Bifurcation from excitability to limit cycle oscillations at the end of the induction period in the classical Belousov–Zhabotinsky reaction

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The appearance of full blown oscillations at the end of the induction period in the classical BZ reaction (substrate: malonic acid) is usually explained by a subcritical Hopf bifurcation. Our perturbation experiments have revealed that the classical BZ reaction is excitable in its induction period and the threshold of excitability is decreasing gradually to zero during that period. Thus the sudden appearance of limit cycle oscillations at the end of the induction period can be explained by a saddle-node infinite period (SNIPER) bifurcation as well.

I. INTRODUCTION

A. Saddle-node infinite period (SNIPER) bifurcation and excitability

Bifurcations leading to stable periodic orbits—i.e., the appearance of limit cycle oscillations at a critical parameter value—is a topic of current interest in the study of chemical dynamic systems.[1–5] Andronov and his school[6] pointed out nearly half a century ago that there are four fundamental theoretical possibilities for such bifurcations in dynamic systems. Nevertheless it was only recently that Marek[2] and Marek and Epstein[3] realized in general that all these theoretical cases can be studied and classified in chemical systems by experimental means as well. They worked out an experimental method to identify the different types of such bifurcations based on the behavior of the amplitude and the period of the emerging oscillations as a function of the bifurcation parameter and observing the presence or the absence of hysteresis nearby the bifurcation point.

Recently we studied[5] the BZ reaction of oxalic acid[7,8] varying the flow rate of the bromine removing inert gas stream as a bifurcation parameter. According to our experiments there was only a certain interval in the parameter space within which oscillations could be observed. We found that the transitions from the oscillatory to the nonoscillatory states went back and forth via SNIPER bifurcations [Fig. 1(a)]. Also we pointed out that the disappearance of limit cycle oscillations via SNIPER bifurcation leads to excitability [Fig. 1(b)].

In other words if an oscillating system can be transformed to an excitable one and vice versa by changing a parameter then such a behavior can be a proof for a SNIPER bifurcation occurring in that system. Thus, in addition to Marek's method, perturbation techniques[5,9–13] revealing, e.g., excitability can give further information about the type of the bifurcation in a dynamic system. Gáspár and Galambosi[14] also applied a perturbation technique and found SNIPER bifurcation in the BZ reaction of oxalic acid in a CSTR. The same behavior was found by Ševčik and Adamčiková.[15] In the present work we want to show that the classical BZ system (substrate: malonic acid) is excitable in its induction period, therefore the appearance of full blown oscillations at the end of the induction period can be explained by a SNIPER bifurcation.

B. Appearance of full blown oscillations in the classical BZ reaction

It is well known that the classical BZ reaction carried out in closed system has an induction period. During that period some critical amount of bromomalonic acid[16] and probably also some glyoxylic acid[17] have to accumulate before oscillations can start. In real open systems like in a CSTR (continuously flowing well stirred tank reactor[18]) nearly constant bromomalonic and glyoxylic acid concentrations can be maintained (at least within certain limits) during the whole experiment (after some initial transient period). That can be achieved by the means of fixed outer control parameters or "constraints"[19] (inflow concentrations, residence time, etc.) Thus a CSTR remains at a fixed point in the parameter space and bifurcations can be observed only if a control parameter is varied. The behavior of a closed BZ system can be modeled approximately with an open one the control parameters of which are varied slowly in the course of the experiment. That is, in a closed BZ system, the bifurcation parameters are varying slowly and in an autonomous way. At the end of the induction period when a certain amount of the organic intermediates has been accumulated a critical surface of the parameter space is crossed and an oscillatory state appears. Later on that bifurcation will be followed by a second one because the concentration of the malonic acid and the bromate is slowly depleted during the oscillatory period and finally the system will enter into another region of the parameter space where the oscillations will disappear again from the "worn out" BZ system.

The appearance of full blown oscillations at the end of the induction period stirred some speculations[20,21] as model calculations predicted Hopf bifurcation (Fig. 2). Two hypotheses were considered:

(i) Supercritical Hopf bifurcation [Fig. 2(a)]. Here the problem is that no small amplitude oscillations can be ob-

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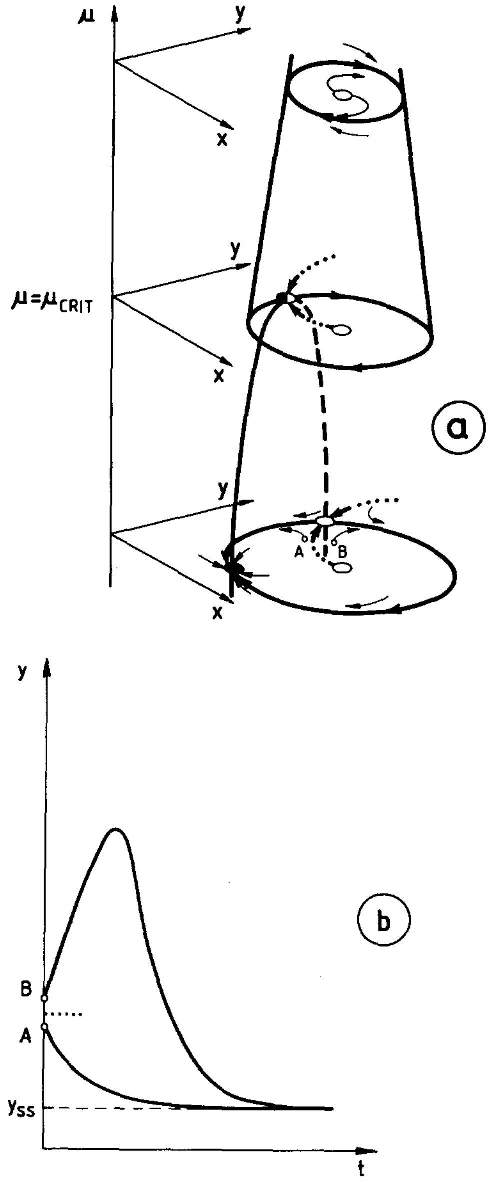

FIG. 1. (a) SNIPER bifurcation. x and y: coordinates of the phase plane (intermediate concentrations) μ: bifurcation parameter. The system is excitable when the parameter μ is below μ_{CRIT}. Limit cycle oscillations of finite amplitude appear above μ_{CRIT}. (b) Responses of an excitable system for subcritical (A) and (B) supercritical perturbations. Y_{SS}: steady state value of variable y. [See also in Fig. 1(a)]. A trajectory starting from point B has to round the separatrix while the other one starting from point A can go directly to the stable node thus the two responses are qualitatively different.

served in the experiments. At least the parameter region within which the limit cycle "grows up" to a finite size must be very narrow if this hypothesis holds.

(ii) Subcritical Hopf bifurcation combined with a previous double loop (or "jug handle") bifurcation [Fig. 2(b)]. This hypothesis explains the sudden appearance of full blown oscillations but it also predicts a parameter region within which "hard" oscillations must appear. (A region where a locally stable steady state and a stable limit cycle coexist.) Hard oscillations were not found experimentally.^{20} Again we could speculate that the region is too narrow for experimental observation.

In the experimental part it will be shown that the classi-

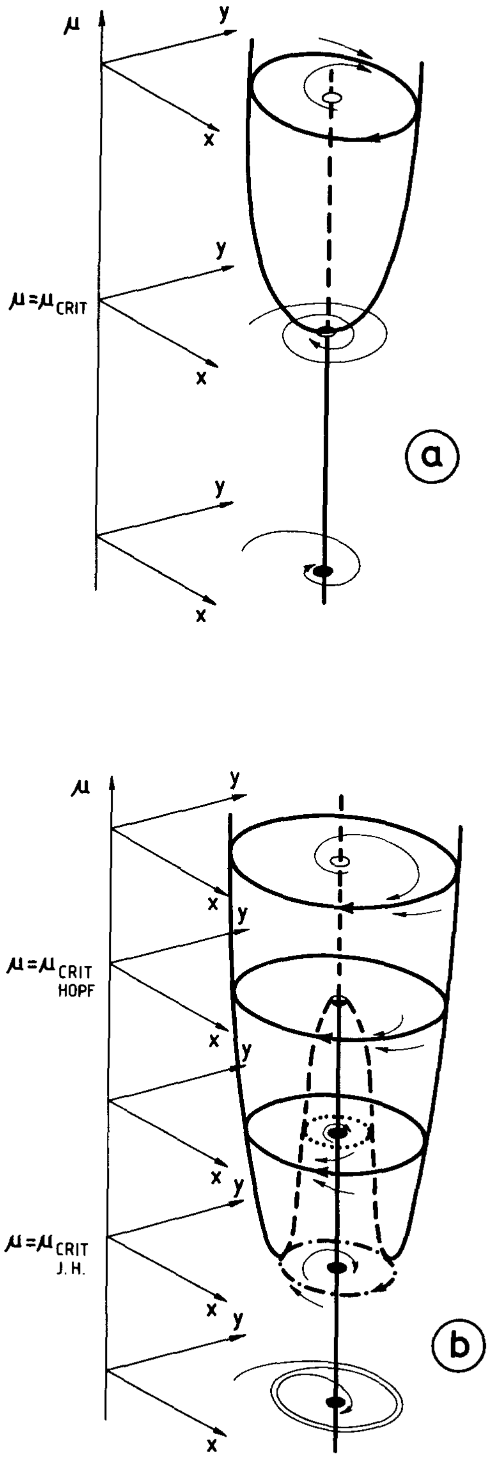

FIG. 2. (a) Supercritical Hopf bifurcation. Perturbations below μ_{CRIT} produce damped oscillations. Limit cycle oscillations can be observed above the critical parameter value only. The amplitude of the oscillations approaches to zero if μ is decreased to μ_{CRIT} from a higher parameter value. (b) Subcritical Hopf bifurcation preceded by a jug handle or "double loop" bifurcation. Below $\mu_{\text{CRIT J.H.}}$ perturbations result in damped oscillation. At $\mu = \mu_{\text{CRIT J.H.}}$ a semistable limit cycle appears which separates to a stable and to an unstable one as μ is increased further. When μ is between $\mu_{\text{CRIT J.H.}}$ and $\mu_{\text{CRIT.HOPF}}$ the system is bistable: perturbations can move the system from the locally stable steady state to the oscillatory state and back. Nearing to $\mu_{\text{CRIT.HOPF}}$ the size of the unstable limit cycle approaches to zero and finally, at the point of the subcritical Hopf bifurcation, the cycle and the stable focus are transformed to an unstable focus. Above $\mu_{\text{CRIT.HOPF}}$ there is only one attractor: the stable limit cycle.

cal BZ system studied by us is excitable in its induction period. The threshold of excitability is gradually decreased to zero by the end of the induction period: consequently the appearance of full blown oscillations can be explained by a SNIPER bifurcation as well.

II. EXPERIMENTAL

The experiments were carried out at 25 °C in a thermostated glass vessel. The applied magnetic stirring was fast enough (~ 300 rpm) to mix the injected perturbing agent rather quickly (within ~ 2 s). Faster stirring was avoided to minimize oxygen effects. Three different reagent solutions A, B, and C were used:

A: 0.2 M MA (malonic acid),

B: 0.1 M $KBrO_3$,

C: 4×10^{-3} M $Ce(SO_4)_2$.

All the three solutions were prepared in 1.5 M H_2SO_4. The chemicals were of reagent grade. To start an experiment 25 ml of solution A and 20 ml of solution B were mixed. After 2–3 min 5 ml of C was added and the registration of the potentiometric trace was started. Thus the initial conditions were the following:

$$[MA]_0 = 0.1\text{ M},\quad [BrO_3^-]_0 = 0.04\text{ M},$$

$$[Ce^{4+}]_0 = 4\times10^{-4}\text{ M},\quad [H_2SO_4] = 1.5\text{ M}.$$

During the induction period in every 40–50 s a small amount (3–16 μl) of 0.1 M KBr solution was injected repeatedly into the reaction mixture with a Hamilton microsyringe. The first emergence of excitability was observed (Fig. 3). Then the whole experiment was repeated applying a higher amount of the perturbing bromide solution. Some perturbations were made in the oscillatory regime as well.

The reaction was monitored by a homemade bromide selective electrode[22] and a double junction calomel electrode was used as a reference. The potential difference was measured by a Radelkis OP-208 *p*H/mV meter and the potentiometric trace was recorded by a line recorder TZ 4200 (Laboratorni Pristroje Praha).

III. RESULTS AND DISCUSSION

A. Bromide ion as a perturbing agent in the induction period

Actually our method to observe excitability can be regarded as an inverse of Ruoff's method. Namely Ruoff[11,12] discovered that a worn out BZ reagent is excitable for a certain time when the oscillatory regime is over. To reveal the excitable behavior he applied perturbations: silver ions were added to the system producing a step-wise decrease in the relatively high bromide level characteristic to the postoscillatory regime.

Now in our case, as the preoscillatory induction period is characterized by just the contrary—i.e., by a very low level of bromide—it seemed to be logical to apply bromide ion as a

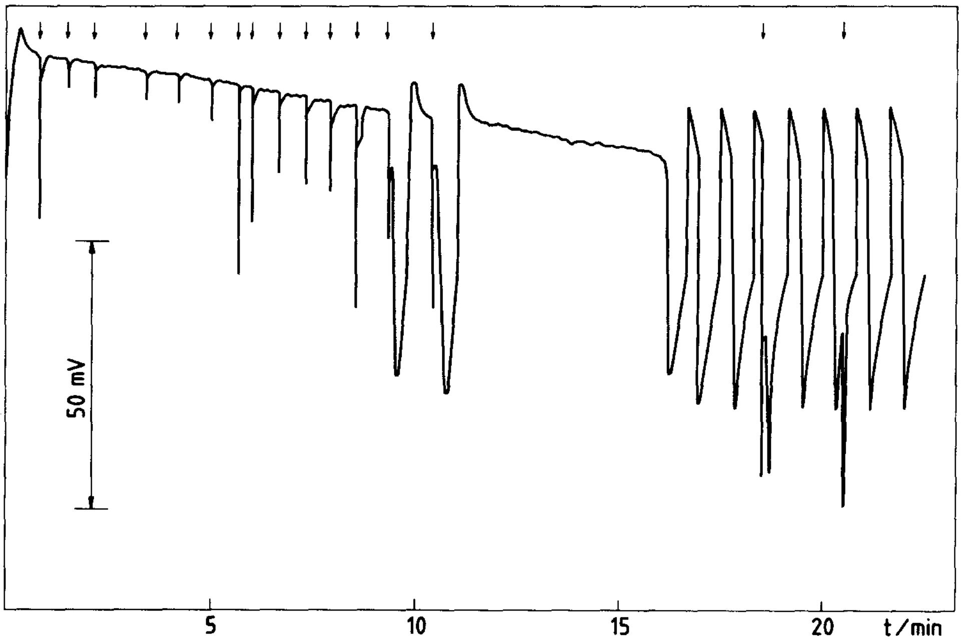

FIG. 3. Perturbations of the classical BZ reaction in the induction period and in the oscillatory regime. The perturbing dosage was 6 μl of 0.1 M KBr solution. (See the text for other experimental data.) Arrows above the recorded potentiometric trace and the simultaneous sudden drops in the potential of the bromide selective electrode mark the repeated injection of the perturbant. As the injected bromide is consumed within the time of mixing the potential jumps up again nearly to its original value. It is the subsequent slow change of the potential which is the real response of the system to the applied perturbation. (The size of the downward strokes depends also on the location of the injection: if that place is nearer to the electrode the resulting stroke is much larger. Naturally the actual perturbation is independent of such effects.) As the figure shows the slow variation of the potential and also the length of the induction period is not affected by the minute amounts of the perturbant injected. After each perturbation the system always returned back asymptotically to the same slow evolution.

perturbing agent. Really bromide ions produced perturbations of the expected type. At the same time bromide has the advantage that it is a real intermediate of our system. Thus after the injection of the perturbing agent we can be sure that the system will evolve along a "natural" trajectory because no new chemical component will be present as a result of the perturbation. For example, in the case of silver ions—if they are applied in an excess compared to bromide ions—a surplus of silver ions will remain in the system right after the perturbation. This new component will provide a new reaction channel; in fact we shall have a new chemical dynamic system. Naturally the silver ion surplus will be consumed sooner or later and we shall get back our original system in a perturbed state. However to find out the real response of our system to the perturbation we have to separate the potentiometric traces recorded before and after the disappearance of silver ions which separation can be a difficult task in some cases.

B. Separation of "perturbation" and "response" periods in the measurements

Another problem in evaluation of the experimental results, even in the case of bromide perturbations too, is the separation of the forced excursion of the system during and under the influence of the applied perturbation from the following response to that perturbation. That is we have to divide the recorded history of a measured signal (e.g., a potentiometric trace) into two parts: a period during of which the perturbing agent is introduced into and mixed homogeneously within the system followed by an autonomous relaxation back to the locally stable steady state. It is only the second part of the recorded curve—i.e., the response to the perturbation—we are really interested in. This separation of the perturbation and the following response can be especially important if we are looking for excitability by an electrochemical detection method because a misinterpretation of the experimental results is a real danger without a clear separation. Namely to find excitability means to find a threshold: a critical value of the applied perturbation or a critical amount of the perturbing agent added to the system. Above that critical limit the response of the system to the perturbation is qualitatively different. Now, if the perturbation is carried out, e.g., with silver ions added to the system to remove bromide ions, an equivalence point can be found beyond of which a bromide selective electrode will give a vastly increased potential response. (This occurs when the bromide ions are just titrated by the silver ions up to the equivalence point.) Naturally this is a property of the applied perturbation and detection methods only and it is not associated with the response of our dynamic system at all. If we apply too large bromide perturbations in the induction period then a "titration" of hypobromous acid may occur accompanied with an increased potentiometric signal just like in the previous case. Therefore a separation of the "perturbation period" from the "response period" is very important. Fortunately the time scales of the two periods are rather different: in a well stirred reactor the perturbation can be carried out relatively fast compared to the following response. Applying a bromide selective electrode with a fast response for bromide ions and for hypobromous acid as well[22,23] the perturbation and the response of the system can be easily separated. As can be seen in Fig. 3 the perturbation is completed within 1–2 s and the following response lasts 15–20 s or more.

C. Measurement of the slow change in the threshold of excitability during the induction period

We may expect that in the course of the induction period the threshold of excitability decreases gradually. According to our expectations during that period a bifurcation parameter (most probably the concentration of bromomalonic acid combined with some other organic intermediates) grows slowly toward its critical value where a stable node will coalesce with a saddle point. As the saddle point and the stable node come nearer and nearer to each other the threshold of excitability must decrease. Really our preliminary experiments pointed out such a monotonous change. Therefore we have to apply a method capable to follow that gradual decrease in the threshold of excitability. On the other hand just because of the continuous change in the parameters of our closed system there is not enough time to perform experiments with different perturbations at a certain fixed value of the bifurcation parameter. Thus we applied a different method with constant perturbations in every 40–50 s and registrating the subsequent responses throughout the entire induction period. At the first some perturbations no excitability was observed in the response as the threshold was too high compared to the applied perturbation. However as the threshold was decreasing continuously after a while it had reached the level of the applied perturbation and starting from this moment a single oscillation appeared as a response following every perturbation (Fig. 3). Then the whole experiment was repeated with another perturbation level. This way we could map the threshold of excitability throughout the induction period at least semiquantitatively (Fig. 4).

D. Threshold of excitability

In Fig. 4 the first appearance of excitability is depicted as a function of the injected bromide amount. If no perturb-

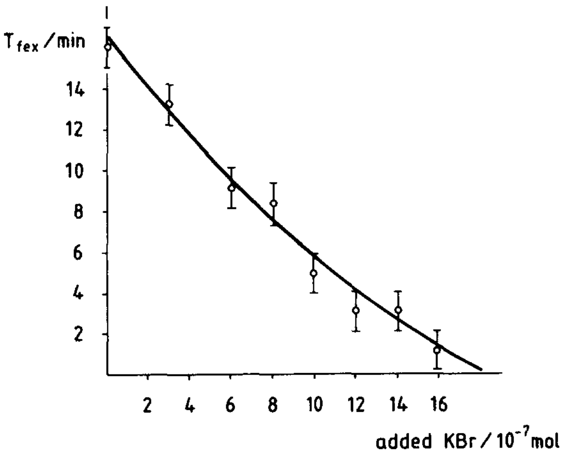

FIG. 4. T_{fex}: the first emergence of excitability as a function of the added KBr perturbant in the course of the induction period of the BZ reaction.

ing agent is added the oscillations appear spontaneously at the end of the induction period ($\sim 16 \pm 1$ min) and 1.6 μmol of injected KBr causes a single oscillation already in the first minute of the induction period. The limited accuracy of the excitability threshold is due to the following disturbing effects:

(i) The perturbed state in the phase space is reached after a forced excursion from a previous state under the influence of the injection of the perturbing agent. Naturally not only the amount of the injected reagent but also the rate and the duration of that injection will have some effect on the final shift from the initial state. In other words a fast and reproducible injection is required. We applied a manual injection of 0.3–0.6 s duration.

(ii) The reproducibility of mixing and the location of the injection is also important to always get the same homogeneous perturbed state. We always tried to inject the perturbing agent into the center of the vortex of the magnetically stirred solution.

(iii) At last some stirring and geometry dependent oxygen effect can also play some disturbing role.

IV. CONCLUSION

Our results prove unambigously that there is an excitable state in the induction period of the classical BZ reaction. The threshold of excitability is decreasing gradually during this period and at the end the threshold vanishes and full blown oscillations appear. The phenomenon can be explained as a saddle-node infinite period (SNIPER) bifurcation: a gradual change of a bifurcation parameter results in the coalescence of a stable node and of a saddle point and a limit cycle is left behind. It is interesting to remark that according to Ruoff's results[11,12] the postoscillatory period is also excitable thus the disappearance of the oscillatory state can also go via SNIPER bifurcation. (In that case a dramatic increase of the time period can be also clearly observed.)

However as it will be pointed out in the following paper by Bar-Eli and Noyes[24] there is always a possibility that the interesting dynamics occurs in a very short interval of the parameter space which is difficult or even impossible to resolve experimentally. Thus we can state only that our observations are consistent with a SNIPER bifurcation within the resolution of our experiments.

At the end it is interesting to remark that Kumpinsky and Epstein[25] (in the case of the minimal bromate oscillator) and Gáspár *et al.*[26] (in the case of oxalic acid BZ system) had to face a similar dilemma: their calculations predicted a Hopf bifurcation while the corresponding experiments suggested a SNIPER bifurcation.

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