Temporary Bistability and Unusual Oscillatory Behavior in a Closed Belousov–Zhabotinsky Reaction System[1]

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When the organic substrate methylmalonic acid is present in stoichiometric excess, the ferroin-catalyzed oxidation by bromate in a closed system exhibits a particularly rich behavior. Thus, we observed more than 1 h during which large-amplitude oxidative excursions separated from each other by several minutes were accompanied by occasional sequences of damped or amplified regular small-amplitude oscillations with periods of about 20 s. These very different types of oscillations were centered on different potentials and could not be considered to be associated with the same steady state. After oscillations had been damped out, the system persisted for over 1 h in a condition such that small perturbations with silver or with bromide ions could initiate transitions between two different steady states each of which was stable to perturbations below a critical threshold magnitude. We believe this is the first time that an extended period of bistability has been observed in a closed system.

Introduction

The Belousov[2]–Zhabotinsky[3] reaction is probably the most investigated and best understood of all chemical oscillators.[4] Many of the previous studies have used the organic substrate malonic acid, $CH_2(CO_2H)_2$, which can undergo many complicated chemical processes.[5]

One of us[6] has recently explored the cerium-catalyzed behavior with methylmaonic acid, $CH_3CH(CO_2H)_2$. Only one hydrogen of this substrate is susceptible to bromination, and at least under some conditions[7] the stoichiometrically significant change in the overall system can evidently be described well to within about 3% by the unique

$$3BrO_3^- + 5CH_3CH(CO_2H)_2 + 3H^+ \rightarrow 2CH_3CO_2H + 3CH_3CBr(CO_2H)_2 + 4CO_2 + 5H_2O \quad (T)$$

We now find that ferrion catalysis of reaction T can generate an unusually rich behavior when the organic reducing agent is in stoichiometric excess. Phenomena which can be observed during a single run include (a) sustained large-amplitude oscillations accompanied by occasional bursts of small-amplitude oscillations taking place around very different average electrode potentials and (b) a long period during which the system can exist in either of two steady states each of which is potentially excitable to the other but is stable to very small perturbations. We believe that these behaviors are unprecedented for closed homogeneous systems.

Materials and Method

All experiments were performed in a stirred thermostated glass beaker at 25 °C. The system was monitored potentiometrically with a bright platinum electrode measured against a double junction Ag/AgCl reference electrode (Orion, Model 90-02). The outer chamber of the reference electrode was filled with a 10% KNO_3 solution. The potential was followed with a conventional x–t recorder (Leeds and Northrup Speedomax).

All chemicals except the methylmalonic acid, MeMA (Fluka, >99%), were of analytical grade. The reaction volume was 50 mL, and oscillations were started by mixing reagents in the order H_2SO_4, MeMA, $NaBrO_3$, KBr. After the yellow color of initially formed bromine had disappeared, ferroin solution (BDH, 1,10-phenanthroline–ferrous sulfate complex solution, 0.025 M) was added.

Perturbations were performed by adding the perturbant dropwise with a conventional Pasteur pipet. As in an earlier study,[8] the average drop size was taken to be 31 μL.

Results

Figure 1 illustrates approximately the first 4 h of a run with the indicated initial composition. After all of the components had been added, the solution first alternated between extended periods of 30–40 min each in reduced and oxidized steady states. Particularly when in the reduced state, the potential exhibited noisy

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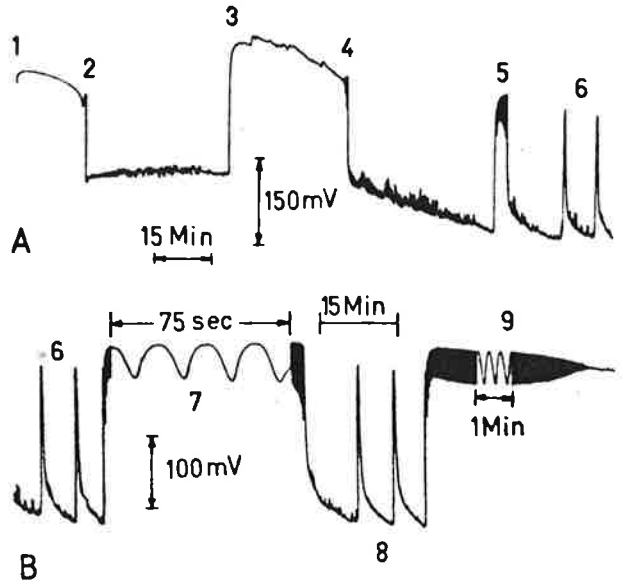

Figure 1. Oscillatory behavior of a ferroin-catalyzed methylmalonic acid BZ system. Initial concentrations: $[H_2SO_4]_0 = 0.5$ M; $[MeMA]_0 = 0.3$ M; $[NaBrO_3]_0 = 0.1$ M; $[KBr]_0 = 0.1$ M. Parts A and B represent a continuation of the same run with an overlap of one "spike". (A) 1: addition of KBr; 2: after bromine color has disappeared, the ferroin is added; 3: after staying for a while in the reduced state, the system goes spontaneously into the oxidized state; The color of the solution changes from red to blue; 4: at the beginning of the oscillating period, oscillations of high frequency and increasing amplitude are observed in the oxidized state; 5: train of small-amplitude oscillations in the oxidized state; 6: oxidizing excursions or "spikes". Note also the considerable "noise" which is observed in the reduced state. (B) 6 and 8: oxidizing excursions; 7: train of small-amplitude oscillations in the oxidized state. Period length in the expanded region is 20 s; 9: at the end of the oscillating region, small-amplitude damped oscillations in the oxidized state are observed (period length in the expanded region is 19 s).

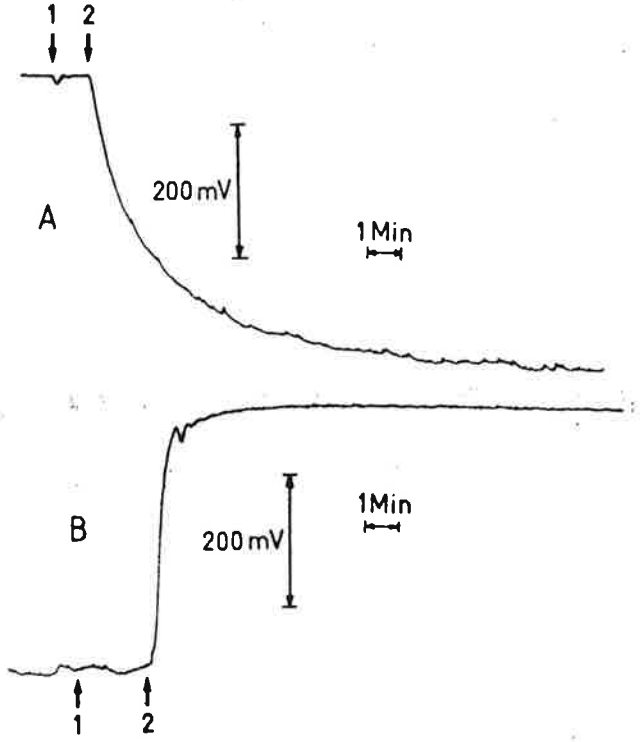

Figure 2. Bistability at the end of the oscillating region in the ferroin-catalyzed methylmalonic acid BZ reaction. The composition corresponds to that at the end of the time in Figure 1. (A) The system starts in the oxidized state. 1: one drop (31 μL) of a 0.004 M KBr solution (2.5×10^{-6} M in 50 mL) shows that the steady state is stable. 2: two drops of a 0.004 M KBr solution drive the system to the reduced state. The color of the solution changes from blue to red. (B) The system starts in the reduced state. 1: five drops of 0.004 M $AgNO_3$ solution (1.3×10^{-5} M) shows that the steady state is stable. 2: eight drops of 0.004 M $AgNO_3$ solution (2.0×10^{-5} M) drives the system to the oxidized state.

fluctuations which seemed to be far too large to explain as instrumental effects.

Then followed a little more than 1 h during which the solution spent most of the time in a reduced state except for seven oxidizing excursions of about 200 mV each. Many of these excursions were sharp "spikes" of oxidation, but during those marked 5 and 7 in Figure 1 the oxidative excursion included several minutes of regular small-amplitude oscillations extending 40–100 mV with period about 20 s each. These small-amplitude oscillations generated a regular envelope as they first damped and then amplified until the system passed a threshold and switched back to a reduced steady state. After the system had exhibited regular small-amplitude oscillations, the time in the reduced state was longer before the next oxidative excursion, and when the time between excursion spikes had been reduced to about 5 min, the next oxidative excursion exhibited small-amplitude oscillations.

At the excursion marked 9 in Figure 1, the small-amplitude oscillations damped instead of being amplified as in excursions 5 and 7. The system then entered an oxidized steady state which persisted for 1 h or more if the system was not perturbed.

Such an oxidized steady state was stable to perturbation by small amounts of bromide ion as shown by point 1 in Figure 2A, but a larger amount of bromide could convert it to a reduced steady state as shown by point 2. That reduced steady state was also stable to perturbation by a small amount of silver ion but could be converted back to the oxidized steady state by a larger perturbation as shown in Figure 2B.

Therefore, the system generated at the end of Figure 1 exhibits a true bistability in that there are two steady states each of which persists for an extended time in the absence of perturbation but each of which can be converted to the other by a sufficient but still very small perturbation. Of course the bistability cannot persist to the final equilibrium state, but we believe this is the first time that such behavior has been demonstrated for an extended duration in a closed system. In fact, bistability has been claimed to be a phenomenon necessarily restricted to open systems.[9]

The features in Figures 1 and 2 were reproducible, although absolute times of transitions varied somewhat from run to run. Because the organic substrate was in stoichiometric excess, a system like that in Figure 1 eventually went to a reduced steady state which persisted for several hours before exhibiting chaotic fluctuations of the order of 100 mV with periods of the order of tens of minutes. Of course these fluctuations eventually died out before the ultimate approach to equilibrium.

Discussion

The observations reported here add still another chapter to the remarkable variety of Belousov–Zhabotinsky systems! The two locally stable steady states of Figure 2 are both presumably undergoing net reaction by the stoichiometry of equation T. The oxidized state has a blue color and a very low concentration of bromide ion. The reduced state has a red color and a concentration of bromide ion in excess of the critical value[10] of about 10^{-7} M. Past experience indicates that the rate of overall reaction is much greater in the oxidized than in the reduced state.

The small-amplitude oscillations are centered on a very different potential than are the large-amplitude excursions. Therefore, each set of oscillations is associated with a different steady state. We believe that dynamic behavior of the system must be influenced by small amounts of other intermediate or product organic species which are present to different extents during different stages of the reaction and whose presence is not recognized in simple process T. Presumably, the relative concentrations of these species determine whether an oxidative excursion will or will not lead to small-amplitude oscillations and whether those oscillations will be amplified until the system goes to a reduced state or will be damped until an oxidized steady state is attained.

Investigation of this remarkably rich behavior is continuing. It is clear that such variety cannot be accomodated either to the original Oregonator model[11] or to an extension used to model large-

and small-amplitude oscillations associated with a single stationary state in a CSTR.[12]

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Registry No. $NaBrO_3$, 7789-38-0; methylmalonic acid, 516-05-2; ferroin, 14708-99-7.