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Complex Oscillations in the Bromate−Oxalic Acid−Acetone−Manganese(II)−Sulfuric Acid Reaction in Batch

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Two characteristically different patterns of oscillations were observed in the bromate−oxalic acid−Mn^{2+}−acetone−sulfuric acid reaction in a stirred batch reactor depending on the method of mixing of the reagents. One of the patterns is a mixture of high- and low-amplitude oscillations, while in the other case a regime of high-amplitude oscillations is followed by a sequence of low-amplitude ones. In both cases, the acetone concentration can control the length of the induction period and the number of small- and high-amplitude oscillations.

1. Introduction

Complex oscillations and chaos have been observed in chemical oscillating systems such as BZ,[1−3] modified BZ systems by using Mn^{2+} and an organic substrate other than malonic acid,[4,5] and fully halogen-based systems such as bromate−iodide[6] and chlorite−bromate−iodide.[7,8]

In this paper, we present another kind of complex oscillation in the system bromate−oxalic acid−Mn(II)−acetone−sulfuric acid that employs acetone to remove bromine. It was shown by Ševčík and Adamčíková[9] and Noszticzius[10−12] that when using oxalic acid as the organic substrate in a BZ system, it is necessary to remove bromine by some way such as flow (in a CSTR), bubbling a gas, or reacting with some additional substance like acetone.

Our original intention was to observe the oscillating chemiluminescence produced by bromate−oxalic acid−Mn(II)−acetone−sulfuric acid in batch reported by Weigt.[13] What we discovered is that this system is a very hard one to work with because it is difficult to reproduce. Later we noticed that the reason for this nonreproducibility was that this system, at low acetone concentrations, is sensitive to the stirring rate. In addition, we observed a remarkable pattern of oscillations that alternate high- and low-amplitude oscillations with some degree of reproducibility, i.e., in the sequence and the number of each kind of oscillations. This pattern can be classified as a transient period doubling behavior determined by the acetone concentration.

2. Experimental Section

The analytical-grade chemicals $NaBrO_3$ (Riedel-deHaën), $MnSO_4{\cdot}H_2O$ (Merck), oxalic acid and $C_2H_2O_4{\cdot}2H_2O$ (Riedel-deHaën), H_2SO_4 (Reagen), and acetone (Merck) were used without further purification. Laboratory water was distilled and further deionized.

Experiments were carried out in a Suprasil standard quartz cuvette using a UV−vis diode array spectrophotometer (HP 8452-A). The cuvette had a 1 cm optical path (Hellma 100-QS) and was closed with an inflatable rubber ball only to prevent liberation of bromine and bromoacetone to the laboratory atmosphere and the pressure increase due CO_2 formation. The total volume of the solution in the cuvette was 3 mL. The cuvette containing a 3 × 5 mm Teflon-coated cylindrical stirring bar was placed inside a jacketed cuvette holder having a water-powered magnetic stirrer. The stirring rate used was low (≅150 rpm) or high (≅1100 rpm). At high stirring rates, no vortices inside the cuvette could be seen. This means that the high stirring rate does not increase very much the loss of bromine or other volatile species to the gas phase compared with the low stirring rates. The temperature was maintained at 20 °C by a circulating bath.

Two methods of mixing the reagents were used.

Method 1. The reagents were thermally conditioned in the circulating bath before being pipetted by a fast delivering digital pipet (Transferpette). Three different solutions of reagents were prepared: (A) 0.42 M sodium bromate; (B) 1.8−3.0 M acetone; (C) 1.875 M sulfuric acid, 0.1875 M oxalic acid, and 0.0039 M $MnSO_4$. After turning on the stirring, equal volumes (1 mL of each) of the solutions A followed by B and then C were added to the cuvette. The time between each addition was approximately 2 min. After this, the cuvette was closed with an inflatable rubber ball. Only a high stirring rate in the cuvette was applied when using method 1.

Method 2. Four different solutions were prepared: (A) 0.28 M sodium bromate; (B) 5.76−6.24 M acetone; (C) 0.25 M oxalic acid; (D) 0.0104 M $MnSO_4$ with 5.0 M sulfuric acid. A 100 mL beaker, stirred by a glass-coated magnetic stirring bar, 2 cm long, at 600 rpm, was placed in a thermostated bath at 20 °C, 20 mL of solution A was added, and the temperature was allowed to equilibrate. After that, both solutions B (5 mL) and C (10 mL) were simultaneously added. The temperature usually went up to ≈24 °C because of some dilution exothermic effect. After 140 s, the temperature was equilibrated again and 5 mL of solution D was added. The temperature went up to ≈23 °C, and the mixture was left in the beaker with continuously stirring for additional 195 s. After that, 3 mL was pipetted to the cuvette, and the cuvette was closed in the same way as before. Only a low stirring rate in the cuvette was applied when using method 2.

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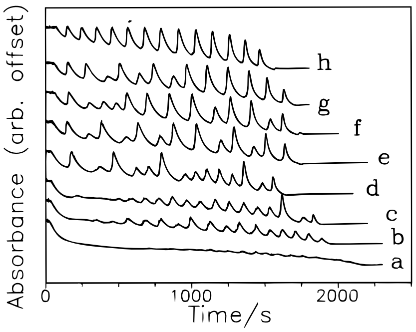

Figure 1. Time series using method 1 to mix reagents. $[BrO_3^-]_0 = 0.14$ M, $[H_2SO_4]_0 = 0.625$ M, $[MnSO_4]_0 = 0.0013$ M, [oxalic acid]$_0 = 0.0625$ M, [acetone]$_0 =$ (a) 0.60, (b) 0.66, (c) 0.72, (d) 0.75, (e) 0.78, (f) 0.80, (g) 0.84, (h) 0.87 M. $\lambda = 310$ nm. $T = 20$ °C. Curves were shifted by some arbitrary offset so as to not superimpose.

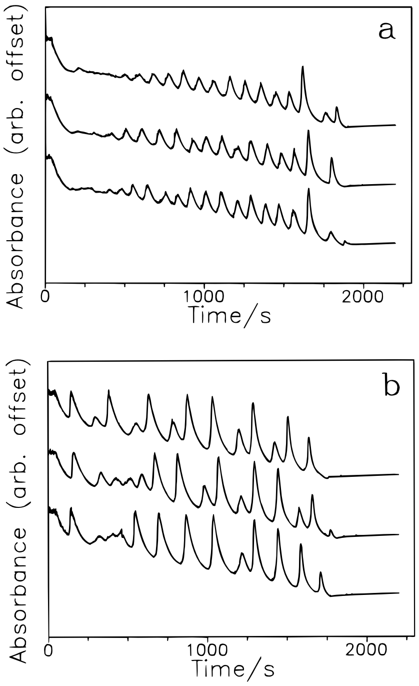

Figure 2. Reproducibility using method 1 to mix reagents. Each curve represents one separated experiment. Curves from each experiment were shifted by some arbitrary offset so as to not superimpose. Experimental conditions are the same as in Figure 1. [acetone]$_0 =$ (a) 0.72, (b) = 0.78 M.

3. Results

In Figure 1, we can see the appearance of oscillations with high and low intermixed amplitude as a function of initial acetone concentration in the range of 0.60−0.87 M. At the low range of the acetone concentration (0.60−0.75 M), we see that low-amplitude oscillations predominate. As the acetone concentration is increased, the induction period decreases and high-amplitude oscillations start to predominate ([acetone] = 0.78−0.84 M). At acetone concentrations greater than or equal to 0.87 M, no low-amplitude oscillations were observed. The exact sequence of low- and high-amplitude oscillations and its number is not exactly the same, but some reproducibility was observed as can be seen in Figure 2 for two different acetone concentrations.

Using method 2, the oscillation pattern changes from the intermixed high- and low-amplitude oscillations to a separated train of high-amplitude oscillations followed by a separated train of small-amplitude and irregular oscillations (Figure 3). In this mixture method, the influence of the acetone concentration over the induction period is more sensitive. As in method 1, increasing the acetone concentration will decrease the induction period and increase the number of high-amplitude oscillations. Small-amplitude oscillations start after 4000 s, almost independently of the induction period size.

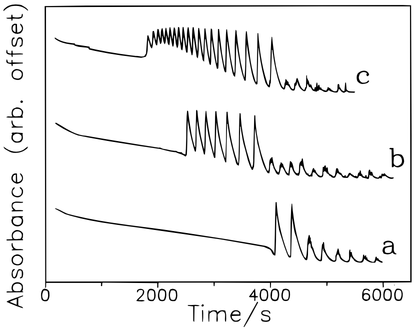

Figure 3. Time series using method 2 to mix reagents. Experimental conditions are the same as in Figure 1. [acetone]$_0 =$ (a) 0.54, (b) 0.60, (c) 0.66 M. Curves were shifted by some arbitrary offset so as to not superimpose.

4. Discussion

The reduction of the induction period when the acetone concentration was increased agrees with the idea that the presence of Br_2 inhibits oscillations, as has been pointed by other authors.[9−12,14] This consideration is based on the very well-known fact that acetone reacts with bromine to produce bromoacetone and consequently reduces the Br_2 concentration.

As this oscillating system contains some volatile species, such as acetone itself and products of the reaction such as bromine and bromoacetone, the two different patterns of oscillations we obtained can be the consequence of the greater facility of method 2 to lose some amount of the volatile components. This can be accomplished by the large solution surface in the 100 mL beaker together with the greater increase of the temperature after mixing the reagents, compared with method 1, which is done fully in a cuvette.

As can be seen from Figure 10 of the Noszticzius and Bódiss paper,[11] bromate and oxalic acid can react slowly without a metallic ion catalyst in 1.5 M sulfuric acid (pH = −0.18). In using method 2 to mix the reagents, we have bromate, oxalic acid, and acetone mixed at an estimated pH of 1.4, during 140 s. As bromate usually reacts following rate laws having a second-order dependence on $[H^+]$,[15,16] we consider that the direct reaction between bromate and oxalic acid should not be the main reason for the different patterns of oscillations observed when using method 1 or 2.

The kind of oscillation we observed for method 1 may suggest the presence of two fundamental frequencies of oscillations. One of them is the high-amplitude oscillation which dominates at high acetone concentrations, and the other one is the low-amplitude oscillations which dominate at low acetone concentrations. Despite the complexity of the solution that contains bromate, oxalic acid, acetone, Mn(II), and sulfuric acid, this system should not contain two intervening oscillating systems, as in the case of chlorite−bromate−iodate, which presents the typical behavior of chlorite−iodate or bromate−iodate oscillation systems, depending on the experimental conditions.[8] We conclude that the complexities arise from the presence of the organic substrate (oxalic acid) and manganese ions by analogy with the BZ system containing manganese and malonic acid, which exhibits complex behavior, too.[5]

What is new in the present case is the capability of the system to show intermixed or separated high- and low-amplitude oscillations, depending on the experimental conditions. Classification of this behavior is difficult because of the batch nature of the experiment. However, some possibilities can be considered. The first of them is the presence of two limit cycles separated by a saddle point as proposed by Masełko et al.[8] to explain the birhythmicity and compound oscillations in the BrO_3^-−ClO_2^-−I^- system. By using their topological model, we can explain the presence of two separated trains of oscillations obtained with method 2 (Figure 3). In this case, we can suppose that the system starts to oscillate as it follows one limit cycle that grows up until it gets closer and closer to a saddle point that will make the system jump to another different limit cycle. Unfortunately, the batch experiment does not allow us to verify if hysteresis is present to allow a decision between the topological models presented by Masełko et al. in their paper (Figure 8II and Figure 8III). Otherwise, the results in Figure 1 are more difficult to explain using this topological model. Although this oscillation pattern has some similarity with period doubling behavior, it is not exactly the same one-to-one, high-to-low oscillation pattern that has been classified as a transient period doubling oscillation.[17,18] Certainly, transient chaotic behavior is a strong possibility for the behavior presented in Figure 1.

Both oscillating patterns we show here are different from the temporary nonoscillatory states observed by Wittmann et al.[19] in bromate−oxalic acid−acetone−Ce(IV)−sulfuric acid in batch. As both of their transitions, from oscillatory to nonoscillatory and from nonoscillatory to oscillatory states, can be classified as subcritical Hopf bifurcations, their system may be understood as having two subcritical Hopf bifurcations connected by a stable focus. As the differences between the system we studied and the Wittmann et al. system are the metal catalyst and sulfuric acid concentrations, we start to believe that the presence of two limit cycles is a fundamental property of this BZ reaction with oxalic acid−acetone mixed substrate.

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