Carbon Dioxide Evolution in a Belousov−Zhabotinsky Type Oscillating Reaction with Acetonedicarboxylic Acid

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Oscillations in the platinum redox potential during the reaction of bromate ions with acetonedicarboxylic acid catalyzed by Mn(II) ions were observed. The volume of gaseous carbon dioxide produced was measured. A nonoscillatory course was found both at the slow and rapid stirring rates for carbon dioxide evolution. The perturbation experiments suggest supersaturation during the Belousov−Zhabotinsky reaction with acetonedicarboxylic acid. Possible reasons for such observations are discussed.

Introduction

The Belousov−Zhabotinsky (BZ) reaction is the most extensively studied oscillating chemical reaction, and it remains a useful way of testing nonlinear dynamics.[1,2]The classical BZ reaction is the bromination and oxidation of malonic acid (MA) by acidified bromate ions in the presence of cerium ions. Replacement of the organic species or metal catalyst may result in quite different nonlinear behavior. The production of the bromide ion control species from organic reactions in the BZ system according to the Field, Körös, and Noyes (FKN) mechanism[3] is also expected when MA is replaced by any easily brominated dicarboxylic acid. Bromination of organic acids occurs via the enol form of the acid with bromine or hypobromous acid as brominating agents. In the case of MA, the products are BrMA and Br_2MA. Recently, it was found[4,5] that oxidation of MA and BrMA is not caused exclusively by the Ce^{4+} ions, but oxidation of BrMA and MA by acidic bromate and the CO_2 formation are well measurable processes.

Acetonedicarboxylic acid (ADA) is easily brominated and it may also give rise to bromide-controlled oscillations. We are aware of some studies of the ADA−cerium−bromate system published by Bhathena and Ojha.[6−7] Unfortunately, these papers, including abstracts, are not available to us.

However, ADA was selected to generate the supersaturated aqueous solution of carbon dioxide[8] according to reaction 1.

$$HO_2CCH_2COCH_2CO_2H \rightarrow 2CO_2(g) + CH_3COCH_3 \quad (1)$$

The critical supersaturation of carbon dioxide is quite large. Measurements from 40 to 50 °C and for $NaClO_4$ concentration up to 3 M indicate[8] that the threshold for nucleation of bubbles of carbon dioxide is 0.3−0.4 M and little dependent on ionic strength. This threshold is about 10 times the solubility of 0.034 M at 101.3 kPa and 25 °C. The supersaturation for carbon dioxide between 273 and 323 K decreases from 0.4 to 0.2 M.[9]

The decomposition of MA and some other dicarboxylic acids in concentrated sulfuric acid is known to give oscillatory gas evolution of carbon dioxide.[10] This reaction is the example of a class of oscillators (GEOs) in which the instability responsible for the oscillations is homogeneous nucleation of a gas bubble in a solution supersaturated with dissolved gas. The appearance of oscillations depends on the build up of supersaturation, and therefore, agitation plays an important role. The best oscillations are found when gentle stirring is maintained, while with vigorous agitation, gas is evolved in a smooth nonoscillatory fashion.[10]

The interesting topic is to speculate whether physical processes associated with supersaturation and gas release might feed back to affect the chemical processes leading to the gas production and to influence the oscillatory parameters of the bromate oscillators. The first, important step should be to find the supersaturation in the oscillatory reaction. It seems that acetonedicarboxylic acid is a good candidate for the formation of the supersaturated solution of carbon dioxide in the bromate oscillator. The present paper describes the CO_2 evolution in a Belousov−Zhabotinsky type oscillatory reaction with acetonedicarboxylic acid.

Experimental Section

All solutions were prepared with redistilled, deionized water and common reagent-grade chemicals (Merck, except $NaBrO_3$, which was from Fluka). 1,3-Acetonedicarboxylic acid (Fluka, purum) was kept at 4 °C. No stock solution of ADA was prepared. The weighted amount of ADA was dissolved in a small volume of water and then added into the reaction vessel. The following initial concentrations were used: 5×10^{-3} M ADA, 0.08 M $NaBrO_3$, 3.33×10^{-3}M $MnSO_4$, and 1.5 M H_2SO_4.

The experiments were carried out in a well thermostated (25.0 ± 0.1 °C) cylindrical glass reaction vessel (diameter 3.5 cm, height 7.2 cm). The volume of the reaction mixture was 30 mL with a free surface area above it of 7.98 cm^2. This value corresponds to the experiments when a commercial platinum indicator macroelectrode and a reference mercury sulfate electrode were inserted into the reaction solution. There were also two other holes in the stopper. One for a glass capillary tube (diameter 0.3 cm in the stopper, but 0.1 cm at the end) immersed into the reaction solution, through which CO_2 gas from a CO_2 pressure vessel was bubbled into the reaction solution to reach saturation before the BZ reaction with ADA was started. The second hole was for a glass tube (diameter 0.5 cm), which was connected via tubing to a 250 mL closed

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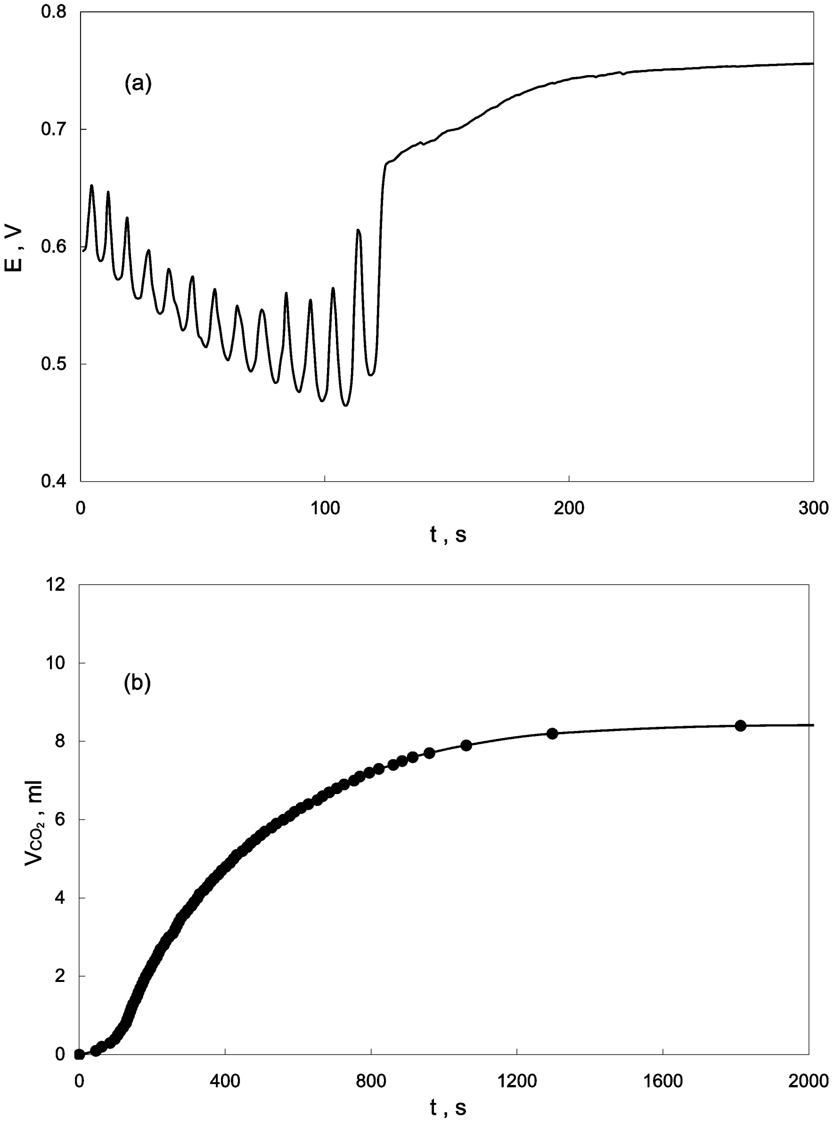

Figure 1. Dynamics of the BZ reaction with ADA. (a) The Pt redox potential, (b) the volume of carbon dioxide produced. Initial concentrations were 1.5 M H_2SO_4, 0.08 M $NaBrO_3$, 5 mM ADA, 3.33 mM Mn(II), at 25 °C, 80 revolutions min^{-1}.

Erlenmeyer-like flask reservoir containing 200 mL of water placed above the level of the reaction vessel.

Carbon dioxide saturation of both the BZ reaction mixture and the water reservoir at 101.3 kPa before the reaction started was reached by CO_2 bubbling (~600 mL min^{-1}) from the pressure vessel for at least 60 min. Then, bubbling was stopped, and the entire amount of CO_2 evolved during the BZ reaction was allowed to enter into the carbon dioxide-saturated water reservoir and accumulate only in the space above the water. The Erlenmeyer flask reservoir was equipped with a tap at the bottom, which, when opened, enabled the outflow of water. It was verified that in this experimental arrangement, the volume of water replaced corresponds to the volume of carbon dioxide produced. The time dependence of the exact volume of water flowing out was measured point-by-point by reading the water level in a calibrated buret. We were able to read the exact volume as often as we wished, because we had available a special sport stopwatch with data memory.

The reaction solutions were added into the reaction vessel in the order aqueous solution of H_2SO_4, Mn(II) ions, acetonedicarboxylic acid, and, finally, a small amount of $NaBrO_3$ (saturated by CO_2) was quickly added, after which the oscillating reaction was started. The reaction solution was stirred magnetically with a Teflon-coated stirrer (polygon-shaped, 2 cm × 0.8 cm). The stirring rate of the magnetic stirrer was kept usually constant at the values 80 or 600 rpm. For comparison, several experiments in the initially nitrogen or oxygen atmosphere were performed. A schematic illustration of the experimental setup used for the similar oxygen gas measurement in the Bray−Liebhafsky system can be found in ref 11 and for carbon dioxide production in the BZ reaction with oxalic acid in ref 12.

Oscillations in the BZ mixture were also followed potentiometrically by recording the time dependence of changes in the platinum redox potential using a Radelkis polarograph and/or Metex connected to a PC.

Results and Discussion

We measured the time dependence of the Pt redox potential and of the volume of CO_2 produced during the uncatalyzed reaction of bromate ions with ADA (5×10^{-3} M in 30 mL of the reaction solution) without a catalyst at 80 and 600 rpm. No potential oscillations were recorded. The curve for CO_2 evolution at slow stirring suggests a slow and autocatalytic reaction. The other possibility is that the reaction solution becomes supersaturated. Typically, the volume of ~1 mL of CO_2 is evolved after a time of about 3000 s at 600 rpm, while at 80 rpm negligible gas evolution was observed at the same time. If we

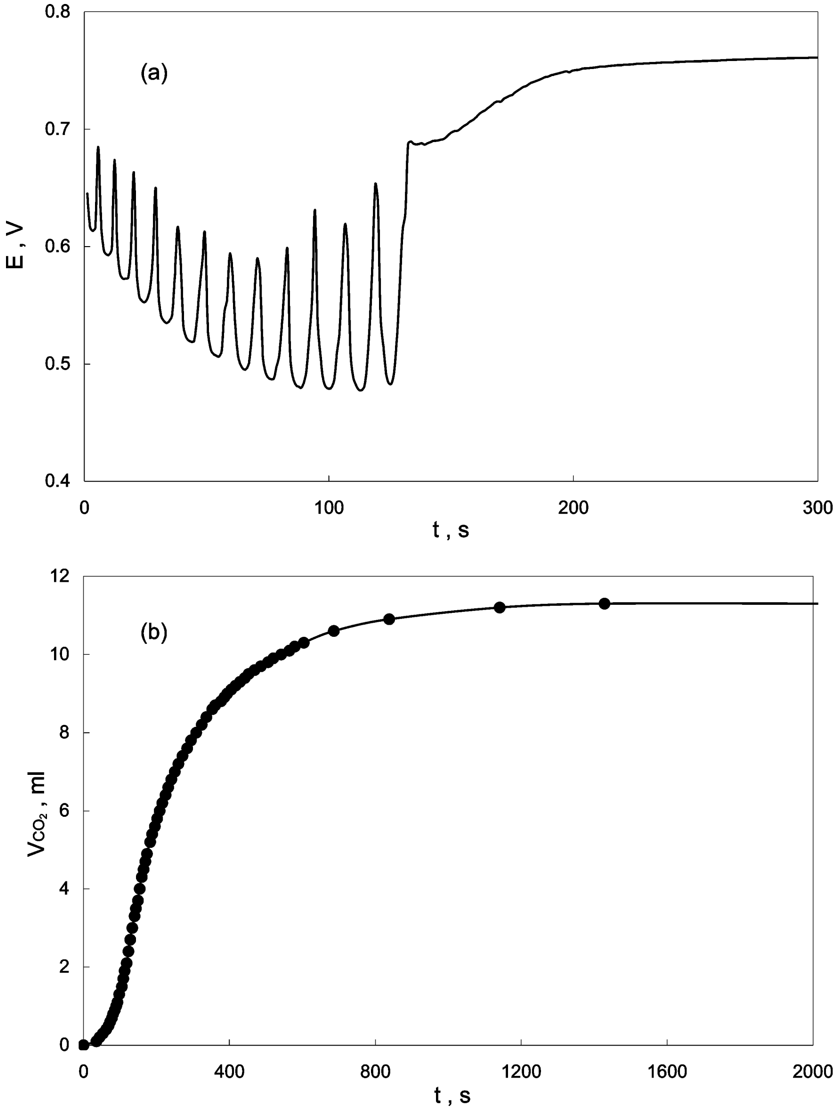

Figure 2. Dynamics of the BZ reaction with ADA. (a) The Pt redox potential, (b) the CO_2 volume. The same reaction conditions as in Figure 1, but only 600 revolutions min^{-1}.

assume an ideal gas, the calculated final volume of CO_2 in the case of the total decarboxylation of both carboxylic groups of ADA should be 7.34 mL. In the case of nonideal behavior, this volume falls to 6.86 mL. However, this amount could be substantially higher if the further oxidation of ADA or various molecular intermediates generates CO_2.

With the Mn(II) catalyst (3.33×10^{-3} M), oscillations in the Pt redox potential were observed under the concentration conditions (1.5 M H_2SO_4, 0.08 M BrO_3^-, and 5×10^{-3} M ADA) in the reaction solution saturated by carbon dioxide (Figure 1a). The oscillating reaction shows no induction period. Oscillations have the amplitude of ~50 mV and last ~120 s. The typical autocatalytic curve was found for the time dependence of the volume of carbon dioxide evolved (Figure 1b), but the supersaturation cannot be ruled out at slow stirring again. More than 8.4 mL of CO_2 is produced after 2000 s. Oscillatory parameters are changed at rapid stirring (Figure 2). The larger amplitude of the redox potential oscillations (up to 185 mV during 130 s) can be observed. Visually, the oscillating color change to pink of Mn(III) ions can also be seen. In Figure 2b the time dependence of the volume of gaseous CO_2 evolved at rapid stirring (600 rpm) is depicted. The amount of carbon dioxide released (11.2 mL) indicates the oxidation of additional carbon atom.

The similar tendency in the oscillatory behavior was found also in the nitrogen and/or oxygen atmosphere. The reaction solution and the water reservoir were purged and saturated with N_2 or O_2 at 101.3 kPa and run as for the CO_2-saturated system. We found no significant difference whether the reaction solution was saturated with nitrogen or oxygen at the same rate of stirring. The larger amplitude of oscillations and final volumes of CO_2 evolved at rapid stirring are as a rule for every case.

Due to the possibility of the spontaneous decomposition of ADA (reaction 1) not only the supersaturated solution of CO_2 but the solution of acetone during the reaction could be formed as well. The global dynamic of the classical BZ reaction with MA was altered with the addition of the methyl ketones.[13] The effect of acetone in the classical BZ reaction is an enlargement of the IP and an increase in the number of oscillations. However, with a very high concentration of acetone the BZ reaction with MA does not oscillate.[13] The addition of 5×10^{-3} M acetone, which can also be easily brominated to our reaction system with ADA, does not influence the oscillatory redox potential traces. Nevertheless, there are some quantitative differences in the amount of the CO_2 gas evolved at both stirring rates. The final volumes of CO_2 were 7.1 and 10.4 mL at 80 and 600 rpm, respectively. These amounts and the shape of the volumetric

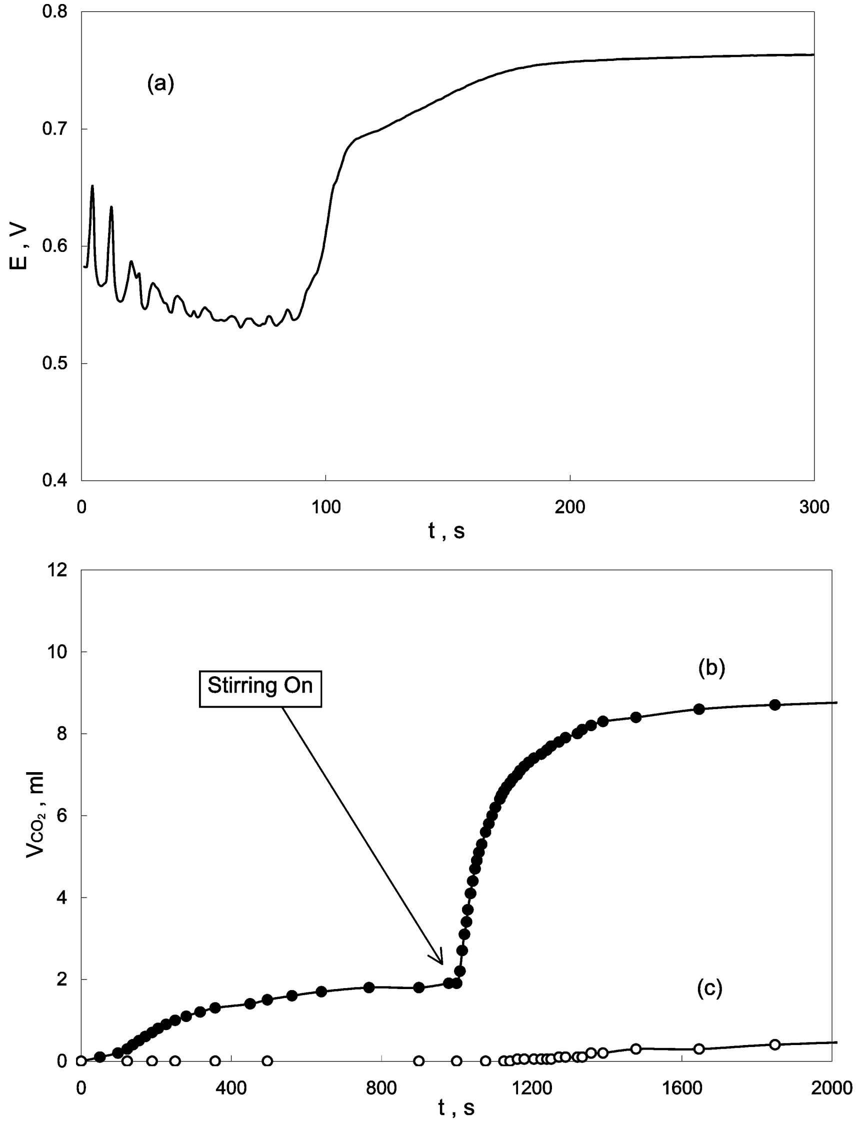

Figure 3. The perturbation of time evolution of the BZ reaction system with ADA initially unstirred but rapidly stirred after 1000 s. (a) The Pt redox potential without a perturbation, (b) the carbon dioxide volume evolved, (c) blank with no ADA added. Initial concentrations are those in Figure 1.

traces do not rule out again supersaturation at slow stirring and decarboxylation of additional carbon atoms.

In continuously stirred tank reactors (CSTR), the stirring effects in nonlinear chemical systems can usually occur because of imperfect mixing of the feed streams.[2,14] In batch reactors, several mechanisms have been proposed. Most of the observed effects can be explained on the basis of concentration fluctuations,[2,15−18] bromine loss to the gas phase,[19−21] or the effect on the rate constant of diffusion-controlled reactions.[22] In the classical BZ reaction, more rapid stirring will increase the rate at which oxygen, which can react with some of the organic intermediates, is taken up by the reaction mixture.[1,2] Our experiments with ADA, performed in a N_2 and O_2 atmosphere, show no observable differences in the potentiometric or volumetric traces at the same rate of stirring. These observations do not support the role of the mass transfer of oxygen in stirring effects in this case.

In general, most of our experiments were done at 101.3 kPa under carbon dioxide atmosphere. The reaction usually proceeds continuously after saturation by CO_2 under constant stirring. Figure 3 shows both potentiometric (part a) and volumetric (part b) traces for the system, which is at first unstirred. At a selected time (in this case after 1000 s), the dissolved CO_2 is released by sudden initiation of rapid stirring (600 rpm). Evolution of CO_2 is fast and the rate of outflow of replaced water at the beginning is limited by the tap diameter of the reservoir. It seems that the perturbation experiment in Figure 3 presents evidence of the supersaturation during the BZ reaction with ADA. The supersaturation of the aqueous solution of carbon dioxide was released by rapid stirring (600 rpm) and the final volume of CO_2 achieved a value similar to that obtained if the reaction solution was stirred continuously and rapidly with no possibility to produce the supersaturation. For comparison, in Figure 3c we can see the response of the reaction system under the same conditions, but with ADA omitted to avoid the carbon dioxide production and supersaturation, suddenly perturbed at 1000 s by rapid stirring. Only a negligible amount of CO_2 was released from the saturated solution after 1000 s and little after 1400 s.

An experimental procedure for measurement of carbon dioxide, as the only final gaseous product of the BZ reaction with oxalic acid[23] and malonic acid,[24] was described. Oscillations of the flame ionization detector signal, corresponding to the oscillations of the carbon dioxide evolution rate, were observed only for appropriate values of the variable control parameter (nitrogen gas flow). In spite of the probability of formation of a supersaturated solution of CO_2, our volumetric traces recorded (Figures 1b, 2b, and 3b) at various stirring do not indicate any evidence for oscillations of the rate of CO_2 production in the BZ reaction with ADA.

However, the rate of production of CO_2 can be varied for various stages of the BZ reaction with ADA, depending on different oxidation states of bromine and a catalyst as well. Therefore, we can hardly exclude the possibility that the concentration of the oxidized form of the catalyst can be varied by an oscillatory manner such as the measured potentiometric traces indicate, while at the same time, the production of carbon dioxide could be monotonous under the experimental conditions applied here, or the volumes of evolved gaseous CO_2 during one potential oscillation are below the limit that we are able to measure.

The basic way in which molecular bromine gas generated by the reaction can be removed from aqueous reactant solution here is stirring. Since Br_2 often has significant effect on the chemistry of the bromate oscillators, one may expect that changes in the rates of stirring will affect the rate of the interphase transport of bromine and the oscillatory behavior.

The role of supersaturation of aqueous solutions of carbon dioxide observed in our experiments remains to be explained. At present, in agreement with reviewers, we can hardly imagine any feedback influence of carbon dioxide unless CO_2 is involved in some sort of reversible reaction or the catalyst is attacked. However, a great number of small bubbles of carbon dioxide, which are formed and escape from the reaction solution to the space above it, might accelerate the vaporization of molecular bromine and in this way contribute to the change of the oscillatory parameters. In addition, the supersaturated solution of carbon dioxide is in metastable equilibrium, and supersaturation is destroyed by rapid stirring. Although the CO_2 is generated by homogeneous chemical reaction, homogeneously nucleated bubbles grow, rise, and escape and in this way they make some heterogenity in the reaction solution. The probability, extent, and distribution of the concentration fluctuations are changed, and dynamic behavior of the system could be affected.

We cannot rule out that the supersaturated solutions of CO_2 are generated during the classical Belousov−Zhabotinsky reaction with malonic acid as well. Another candidate for testing of the possibility that chemical processes may couple with nucleation, supersaturation, and gas evolution is the oscillatory Briggs−Rauscher (BR) reaction with malonic acid as a substrate. Organic radical species, produced from malonic acid during the BR reaction, could react with oxygen, which is the dominant gaseous product of the BR reaction, and just the supersaturated solution of oxygen was prepared by the iodide-catalyzed decomposition of hydrogen peroxide, which is one of the reactants in the BR reaction.[9,25] Research is in progress to test the above hypothesis and it will be the subject of our next paper.

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