Some disagreement exists between our results and those of Dayantis and Sturm.<sup>10</sup> The first part of our present work gives the quantitative dependence of the ferroin-catalyzed period on initial concentrations of bromate ions, malonic, and sulfuric acids, and catalyst, for a temperature of 24.9°C. This expression can be used to predict the period of bulk oscillation in the distributed system consisting of a thin layer of reacting solution between two flat plates.<sup>26</sup> It is not possible to compare this experimental period with a chemical mechanism since none is available for the ferroin-catalyzed oscillations. But clearly, the mechanisms for ferroin and cerium-catalyzed oscillations do not coincide<sup>57</sup> since the periods show a different dependence on initial concentrations.

The waveforms of the homogeneous oscillations also depend on the initial concentrations. An interesting measure of this influence is given by the oxidized fraction of the period. This quantity is defined as the half-width of the high transmittance peak (at 546 nm) divided by the period. Changes in the oxidized fraction of the period are interesting for two reasons. The first one is the existence of a direct correlation between the oxidized fraction of the period in the homogeneous stirred system and the oxidized fraction of the wavelength in the distributed system.<sup>27</sup> For instance, when malonic acid is in low concentration, one observes the formation of oxidized plateaux in the homogeneous transmittance oscillations and the thickening of the blue wavefronts in the distributed system. The second reason is that a sufficient increase in the oxidized fraction of the period

leads to the appearance of an oxidized steady state. Similarly, a progressive decrease of the oxidized fraction culminates in a reduced steady state. These two bifurcations<sup>28</sup> correspond to transitions between a steady state and finite (large) amplitude, low frequency, relaxation oscillations. The same bifurcations are observed in the distributed system. Striking new spatio-temporal patterns are found when one approaches the oxidized steady-state transition.<sup>27</sup> The possibility of a third bifurcation will be mentioned below. It would be another type of bifurcation, a transition from an intermediate steady state to small amplitude, high frequency, sinusoidal oscillations.

Another important characteristic of the period of oscillations is its instability<sup>22</sup> under various conditions. The oscillations are far more chaotic<sup>29-31</sup> than periodic, near the two bifurcations to finite amplitude oscillations or at relatively high concentration of the catalyst or when the reaction has proceeded for some time. Since chaos and stochastic oscillations cannot be distinguished in this case, we will describe our results in terms of the familiar concept of fluctuations. The period fluctuations might be of great interest as a case of fluctuation chemistry.<sup>32</sup> Furthermore, if the period fluctuations can be as large as observed in the homogeneous system, they ought to be even larger in small volume elements of the distributed system. This might give us a clue concerning the possibility of homogeneous initiation of the centers of wave propagation.<sup>14,26</sup>

## II. EXPERIMENTAL SECTION

Merck 1,10-phenanthroline monohydrate (GR) and iron (II) sulfate heptahydrate (GR) were used to prepare the ferroin solution. (Some commercially available ferroin solutions contain large amounts of chloride ions which make them inappropriate for the Zhabotinskii oscillations.) Merck sulfuric acid (GR), malonic acid (LAB); and Fisher sodium bromate (Fisher certified) were used without further purification. Bromide appears as an impurity in the sodium bromate (max. 0.05% by weight). Bidistilled water was used in all cases. All solutions were filtered before use.

The reacting mixture was prepared by addition of sulfuric acid, malonic acid, and ferroin to sodium bromate at intervals of one minute. Immediately after the last addition, the sample was transferred to a thermostated cuvette in which the temperature was maintained at  $24.9 \pm 0.1^\circ\text{C}$ . At least two minutes before the beginning of the measurements, the stirring was started. Throughout the set of measurements, constant and adequate mixing was provided. The transmittance of the sample at  $546\text{ nm}$ <sup>33</sup> was followed with a recording monochromatic filter photometer (Eppendorf). Ten consecutive periods were recorded. Our observations began four minutes after addition of the last reactant. The first oxidation peak observed thereafter was taken as the beginning of the first period. With ferroin, the oscillations start immediately, without the induction period observed in the equivalent cerium-catalyzed system.<sup>7</sup>

## III. RESULTS

In the strict mathematical sense, a periodic function of period  $T$  is defined as a function for which  $f(t) = f(t + T)$  for all  $t$ 's, with  $T$  constant. Since our observations are made in a batch reactor,<sup>34</sup> the system does not oscillate around a fixed steady state but rather around a so-called quasisteady state of slowly decreasing free energy. Indeed, reactants are consumed, products are formed, and the system slowly approaches equilibrium. This situation excludes truly periodic oscillations. To avoid this problem, as much as possible, our measurements were limited to ten early oscillations. With high frequency oscillations, we can then obtain constant period and amplitude over the time interval of observations. But with smaller frequencies, a second difficulty is encountered. Superposed to the above-mentioned monotonic change, we observe irregular jumps in amplitude and especially in period. Strictly speaking, the oscillations are aperiodic. However, for practical purposes, it is useful to define an average period over  $N$  oscillations as  $\bar{T} = \sum_{i=1}^N T_i$ , with  $N$  small and  $T_i$ , the time interval for the  $i$ th oscillation. One considers each  $|\bar{T} - T_i|/\bar{T}$  as the degree of irregularity in the period of the  $i$ th oscillation. We will see that the degree of irregularity increases with  $\bar{T}$ , with the extent of the reaction, and with the concentration of ferroin.

### A. Period dependence on initial concentrations

We have investigated the effect of the concentrations of bromate ion, sulfuric and malonic acids, and catalyst. The ranges of initial concentrations used are given in Table I. The minimum concentrations used in the cases of bromate ion and malonic acid were determined by the presence of bifurcations to steady states. With low sulfuric acid concentrations, we did not reach a bifurcation. However, the high level of irregularity of the period at low concentrations of sulfuric acid could be explained by the approach of a bifurcation from finite amplitude, low frequency oscillations to a stable steady state.

The period as a function of the initial concentrations of bromate ion, sulfuric acid, and malonic acid is given in Figs. 1-3. Each dot represents the mean period  $\bar{T}$ , averaged over ten consecutive oscillations in a single sample. The limits given for the period correspond to the limits of error of the mean,  $\lambda_m$ .<sup>35</sup> For concentrations, the limits of error are estimated to be 0.5%. Solid lines are obtained by the method of least squares.<sup>35,36</sup> The limits of errors on slope and intercept are determined graphically.<sup>35</sup> The dashed lines correspond to a graphical fit with slope constrained to a given value. Both slope and intercept of the dashed lines are within the error limits of the slope and intercept for the corresponding solid lines.

In Fig. 1, the dependence of the period on the initial concentration of bromate ion is given by (1),

$$T(s) = x[\text{BrO}_3^-]_0^y (\text{mol dm}^{-3})^y s \quad (1)$$

with  $y = 1.6 \pm 0.1$  and  $x = 0.75 \pm 0.15$  [conditions (1) in Table I]. The dashed line is constrained at  $y = 1.5$  and corresponds to  $x = 0.90$ .

TABLE I. Ranges of initial concentrations of bromate ion, sulfuric and malonic acids, and catalyst.

Conditions	$[\text{BrO}_3^-]_0$ (mol dm <sup>-3</sup> )	$[\text{H}_2\text{SO}_4]_0$ (mol dm <sup>-3</sup> )	$[\text{MA}]_0$ (mol dm <sup>-3</sup> )	$[\text{Ferriin}]_0$ (mol dm <sup>-3</sup> )	$\bar{T}$ (s)
(1)	0.0560–0.3410	0.8500	0.08730	$2.270 \times 10^{-3}$	150–4
(2)	0.1820	0.2830–1.416	0.08730	$2.270 \times 10^{-3}$	290–2.7
(3)	0.1820	0.7080	0.0130–0.3500	$2.270 \times 10^{-3}$	29–10
(4)	0.1820	0.5660	0.08730	$4.500 \times 10^{-4}$ – $4.500 \times 10^{-3}$	17–43

Temperature =  $24.9 \pm 0.1^\circ\text{C}$ . Constant stirring.

For (1) and  $[\text{BrO}_3^-]_0 < 0.0560$  mol. dm<sup>-3</sup>,  $\bar{T} > 3600$  s (reduced)

For (2) and  $[\text{H}_2\text{SO}_4]_0 < 0.1420$  mol. dm<sup>-3</sup>,  $\bar{T} > 5400$  s (reduced)

For (3) and  $[\text{MA}]_0 < 0.0040$  mol. dm<sup>-3</sup>,  $\bar{T} = \infty$  (oxidized)

Figure 2 shows the dependence on sulfuric acid (2),

$$T(s) = x[\text{H}_2\text{SO}_4]_0^y (\text{mol dm}^{-3})^y s \quad (2)$$

with  $y = 2.7 \pm 0.2$  and  $x = 7.03 \pm 0.07$  [conditions (2) in Table I]. The dashed line is constrained at  $y = 2.5$  and corresponds to  $x = 7.03$ .

The period dependence on the initial concentration of malonic acid is shown in Fig. 3. We obtain Eq. (3),

$$T(s) = x[\text{MA}]_0^y (\text{mol dm}^{-3})^y s \quad (3)$$

with  $y = 0.27 \pm 0.05$  and  $x = 8 \pm 1$  [conditions (3) in Table

I]. A line constrained to  $y = 0.25$  would be almost superposed to the one shown. Equation (3) cannot be extrapolated for concentrations of malonic acid below  $0.0100$  mol dm<sup>-3</sup>. This is because for these very low concentrations the "period"  $T_i$  shows a significant increase from one oscillation to the next. It might be due to an excessive decrease in the concentration of malonic acid within one oscillation.

The above results can be summarized in the general expression (4),

$$T(s) = 0.22 [\text{BrO}_3^-]_0^{1.6} [\text{H}_2\text{SO}_4]_0^{2.7} \times [\text{MA}]_0^{0.27} (\text{mol dm}^{-3})^{4.57} s \quad (4)$$

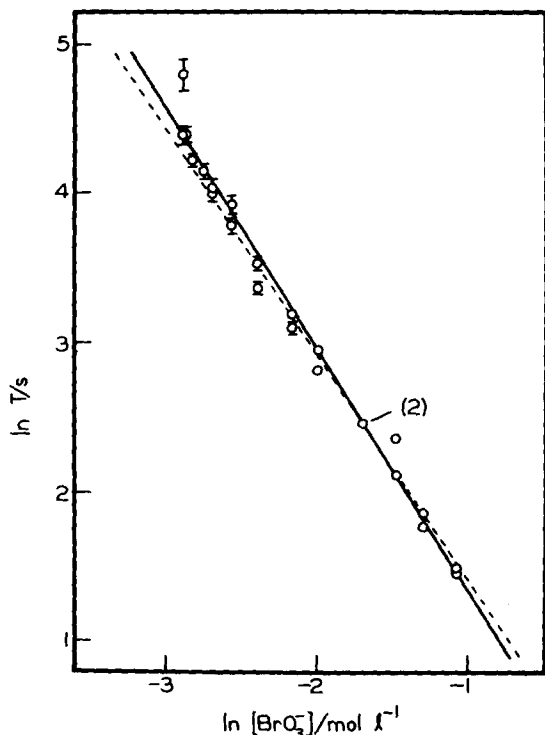


FIG. 1. Period as a function of the initial concentration of sodium bromate. Initial concentrations of other reactants: conditions (1) in Table I. Dots represent mean period, averaged over 10 successive oscillations. Limits are estimated error of the mean. Solid line: slope =  $-1.6$ . Dashed line: slope constrained at  $-1.5$ .

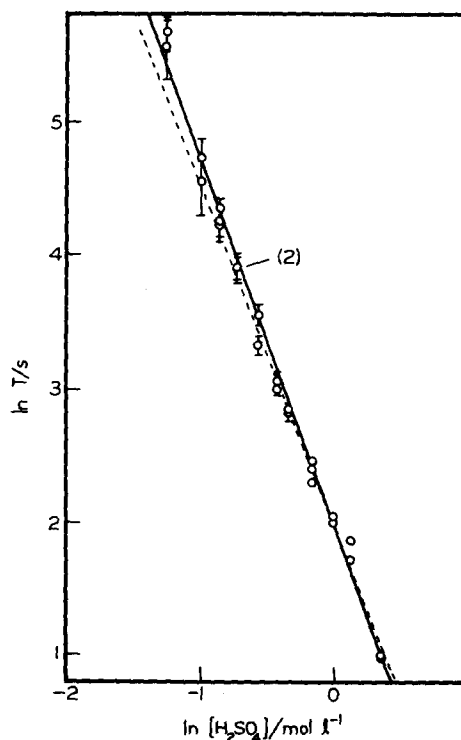


FIG. 2. Period as a function of the initial concentration of sulfuric acid. Initial concentrations of other reactants: conditions (2) in Table I. Dots and limits as in Fig. 1. Solid line: slope =  $-2.7$ . Dashed line: slope constrained at  $-2.5$ .

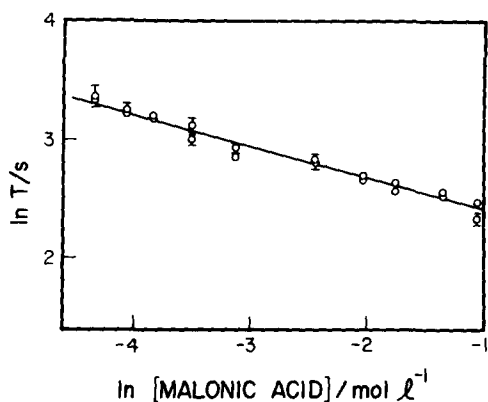


FIG. 3. Period as a function of the initial concentration of malonic acid. Initial concentrations of other reactants; conditions (3) in Table I. Dots and limits as in Fig. 1. Slope = -0.27.

with  $[\text{Ferroin}]_0 = 2.27 \times 10^{-3} \text{ mol dm}^{-3}$  and  $\text{Temp.} = 24.9 \pm 0.1^\circ\text{C}$ . The validity of Eq. (4) is established by plotting together all data obtained with the appropriate catalyst concentration and temperature. Our results are shown in Fig. 4. A least square fit gives a slope of -1.02 for the combined 64 measurements.

The period dependence on the initial concentration of catalyst<sup>56</sup> is given in Fig. 5. For the range of concentrations investigated [conditions (4), Table I], we have the linear relationship (5)

$$T(s) = 16.4 \text{ s} + 4490 (\text{s mol}^{-1} \text{ dm}^3) [\text{Ferroin}]_0. \quad (5)$$

The data also show a decrease in the stability of the average period with an increase in the catalyst concentration, all other factors being constant. We will return to this question later.

### B. Oxidized fraction of the period and bifurcations<sup>28</sup>

Our transmittance measurements were made at a wavelength of 546 nm. At this wavelength, an increase in transmittance corresponds to the oxidation of ferroin (deep red) into ferriin (pale blue). Indeed, the tris-

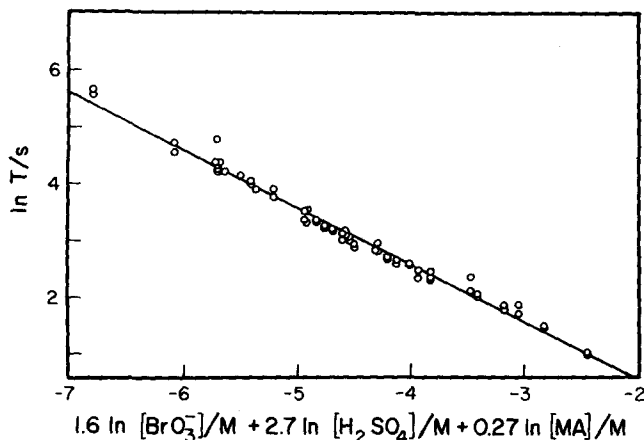


FIG. 4. Period as a function of the initial concentrations of sodium bromate, sulfuric acid, and malonic acid. Verification of Eq. (4). Slope = -1.02 (see text).

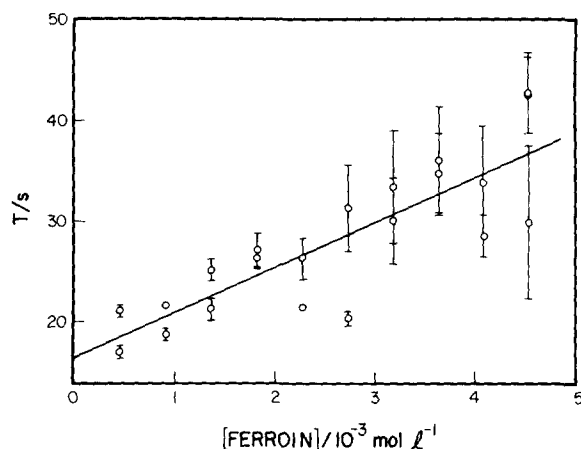


FIG. 5. Period as a function of the initial concentration of ferroin. Initial concentrations of other reactants; conditions (4) in Table I. Dots and limits as in Fig. 1. Slope = 4.490.

1,10-phenanthroline iron (II) complex, called ferroin, has an absorption maximum at  $\lambda_{\text{max}} = 510 \text{ nm}$ ,<sup>33</sup> with molar absorptivity of  $11\,100 \text{ units dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . In contrast, the iron (III) complex, called ferriin, has an absorption maximum at  $\lambda_{\text{max}} = 590 \text{ nm}$ , with molar absorptivity of  $600 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .<sup>33</sup>

Figure 6 represents three waveforms for different concentrations of sulfuric acid, with conditions (2) in Table I. From top to bottom,  $[\text{H}_2\text{SO}_4]_0 = 0.2830, 0.5660,$  and  $1.416 \text{ mol dm}^{-3}$ . The corresponding average periods are 289.08, 34.94, and 2.66 s. Because of the large differences in periods, two time scales had to be used, with a fivefold scale reduction for the upper part of Fig. 6. With increasing periods, one observes clear increases in the relaxational<sup>28,31</sup> character of the oscillations and in the oxidized fraction of the period. For sufficiently low  $[\text{H}_2\text{SO}_4]_0$ , we anticipate a switch from high amplitude, small frequency oscillations to a reduced steady state. On the other hand, for  $[\text{H}_2\text{SO}_4]_0$  sufficiently high, we expect a transition between low ampli-

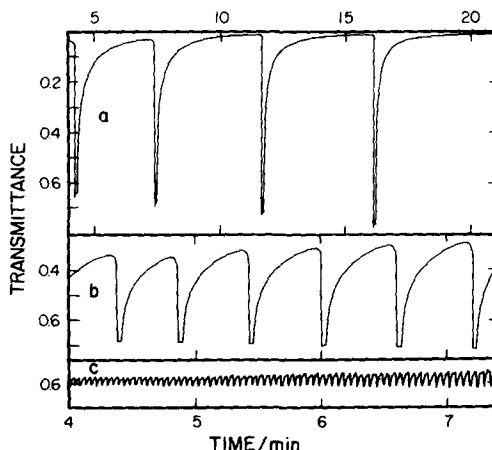


FIG. 6. Influence of the initial concentration of sulfuric acid on the transmittance oscillations at  $\lambda = 546 \text{ nm}$ . From top to bottom:  $[\text{H}_2\text{SO}_4]_0 = 0.2830, 0.5660,$  and  $1.416 \text{ mol dm}^{-3}$ . With  $\bar{T} = 289.08, 34.94,$  and  $2.66 \text{ s}$ . Other initial concentrations; conditions (2) in Table I.

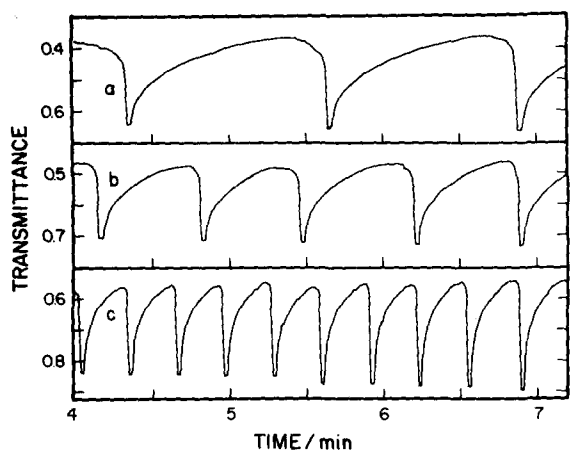


FIG. 7. Influence of the initial concentration of bromate on the transmittance oscillations at  $\lambda = 546$  nm. From top to bottom:  $[\text{BrO}_3^-]_0 = 0.05690, 0.07730, \text{ and } 0.1360 \text{ mol dm}^{-3}$ , and  $\bar{T} = 80.8, 43.4, \text{ and } 19.1$  s. Other initial concentrations: conditions (1) in Table I.

tude, high frequency oscillations, and an intermediate steady state. In this intermediate state, the iron complex will be neither fully oxidized nor fully reduced and the transmittance will be close to the average transmittance in the oscillations of Fig. 6(c).

Figure 7 shows the changes in waveform due to a change in the initial concentration of bromate, with conditions (1) in Table I. We have, from top to bottom,  $[\text{BrO}_3^-]_0 = 0.05960, 0.07730, \text{ and } 0.1360 \text{ mol dm}^{-3}$ . With a decrease in  $[\text{BrO}_3^-]_0$ , we observe an increase in the relaxational character of the waveform and a decrease in the oxidized fraction of the period. High  $[\text{BrO}_3^-]_0$  produces quasisinusoidal, low amplitude oscillations which suggest the approach of a bifurcation to an intermediate steady state, like in the case of sulfuric acid. The other bifurcation, at low  $[\text{BrO}_3^-]_0$ , corresponds to a transition

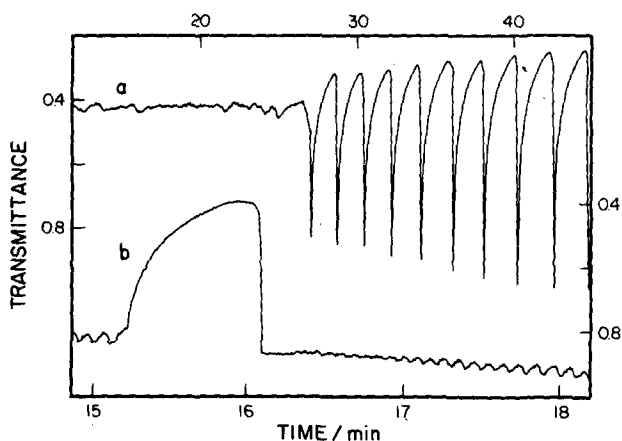


FIG. 8. Transitions between steady states and oscillations in bifurcation regions. (a) *Low bromate concentration*:  $[\text{BrO}_3^-]_0 = 55.90 \times 10^{-3} \text{ mol dm}^{-3}$ . (Other conditions as in Fig. 1.) Reduced steady state. (Use left and top coordinate axes). (b) *Low malonic acid concentration*:  $[\text{MA}]_0 = 7.850 \times 10^{-3} \text{ mol dm}^{-3}$ . (Other conditions as in Fig. 3 except for  $[\text{H}_2\text{SO}_4]_0 = 0.4250 \text{ mol dm}^{-3}$ ). Oxidized steady state. (Use right and bottom coordinate axes).

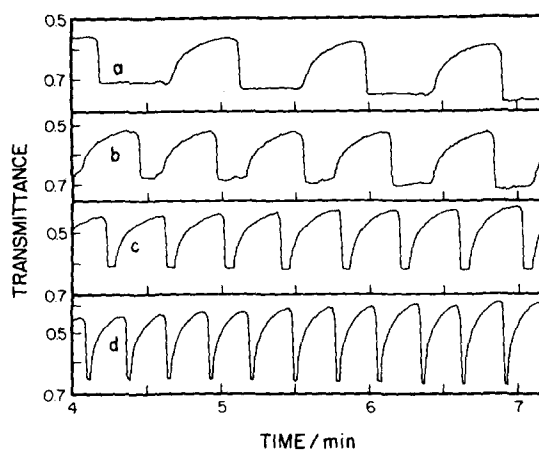


FIG. 9. Influence of the initial concentration of malonic acid on the transmittance oscillations at  $\lambda = 546$  nm. From top to bottom:  $[\text{MA}]_0 =$  (a)  $6.110 \times 10^{-3}$ , (b)  $8.730 \times 10^{-3}$ , (c)  $21.80 \times 10^{-3}$ , and (d)  $87.30 \times 10^{-3} \text{ mol dm}^{-3}$ .  $\bar{T} =$  (a) 60.0, (b) 43.7, (c) 24.6, and (d) 16.9 s. Other concentrations: conditions (3) in Table I.

from large amplitude oscillations to a reduced steady state. An example is shown in Fig. 8(a), with  $[\text{BrO}_3^-]_0 = 0.05590 \text{ mol dm}^{-3}$  and conditions (1) in Table I. The complete series of events is as follows: A first oxidation occurs two minutes after the start of the reaction; the system then returns to a reduced state in which the transmittance is almost constant (at 0.42); after 12 min, the steady state becomes increasingly sensitive to noise; a complete destabilization occurs at  $t = 27$  min with the start of large amplitude oscillations; after 19 oscillations of increasingly irregular period, the system reaches its final reduced steady state (transmittance  $\sim 0$ ). The same qualitative behavior is observed for other trials under the same conditions. However, there is no quantitative reproducibility of the exact time at which the transition between steady and oscillatory state occurs. The bifurcation region is fairly well defined in terms of bromate concentrations. At slightly higher bromate concentrations ( $0.05680 \text{ mol dm}^{-3}$ ), the oscillatory state is the stable state, and large amplitude oscillations are observed immediately after mixture of the reactants. But at slightly lower concentrations ( $0.05450 \text{ mol dm}^{-3}$ ), it is the steady state which is stable. After a first oxidation, the system reaches a reduced steady state which shows irregular transmittance fluctuations but does not switch to a large amplitude oscillatory state.

Figure 9 indicates the effect of initial concentrations of malonic acid. The conditions (3) of Table I are used except that we allow lower values for  $[\text{MA}]_0$ . From top to bottom,  $[\text{MA}]_0 = 6.110 \times 10^{-3}, 8.730 \times 10^{-3}, 21.80 \times 10^{-3}$ , and  $87.30 \times 10^{-3} \text{ mol dm}^{-3}$ . A decrease in  $[\text{MA}]_0$  increases the oxidized fraction of the period.<sup>38</sup> For sufficiently low values of  $[\text{MA}]_0$ , a new bifurcation occurs. It is again a transition between large amplitude oscillations and steady state, but in this case it is an oxidized steady state. The bifurcation is illustrated in Fig. 8(b). The conditions are still given by (3) in Table I, except for  $[\text{H}_2\text{SO}_4]_0 = 0.4250 \text{ mol dm}^{-3}$  and  $[\text{MA}]_0 = 7.850 \times 10^{-3} \text{ mol dm}^{-3}$ . The reduction burst shown in Fig. 8(b) is the

fifth and last burst observed. Between bursts, the system remains in an oxidized state. For a while, this state is stable. Later, there is a sudden increase in noise. The noise observed around the oxidized steady state resembles undamped, low amplitude, high frequency oscillations. Since these oscillations are observed near a bifurcation from steady state to large amplitude oscillations, one could think that a hard excitation<sup>28</sup> is taking place. This would be a hasty conclusion since we measure only one variable, the transmittance of the system. We lack information concerning the relative location of the steady state and the periodic trajectory in phase space. We return to this point in the discussion below.

### C. Instability of the period. Fluctuation chemistry<sup>32</sup>

In the ferroin-catalyzed system, under batch reactor conditions, at least two conditions must be met in order to obtain a stable, reproducible period of oscillations. First, the initial concentrations of malonic acid, sulfuric acid, and bromate ions must each be relatively high. Second, the concentration of catalyst must be relatively low. A possible third condition will be discussed below. It involves the concentration of products.

The first condition is given a quantitative expression in Figs. 1–3. Indeed, the error limits are a measure of the irregularity in the period of ten consecutive oscillations. Note that the logarithmic scale tends to minimize the importance of the irregularities. Furthermore, the present work was done in order to obtain an expression for the period such as Eq. (4). For this reason, we avoided the regions of highest irregularity where the concept of period definitively loses any meaning. Such regions occur, for instance, near the bifurcations to the reduced or the oxidized steady states. If we combine the conditions of low  $[MA]_0$  and low  $[H_2SO_4]_0$ , the irregularities are amplified by the conflicting bifurcations: Low  $[MA]_0$  stabilizes the oxidized steady state and low  $[H_2SO_4]_0$  stabilizes the reduced one. If bistability exists in the ferroin-catalyzed system, it will occur in such a region.

The second condition for stability of the period is that the concentration of catalyst be low. Figure 5 shows the destabilization of the period due to an increase in the catalyst concentration. We remember that each dot corresponds to an average period for ten oscillations. The error limits show the magnitude of the irregularities in period. Although there is generally an overall increase in period between the first and last oscillations in the series of ten, the increase is by no means monotonic. This is illustrated in Fig. 10. Figures 10(a) and 10(c) correspond to  $[Ferroin]_0 = 2.27 \times 10^{-3}$  mol dm<sup>-3</sup>. Figures 10(b) and 10(d) correspond to  $[Ferroin]_0 = 4.54 \times 10^{-3}$  mol dm<sup>-3</sup>. On the right, Figs. 10(c) and 10(d) give the simple sequence of periods ( $T_i$ 's). The low concentration case [Fig. 10(c)] shows a relatively stable period around 21 s while the high concentration case [Fig. 10(d)] indicates an unstable period with apparently random jumps from a lower value around 25 s to a higher value around 42 s. Because the jumps in the high concentration case [Fig. 10(d)] do not alternate regularly,

this is not an example of double periodicity<sup>39</sup> as observed in the glycolytic oscillations. On the left side of Fig. 10, the same results are plotted in a different representation: The  $(n+1)$ th period vs the  $n$ th one. This transition function is used in chaos theory.<sup>29–31</sup> In this representation, a stable period gives a single point on the diagonal, while double periodicity gives two points symmetric with respect to the diagonal. As its name indicates, the transition function emphasizes the jumps in chaotic oscillations. There are no jumps when the points are located on the diagonal. The points on the left of the diagonal indicate jumps with  $T_{n+1} > T_n$ . The points on the right of the diagonal correspond to jumps with  $T_n > T_{n+1}$ . We see that jumps in period are large and frequent for high catalyst concentrations.<sup>40</sup>

A possible third stability condition is that the concentrations of the products of reaction should remain low. Or, for batch reactor conditions, the reaction should not have proceeded for a long time. Indeed, the period irregularities increase with the duration of the reaction. However, in the course of reaction, formation of products is paralleled by consumption of reactants. In the ferroin-catalyzed reaction, there is a progressive decrease in  $[MA]$  and  $[BrO_3^-]$  and thus a progressive breakdown of the first stability condition (see above). Since we have not isolated the effects of product formation from the effects of reactant consumption, the third stability condition remains tentative and requires further investigation.

## IV. DISCUSSION

The period and waveform of the ferroin-catalyzed oscillations depend on the initial concentrations of reactants. This result is not surprising if one assumes that these oscillations are of the limit cycle type. In "chemical" limit cycles, the period and waveform are independent of the initial concentrations of the oscillatory intermediates but depend on some constrained concentrations and temperature. For instance, in the Bautin limit cycle (Appendices), the period (A5) and waveform (A2) are independent of  $X(0)$  and  $Y(0)$  but they depend on the parameters  $a$ ,  $E_1$ , and  $E_2$  in the rate equations (A1). In the ferroin-catalyzed system, under batch conditions, no concentrations are truly constrained. However, in first approximation, the initial concentrations of  $BrO_3^-$ ,  $H_2SO_4$ ,  $MA$ , and catalyst<sup>56</sup> play the role of fixed parameters. Their control over the period and waveform of the ferroin-catalyzed oscillations is thus in good agreement with the assumption of limit cycle oscillations.

It is instructive to compare the periods of the Zhabotinskii oscillations for various catalysts. In the ferroin-catalyzed oscillations, the period is given by

$$T(s) = C [BrO_3^-]_0^{1.6} [H_2SO_4]_0^{-2.7} [MA]_0^{-0.27} s \text{ (mol dm}^{-3}\text{)}^{4.57}.$$

For cerium, Rastogi and Yadava<sup>21</sup> have found that the period depends on  $[MA]_0$  as

$$T(s) = C'(s) + C''[MA]_0^{1.0} s \text{ (mol dm}^{-3}\text{)}.$$

They report only an unspecified inverse relationship between period and initial concentrations of bromate and

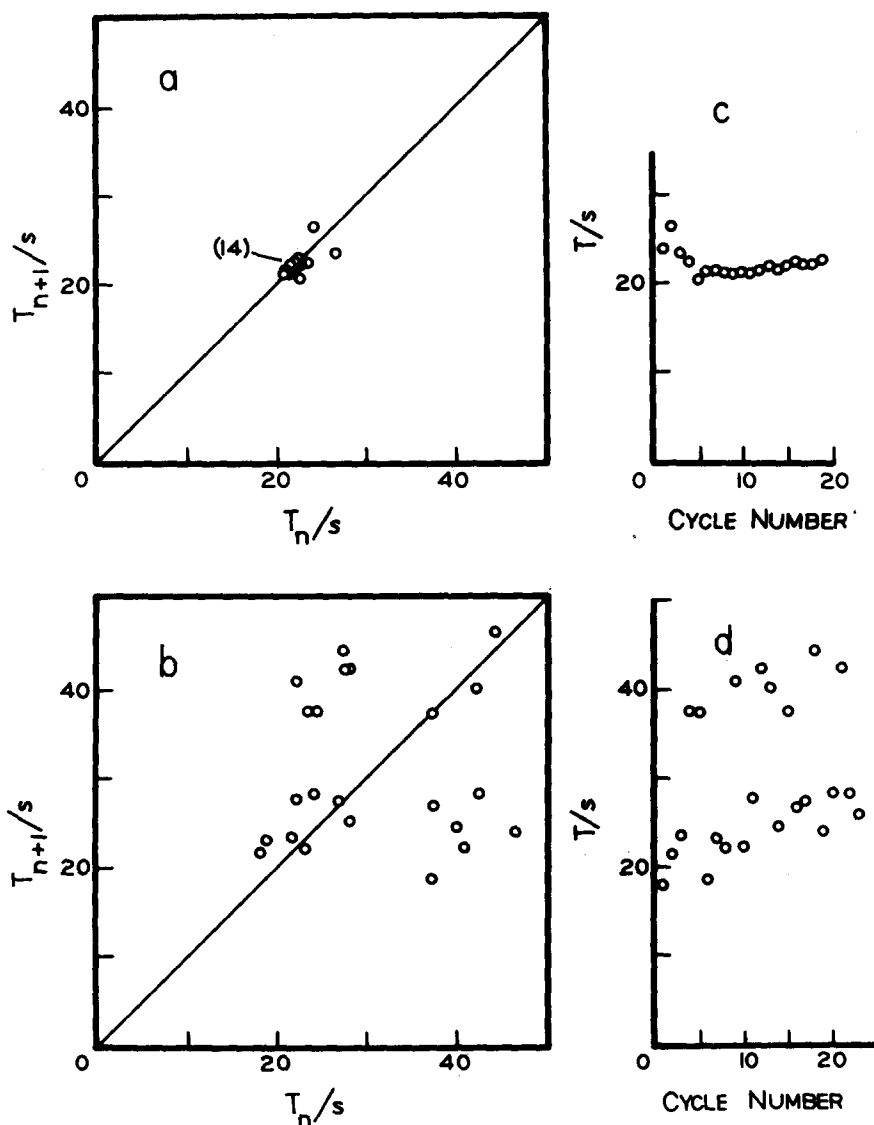


FIG. 10. Transition function:  $(n+1)$ th period as a function of  $n$ th period. Concentrations and temperatures as in Fig. 5. (a) and (c):  $[\text{Ferroin}]_0 = 2.270 \times 10^{-3} \text{ mol dm}^{-3}$ . (b) and (d):  $[\text{Ferroin}]_0 = 4.540 \times 10^{-3} \text{ mol dm}^{-3}$ . See text.

sulfuric acid. The same authors<sup>18</sup> found that for manganese

$$T(s) = C''' [\text{BrO}_3^-]_0^{-0.5} [\text{H}_2\text{SO}_4]_0^{-1.0} [\text{MA}]_0^{-0.5} \text{ s (mol dm}^{-3})^{2.0}.$$

In view of these differences, we may expect some differences<sup>57</sup> in the mechanisms for cerium, manganese, and ferroin-catalyzed oscillations. Further evidence is provided by the difference in energy of activation for the frequencies obtained with these three catalysts. For cerium and manganese,<sup>20</sup> the activation energy is 67.5 kJ mol<sup>-1</sup> while it is 100 kJ mol<sup>-1</sup> for ferroin.<sup>19</sup> Moreover, the ferroin-catalyzed oscillations do not show an induction period<sup>7</sup> for conditions in which the cerium-catalyzed oscillations do. Finally, Körös and his collaborators have shown a difference in the heat produced per period with various catalysts.<sup>7</sup> Noyes has made some predictions concerning the difference in critical values of bromide ions in the cerium and ferroin systems.<sup>41</sup> To our knowledge, there has been no verification yet. In fact, the ferroin system is surprisingly underinvestigated in view of its interest for the understanding of the ferroin-catalyzed waves. The fact that ferroin decomposes<sup>8</sup> slowly is often used as a justifica-

tion for this neglect. But the decomposition could be taken into account as part of the global mechanism since decomposition is just another chemical process.

Besides the effect of the slow decomposition of ferroin, several other effects remain to be investigated. One of them is the effect of the products. Another one is the alleged oxygen effect. Oxygen has been mentioned as preventing oscillations and maintaining the system in an "excitable"<sup>42</sup> reduced state. The stirring effect should also be investigated. It must be uncoupled from the oxygen effect.<sup>43</sup> One of the effects related to the stirring is due to the spontaneous desynchronization of the oscillations occurring in various volume elements of the system.<sup>27</sup> This desynchronization can explain the damping of transmittance oscillations when stirring is inadequate.<sup>4</sup> It remains unclear if there is any genuine effect of the rate of stirring on the period. To conclude, let us mention that the origin of the large fluctuations in period is still an open question.

In the three-dimensional parameter space with coordinate axes  $[\text{BrO}_3^-]_0$ ,  $[\text{H}_2\text{SO}_4]_0$ , and  $[\text{MA}]_0$ , the oscillation domain is a three-dimensional volume. We have only

analyzed the behavior of the system along a few lines parallel to the coordinate axes (see Table I). The bifurcations described in our results correspond to the intersections of three such lines with the surface bounding the domain of stable oscillations. It would be helpful to map the bifurcation surface more completely in order to clarify the dynamic behavior of the ferroin-catalyzed system. However, the information available is already interesting in several respects. The first result of interest concerns the transition from steady state to finite, full-blown (rather than infinitesimal) amplitude oscillations. This type of transition may correspond to various types of dynamic behavior in phase space. We can distinguish at least two groups. In the first one, the steady state is separated from, and surrounded by the periodic trajectory. In a two-dimensional phase space, this corresponds to a hard excitation and an unstable limit cycle surrounded by a stable one. For the second group, the steady state is located on the trajectory. It disappears to give rise to the periodic behavior. In the two-dimensional phase space this corresponds to a saddle-node transition. The hard excitations, with unstable limit cycle are familiar but the possibility of a saddle-node transition is apparently never mentioned in the chemical literature. A topological description of the saddle-node transition is given by Andronov *et al.*<sup>23</sup> and an interesting analytical example arises in the asymmetric Bautin system (Appendix B). We believe that a clear understanding of the dynamic difference between unstable limit cycle transition and saddle-node transition in two-dimensional phase space can help understand these two groups of transitions in higher-dimensional phase space. This, in turn, should lead to the appropriate investigation of the nature of the transition observed in the ferroin-catalyzed Zhabotinskii system. A first conclusion that can be drawn is that as many variables as possible should be measured simultaneously in order to obtain the relative positions of the periodic trajectory and the steady states. The one variable measurements of Graziani *et al.*<sup>44</sup> are certainly interesting but a many variables study would be more fruitful.

Another interesting point is that we have found two distinct steady states from which finite amplitude oscillations bifurcate: a reduced state for low  $[\text{BrO}_3^-]_0$  and for low  $[\text{H}_2\text{SO}_4]_0$ , and an oxidized state for low  $[\text{MA}]_0$ . We have not yet observed bistability, the simultaneous stability of reduced and oxidized steady states, in the ferroin-catalyzed system. However, it is likely that the combination of low  $[\text{BrO}_3^-]_0$  (and/or low  $[\text{H}_2\text{SO}_4]_0$ ) with low  $[\text{MA}]_0$  will produce a bistable system. Bistability has been reported in cerium-catalyzed systems under flow conditions.<sup>43</sup> With cerium, bistability occurs at low  $[\text{MA}]_0$  and low  $[\text{BrO}_3^-]_0$ . In the ferroin-catalyzed system, the existence of a reduced steady state has been known for some time.<sup>5,42</sup> But the low  $[\text{MA}]_0$  steady state and its bifurcation to finite amplitude oscillations have not been reported previously.<sup>45</sup> The observation of this new oxidized steady state is of great interest in terms of the corresponding chemical waves occurring in the distributed ferroin-catalyzed system. At low  $[\text{MA}]_0$ , we have found that both blue and red centers can occur in the distributed system. To the blue centers correspond

oxidizing waves and to the red centers, reducing waves. The speeds of propagation of oxidizing and reducing waves are not equal. The blue (oxidizing) waves move faster but they decelerate when they approach the red (reducing) wave fronts from behind. We have summarized our preliminary observations elsewhere<sup>27</sup> and a detailed publication is in preparation.

In the years preceding the application of chaos theory<sup>29</sup> to chemical oscillations,<sup>46</sup> there were surprisingly few reports of period irregularities<sup>13,17,22,47</sup> in the literature. The only theoretical models available were of the limit cycle type. As a result, perfect reproducibility of the period was expected (erroneously, as will be shown below). The rise of chaos theory has encouraged the reporting of, and search for, irregularities. Reports of chaos in the ferroin<sup>48</sup>- and manganese<sup>49</sup>-catalyzed Zhabotinskii system and in the horseradish peroxidase<sup>30</sup> oscillations have appeared recently. A common feature of these experiments is that they involve a continuous stirred tank reactor (CSTR).<sup>34</sup> Unfortunately, this raises the possibility of coupling between trivial oscillations<sup>50</sup> (due to the CSTR process itself) and intrinsic oscillations (due to the chemical rate equations). Recent work by Gollub *et al.*<sup>51</sup> indicates that coupling of two nonlinear oscillators may result in chaotic oscillations. The present work is done under batch reactor conditions and the possibility of chaos due to trivial oscillations is thus eliminated. We find that the period is sometimes quite irregular, but the irregularities do not fit a well-defined cap-shaped transition function.<sup>30</sup> On the contrary, in most cases the period irregularities appear random except for the general increase in period with time due to consumption of the reactants. If we are dealing with chaos, it is thus the type of chaos which cannot be distinguished from a random stochastic process.

As we have just mentioned, one cannot generally expect period reproducibility in oscillations of the limit cycle type. In particular, if an orbitally stable limit cycle lacks asymptotic and structural stability, the oscillations may show various degrees of irregularity in their period. This is due to the effect of random fluctuations in the physical variables and parameters describing the system. The very interesting experiments of Blandamer and Roberts<sup>52</sup> indicate that the cerium-catalyzed oscillations have the combined properties of orbital stability and asymptotic and structural instabilities. Our own experiments indicate that the ferroin-catalyzed oscillations have the same general stability characteristics. Other oscillatory systems, such as the glycolytic oscillations<sup>58</sup> exhibit the same stability properties. Indeed, most oscillatory chemical mechanisms give rise to asymptotic and structural instabilities, and thus to period irregularities.

In order to illustrate the meaning of these various types of stability and the reason why fluctuations in concentrations and temperature can bring about the period irregularities, any limit cycle with asymptotic and structural instabilities will be adequate. Because the symmetric Bautin limit cycle has the powerful property of being analytically soluble, besides having the required



stability characteristics, it is a most appropriate model for our discussion here. This limit cycle corresponds to the rate equations (A1) in Appendix A. Consider the solution (A2). For  $(E_2 + E_1) > 0$ , the exponential term in the denominator of  $X$  disappears in the asymptotic limit. Since this term is the only one containing  $X(0)$ , the asymptotic value of  $X(t)$  is independent of its initial value. Hence, the periodic trajectory possesses orbital stability.<sup>28</sup> However, there is no asymptotic stability in the sense of Liapounov.<sup>28</sup> The relationship (A3) establishes a dependence between  $\phi(t)$ , the instantaneous phase, and  $C_0$ . But  $C_0$  depends on the initial value of the phase,  $\phi(0)$ , as shown in (A4). Since  $\phi(t)$  depends on  $\phi(0)$ , there is no asymptotic stability. There is also a lack of structural stability.<sup>28</sup> Indeed, the Bautin system has an infinity of limit cycles (and phase planes) corresponding to as many values of the parameters  $a$ ,  $E_1$ , and  $E_2$ . Each individual cycle and its period are unstable with respect to perturbation of any of these three parameters. If a parameter varies continuously with time, the system slips continuously from one trajectory to the next (in a different phase plane). This behavior differs from the Volterra-Lotka<sup>32</sup> instability since the latter involves perturbations of the oscillatory intermediates,  $X(0)$ ,  $Y(0)$ , in a fixed phase plane (orbital instability). The consequences of structural and asymptotic instability in terms of period irregularities are clear when one writes the period as below.

$$T = \int_{\phi_0}^{\phi_0 + 2\pi} \frac{dt}{d\phi} d\phi.$$

In the Bautin system, if  $C_0$ ,  $a$ ,  $E_1$ , and  $E_2$  are fixed,  $T$  is given by (A5). However, almost any time-dependent perturbation of one of these four parameters will destroy the strict periodicity of the oscillations and introduce period irregularities. The example of the Bautin limit cycle shows that the period irregularities observed in the ferroin-catalyzed Zhabotinskii oscillations do not preclude the use of limit cycle models for such oscillations.

## V. CONCLUSION

The above results are far from complete. They are mostly an indication of some interesting avenues for further research. If we want to understand the waves occurring in the ferroin-catalyzed Zhabotinskii system, it may no longer be satisfactory to study only the cerium-catalyzed system. We should be aware of the differences between these two systems, not so much in terms of their chemical mechanisms<sup>57</sup> as in terms of their phase space trajectories and bifurcation spaces. It would be interesting to try to answer the questions raised by the bifurcations from steady state to finite amplitude oscillations. Do they indicate an unstable limit cycle, a saddle-node transition or still something else? This requires simultaneous measurement of several oscillatory intermediates in order to obtain a phase

space representation of the system trajectory. The period irregularities in the oscillatory state and the sensitivity of the steady states to perturbations deserve further attention. They could provide information concerning the centers of propagating waves in the distributed system. For instance, is there a possibility of spontaneous, homogeneous, localized "ignition" at the centers? But the most interesting result is the existence of an oxidized steady state at low concentration of malonic acid. Its discovery had led us to a variety of new results in the distributed system. The central new fact is the existence of both oxidizing and reducing waves. It opens up a wealth of new properties of the chemical waves.

## ACKNOWLEDGMENTS

Part of this work was done at the Max Planck Institute (Ernährungsphysiologie) in Dortmund, West Germany. I am very grateful to Professor T. M. Dunn and the Chemistry Department at the University of Michigan for their hospitality and support.

## APPENDIX A: SOME PROPERTIES OF THE SYMMETRIC BAUTIN SYSTEM<sup>23-25,28</sup>

The Bautin system (A1)

$$\frac{dX}{dt} = aY + E_1X - X^3 - XY^2 \quad (\text{A1})$$

$$\frac{dY}{dt} = -aX + E_2Y - Y^3 - YX^2$$

is soluble in closed form and exhibits a number of interesting dynamic properties such as limit cycle oscillations and bistability. The Bautin bifurcations include amongst others a transition from bistability to low frequency, finite amplitude, relaxation oscillations, and a transition from stable focus to high frequency, small amplitude, sinusoidal oscillations. This Appendix summarizes the results of interest for our discussion of the ferroin-catalyzed Zhabotinskii system.

$X'$ ,  $Y'$ , the concentrations of intermediates defined by

$$X' \equiv X + X_c \quad \text{and} \quad Y' \equiv Y + Y_c$$

will always be positive<sup>23</sup> if

$$E_1 < X_c^2 - \frac{a^2}{4X_c^2} \quad \text{and} \quad E_2 < Y_c^2 - \frac{a^2}{4Y_c^2}$$

and  $X'(0)$ ,  $Y'(0)$  are positive. At  $X' = X_c$ ,  $Y' = Y_c$ , a singularity exists for all possible values of the parameters  $a$ ,  $E_1$ ,  $E_2$ . This singularity is located at the origin of the coordinate system of the excess concentrations  $X$ ,  $Y$ .

For  $(E_2 + E_1) > 0$ , there is a limit cycle if  $|E_2 - E_1| < |2a|$ . The waveform<sup>25</sup> (A2) becomes periodic in the infinite time limit.

$$\lim_{t \rightarrow \infty} X(t) = \lim_{t \rightarrow \infty} \left\{ \frac{\cos(C_0 - az_2 t)}{\alpha_1 + \beta_1 \cos(2C_0 - 2az_2 t) + \gamma_1 \sin(2C_0 - 2az_2 t)} \right\}^{1/2} \cdot \left\{ + ((\cos^2 C_0 / X^2(0)) - \alpha_1 - \beta_1 \cos(2C_0) - \gamma_1 \sin(2C_0)) \exp(-(E_2 + E_1)t) \right\} \quad (\text{A2})$$

The phase is given by (A3). It is not a linear function of time, in general:

$$\phi(t) = \tan^{-1}(Y/X) = \tan^{-1}(z_1 + z_2 \tan(C_0 - az_2 t)) \neq \frac{2\pi}{T} t. \quad (\text{A3})$$

The various parameters are defined in (A4).

$$\begin{aligned} C_0 &\equiv \tan^{-1}((\tan\phi(0) - z_1)/z_2) \\ z_1 &\equiv (E_2 - E_1)/2a \\ z_2 &\equiv (1 - z_1^2)^{1/2} \\ \alpha_1 &\equiv 2/(E_2 + E_1) \\ \beta_1 &\equiv z_1(z_1 E_1 + a)/(E_2 E_1 + a^2) \\ \gamma_1 &\equiv z_1 z_2 E_1/(E_2 E_1 + a^2). \end{aligned} \quad (\text{A4})$$

The waveform (A2) corresponds to relaxation oscillations when  $|z_1| \rightarrow 1$  and to harmonic oscillations when  $|z_1| \rightarrow 0$ .<sup>23</sup> The amplitude grows with an increase in  $(E_2 + E_1)$ .<sup>25</sup> The period

$$T = \frac{4\pi}{(4a^2 - (E_2 - E_1)^2)^{1/2}} \quad (\text{A5})$$

is infinite for  $|z_1| = 1$  (transition to bistable regime). It reaches a maximum of  $2\pi/a$  for  $z_1 = 0$ .

For  $(E_2 + E_1) > 0$  but  $|E_2 - E_1| > |2a|$ , the symmetric Bautin system is bistable. The transition between bistability ( $|z_1| > 1$ ) and limit cycle ( $|z_1| < 1$ ) is of interest for our discussion of the present work. In the transition region, the bistable Bautin system possesses five singularities.<sup>23,28</sup> For  $a > 0$ , there are two stable nodes at a distance

$$R_0^* = (a(z_1 + z_3) + E_1)^{1/2}$$

from the origin, on the separatrix<sup>28</sup> through the origin defined by

$$\tan\phi_0^* = z_1 + z_3$$

with  $z_3 \equiv iz_2$  ( $z_2$  is imaginary in the bistable region). The origin is an unstable node and there are two saddle points at a distance

$$R_0^- = (a(z_1 - z_3) + E_1)^{1/2}$$

from the origin, along the separatrix through the origin

$$\tan\phi_0^- = z_1 - z_3.$$

The transition to limit cycle occurs for  $|z_1| = 1$ , by fusion of the separatrices and their stable nodes and saddle points. We are left with a pair of saddle nodes at a distance

$$R_0 = (az_1 + E_1)^{1/2}$$

from the origin, along the unique separatrix given by

$$\tan\phi_0 = z_1.$$

For an infinitesimal decrease in  $|z_1|$ , the separatrix disappears, giving rise to a limit cycle of finite amplitude

$$\lim_{|z_1| \rightarrow 1} X_{\max} = \lim_{|z_1| \rightarrow 1} Y_{\max} = ((E_1 + az_1)/2)^{1/2}.$$

This type of transition will be called a saddle-node transition.

## APPENDIX B: SOME PROPERTIES OF AN ASYMMETRIC VERSION OF THE BAUTIN SYSTEM<sup>53</sup>

The asymmetric version of interest is

$$\begin{aligned} \frac{dX}{dt} &= aY + E_1X + C_1X^2 - X^3 - XY^2 \\ \frac{dY}{dt} &= -aX + E_2Y - Y^3 - YX^2. \end{aligned} \quad (\text{B1})$$

Although Bautin did not study this system, it is convenient to call (B1) the asymmetric Bautin system since for  $C_1 = 0$ , one recovers the original symmetric system (A1). The limit cycle is egg shaped and the waveform asymmetric. For appropriate values of the parameters, there is a saddle-node transition involving a monostable rather than a bistable regime. For instance, with  $E_2 = 4.5$ ,  $E_1 = 1.0$ , and  $a = 2.0$ , if  $C_1 = 0.8$ , the system is monostable with three singularities: stable node (at  $Y = -1.45$ ,  $X = -1.0$ ), saddle point (at  $Y = -0.65$ ,  $X = -1.0$ ), and unstable focus-node (a multiple singularity)<sup>28</sup> at the origin.<sup>53</sup> If  $C_1$  is decreased below 0.4, the system exhibits finite amplitude limit cycle oscillations around an unstable focus at the origin. For  $C_1$  slightly larger than 0.4, the saddle-node transition occurs through fusion of the saddle point with the stable node.

The saddle-node bifurcation from monostable regime to limit cycle has been discussed by Andronov *et al.* (Ref. 28, Fig. 318). A typical feature is that two separatrices join the saddle point to the stable node in the monostable regime. When these two singularities fuse and disappear, the limit cycle formed follows the trajectory of the separatrix which becomes a closed loop in the transition.<sup>54</sup> The transition is reversible, without hysteresis.<sup>32</sup> It occurs always when  $C_1$  reaches the saddle-node value, irrespective of the previous value of  $C_1$ . The effect of fluctuations of  $X$  and  $Y$  in the transition region is the following: The monostable regime, close to the transition value of  $C_1$ , may show excitability.<sup>42</sup> The fluctuations must be large enough to pass a threshold. The threshold is defined by the position of the separatrices which do not join the saddle point to the node. If the system is in the limit cycle regime, near the transition region, its period is nearly infinite and very sensitive to small fluctuations in the parameters or to fluctuations affecting the phase ( $C_0$ ). Because the single excursion of the excitable perturbed system and the limit cycle trajectory are very similar for systems near the saddle-node transition, it will not be possible to distinguish between excitable system and oscillations with very long period.

<sup>1</sup>B. P. Belousov, Ref. Radiat. Med. 1958, Medzig, Moscow, 145 (1959).

<sup>2</sup>A. M. Zhabotinskii, Dokl. Akad. Nauk. SSSR 157, 701-704 (1964) (in English translation).

<sup>3</sup>D. O. Cooke, Progr. React. Kinet. 8, (3), 185-229 (1977).

<sup>4</sup>B. F. Gray, React. Kinet. 1, 8 (1975).

<sup>5</sup>R. M. Noyes and R. J. Field, Acc. Chem. Res. 10 (8), 273-280 (1977).

<sup>6</sup>R. M. Noyes, R. J. Field, and E. Körös, J. Am. Chem. Soc. 94, 1394 (1972); R. J. Field, E. Körös, and R. M. Noyes, *ibid.* 94, 8649-8664 (1972); D. Edelson, R. J. Field, and

- R. M. Noyes, *Int. J. Chem. Kinet.* **7**, 417-432 (1975).
- <sup>7</sup>E. Körös, M. Burger, V. Friedrich, L. Ladanyi, Zs. Nagy, and M. Orban, *Faraday Symp. Chem. Soc.* **9**, 28-37 (1974).
- <sup>8</sup>E. Körös, *ibid.*, p. 94.
- <sup>9</sup>(a) G. Schmitz, *Can. J. Chem.* **55**, 3147-3155 (1977); (b) R. M. Noyes and K. Bar-Eli, *ibid.* **55**, 3156-3160 (1977).
- <sup>10</sup>Z. Varadi and M. T. Beck, *J. Chem. Soc. Chem. Commun.* **2**, 30-31 (1973); J. Dayantis and J. Sturm, *C. R. Acad. Sci. Paris Ser. C* **280**, 1447-1450 (1975).
- <sup>11</sup>R. J. Field and R. M. Noyes, *J. Am. Chem. Soc.* **96**, 2001-2006 (1974).
- <sup>12</sup>A. T. Winfree, *Science* **175**, 634-635 (1972).
- <sup>13</sup>M-L. Smoes, *Faraday Symp. Chem. Soc.* **9**, see plate facing p. 75 and discussion (1974).
- <sup>14</sup>A. M. Zhabotinskii and A. N. Zaikin, *J. Theor. Biol.* **40**, 45-61 (1973).
- <sup>15</sup>A. N. Zaikin and A. M. Zhabotinskii, *Nature (London)* **225**, 535-537 (1970).
- <sup>16</sup>V. A. Vavilin, A. M. Zhabotinskii, and L. S. Yaguzhinski, *Oscillatory Processes in Biological and Chemical Systems* (Nauka, Moscow, 1967), p. 181 (in Russian).
- <sup>17</sup>A. M. Zhabotinskii, A. N. Zaikin, M. D. Korzhukhin, and G. P. Kreitzer, *Kinet. Katal.* **12** (3) 516-521 (1971) (in English translation).
- <sup>18</sup>R. P. Rastogi, K. D. S. Yadava, and K. Prasad, *Ind. J. Chem.* **12**, 974-976 (1974).
- <sup>19</sup>D. Thoenes, *Nature Phys. Sci.* **243**, 18-20 (1973).
- <sup>20</sup>E. Körös, *Nature* **251**, 703 (1974).
- <sup>21</sup>R. P. Rastogi and K. D. S. Yadava, *Ind. J. Chem.* **12**, 687-690 (1974).
- <sup>22</sup>M-L. Smoes, *J. Theor. Biol.* **58**, 1-14 (1976).
- <sup>23</sup>M-L. Smoes, Ph.D. thesis, University of Colorado (1973).
- <sup>24</sup>J. Dreitlein and M-L. Smoes, *J. Theor. Biol.* **46**, 559-572 (1974). Note: Figure 1 is incorrect. See Refs. 23 and 25 for correct waveforms.
- <sup>25</sup>M-L. Smoes, "The Autonomous Bautin System and Some Non-Autonomous Applications to Chemical Oscillations." *Proceedings of the International Conference on Nonlinear Oscillations* (1975) *Abhandlungen der Akademie der Wissenschaften der DDR*, p. 385-390 (in press).
- <sup>26</sup>M-L. Smoes, 175th ACS National Meeting, Anaheim, California, March 1978. Abstracts of Papers (\*Phy 086) and paper in preparation.
- <sup>27</sup>M-L. Smoes, *Bull. Amer. Phys. Soc.* **23**(4), 534 (1978). Also 176th ACS National Meeting, Miami Beach, Florida, September 1978. Abstracts of Papers. Also, paper in preparation.
- <sup>28</sup>A. A. Andronov, A. A. Vitt, and S. E. Khaikin, *Theory of Oscillators* (Addison-Wesley, Reading, MA, 1966). Note: The Bautin system is discussed on pp. 336-340. A saddle-node transition is illustrated in Fig. 318.
- <sup>29</sup>R. M. May and G. F. Oster, *Am. Nat.* **110** (974), 573-599 (1976) and references therein.
- <sup>30</sup>L. F. Olsen and H. Degn, *Nature* **267**, 177-178 (1977).
- <sup>31</sup>O. E. Rössler, *Bull. Math. Biol.* **39**, 275-289 (1977) and references therein; O. E. Rössler, *Z. Naturforsch.* **31**, 259-264 (1976).
- <sup>32</sup>G. Nicolis and I. Prigogine, *Self-Organization in Nonequilibrium Systems-From Dissipative Structures to Order Through Fluctuations* (Wiley-Interscience, New York, 1977). See p. 464 for fluctuation chemistry.
- <sup>33</sup>A. A. Schilt, *Analytical Applications of 1,10-Phenanthroline and Related Compounds* (Pergamon, New York, 1969).
- <sup>34</sup>R. Aris, *Introduction to the Analysis of Chemical Reactors* (Prentice-Hall, New Jersey, 1965).
- <sup>35</sup>D. P. Shoemaker and C. W. Garland, *Experiments in Physical Chemistry* (McGraw-Hill, New York, 1967); H. D. Young, *Statistical Treatment of Experimental Data* (McGraw-Hill, New York, 1962).
- <sup>36</sup>E. B. Wilson, Jr., *An Introduction to Scientific Research* (McGraw-Hill, New York, 1952).
- <sup>37</sup>A. H. Nayfeh, *Perturbation Methods* (Wiley, New York, 1973).
- <sup>38</sup>In the corresponding chemical waves, there is a clear increase in the oxidized fraction of the wavelength, when  $[MA]_0$  is decreased. The fraction can even reach unity for very low  $[MA]$  (see Ref. 27).
- <sup>39</sup>B. Hess and A. Boiteux, in *Biological and Biochemical Oscillators*, edited by B. Chance, E. K. Pye, A. K. Ghosh, and B. Hess (Academic, New York, 1973), pp. 229-241.
- <sup>40</sup>Such concentrations are often used in the study of chemical waves (see Ref. 11 for instance).
- <sup>41</sup>R. M. Noyes, Discussion remarks in *Faraday Symp. Chem. Soc.* **9**, 93-94 (1974).
- <sup>42</sup>R. J. Field and R. M. Noyes, *Faraday Symp. Chem. Soc.* **9**, 21-27 (1974).
- <sup>43</sup>P. De Kepper, A. Rossi, and A. Pacault, *C. R. Acad. Sci. Paris Ser. C* **283**, 371-375 (1976).
- <sup>44</sup>K. R. Graziani, J. L. Hudson, and R. A. Schmitz, *Chem. Eng. J.* **12**, 9-21 (1976).
- <sup>45</sup>J. J. Tyson, *J. Chem. Phys.* **66**, 905-915 (1977).
- <sup>46</sup>*Synergetics: A Workshop*, edited by H. Haken (Springer-Verlag, Berlin, 1977). See article by O. E. Rössler, p. 174.
- <sup>47</sup>M-L. Smoes and J. Dreitlein, *J. Chem. Phys.* **59**, 6277-6285 (1973).
- <sup>48</sup>R. A. Schmitz, K. R. Graziani, and J. L. Hudson, *J. Chem. Phys.* **67**, 3040-3044 (1977).
- <sup>49</sup>O. E. Rössler and K. Wegmann, *Nature* **271**, 89-90 (1978).
- <sup>50</sup>D. A. Frank-Kamenetskii, *Diffusion and Heat Transfer in Chemical Kinetics* (Plenum, New York, 1969), p. 517.
- <sup>51</sup>J. P. Gollup, T. O. Brunner, and B. G. Danly, *Science* **200**, 48-50 (1978).
- <sup>52</sup>M. J. Blandamer and D. L. Roberts, *J. Chem. Soc. Faraday Trans.* **1636-1645** (1977).
- <sup>53</sup>M-L. Smoes, in preparation.
- <sup>54</sup>W. H. Ray, *Applications of Bifurcation Theory*, 285-315 edited by P. H. Rabinowitz (Academic, New York, 1977), pp. 285-315.
- <sup>55</sup>The ability of a proposed mechanism to reproduce the properties of the experimental period of oscillations represents a necessary (but not sufficient) condition for the proposed mechanism to be valid. It is a necessary condition because the correct mechanism of a given chemical oscillation must correspond to rate equations which give a correct period of oscillations when integrated over a cycle. The only expected discrepancy between experimental and theoretical period comes from the effect of fluctuations. Such effects will be seen in the experimental period only since the theoretical rate equations are deterministic. This is not only true for the period but also for the waveforms.
- <sup>56</sup>The concentration of catalyst is a fixed parameter. Although the concentration of ferroin oscillates, the total concentration of ferroin and ferrin remains constant. This total concentration of catalyst is abbreviated as  $[Ferroin]_0$  in the text, table, and figures. There should be no confusion.
- <sup>57</sup>We agree with one of our referees that the differences in the chemical mechanisms for the cerium- and ferroin-catalyzed Zhabotinskii systems are very likely to be limited to differences in rate constant values, exothermicities of various steps, and existence and effects of various side and competing reactions.
- <sup>58</sup>*Biological and Biochemical Oscillators*, edited by B. Chance, E. K. Pye, A. K. Ghosh, and B. Hess (Academic, New York, 1973).