Perturbation of the Oscillatory BZ Reaction with Methanol and Ethylene Glycol: Experiments and Model Calculations

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This study is initiated by a recent discovery, according to which a water soluble polymer, poly(ethylene glycol) (PEG), affects the dynamics of the Belousov−Zhabotinsky (BZ) reaction in a characteristic way. As various polymers and polymer-based hydrogels are often applied in nonlinear chemical experiments, it is an interesting question whether the effect of a polymer can be attributed exclusively to its reactive endgroups (here primary alcoholic groups) or if the macromolecular nature of the perturbant might be also important. In this paper, as a first step, the results of batch experiments are presented applying only small molecules, namely ethylene glycol (the monomer of PEG) and methanol (a more simple primary alcohol), as perturbants of the BZ reaction. The reaction was followed by monitoring the rate of the carbon dioxide evolution. The experimental results are compared with model calculations, applying the latest model of the BZ reaction, the Marburg-Budapest-Missoula (MBM) mechanism extended with the perturbing reactions. The rate of the perturbing reactions (reaction of the acidic bromate with the alcohol producing the autocatalytic intermediate bromous acid) was determined in separate spectrophotometric experiments. Experiments and model calculations show a good qualitative agreement (alcoholic perturbations increase the induction period and the frequency of the oscillations and decrease the amplitude), but disagreements were found on a quantitative level. Because the mechanism of the alcoholic perturbation, especially in the case of methanol, is mostly clarified, it is the MBM mechanism which should be modified somewhat in the future. As the reaction dynamics responds to the alcoholic perturbations rather sensitively, simulating these perturbation experiments can help to test new mechanistic proposals for the BZ reaction.

Introduction

This paper presents experimental data and model calculations on alcoholic perturbations of the oscillatory BZ reaction. This work, however, is only the first part of a longer program of perturbation experiments planned with water-soluble polymers. The present introduction discusses the preliminaries and explains the motivations of the whole research program.

Polymers in Nonlinear Chemistry. Study of various nonlinear phenomena in chemistry such as oscillations, chaos, waves, and pattern formation became a field of traditional research in the past decades.[1−4] Macromolecules play a more and more important role in those investigations.[5] Among the first polymers introduced in this field were hydrogels (cross-linked polymeric networks) applied in continuously fed unstirred reactors (in short: CFURs) to establish a convection-free inert medium for reaction diffusion systems. Chemical waves[6] and later on Turing patterns[7] were studied in such reactors. (Historically, gels were applied even earlier in Petri dish batch reactors. These gels, however, were mainly inorganic hydrogels, namely silica gel, used by Kuhnert[8] or fumed silica (Cabosil) introduced by Winfree.[9] For a review of the various gels applied in the BZ reaction, see Yamaguchi et al.[10])

Very soon, however, it was realized that in many experiments the gel medium was not completely inert: e.g., the gel was able to change the velocity of a propagating chemical wave[11,12] or it could contribute to the formation of a "fossil type" Turing structure.[13] Especially when water soluble polymers, such as soluble starch or poly(vinyl alcohol) (PVA), were applied as Turing pattern indicators,[14] these macromolecular reagents proved to be crucial not only in the observation but also in the very formation of these patterns. This is because a selective and reversible reaction of the macromolecule with the activator species of an activator−inhibitor type reaction system slows down the apparent diffusion of the activator compared to that of the inhibitor, which is an important prerequisite for the experimental observation of a Turing bifurcation. Another interesting example for the application of polymeric reagents is the creation of a self-oscillating gel[15] by coupling chemical oscillations with osmotic swelling. The above examples were mentioned only to demonstrate that perturbation of nonlinear chemical systems with polymeric reagents can lead to various new dynamic phenomena, thus it is worth to study the chemical mechanism of these perturbations.

Finally, we can mention that polymers can be not only reagents in the BZ reaction but products as well: in the presence of an appropriate monomer such as acrylonitrile, free radicals (e.g., malonyl radicals) formed in a BZ system can initiate the polymerization of the monomer.[16−18]

Separating the Effect of the Polymer Backbone and Its Side Groups: Perturbation of the BZ System with Poly(vinyl alcohol) (PVA). When investigating the chemical mech-

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anism of a perturbation with a polymer, it is an important question whether the polymer affects the reaction system by its reactive side groups only or the polymeric nature of the reagent also matters. This question can be answered by conducting parallel experiments with the polymer and with a low molecular weight reagent containing the same reactive side group. Recently, Horváth et al.[12] studied such a problem, namely the interaction of PVA with the BZ reaction mixture. They compared the effect of PVA with that of 2-propanol, a small molecular weight secondary alcohol. (The structure of this small molecule is rather close to that of the polymer repeating unit in PVA.) In a batch reactor both reagents increased the frequency and decreased the amplitude of the oscillations, but the secondary alcoholic group of the 2-propanol proved to be a stronger perturbant compared to the same group in PVA. Quantitative modeling of the observed perturbation effects was not attempted, however, because one of the component reactions—the reaction between PVA and acidic bromate—proved to be too complicated for a thorough kinetic study.[12] Another problem was that in the case of the 2-propanol-bromate reaction the product acetone can be brominated, which makes the PVA-2-propanol comparison more difficult.

A Versatile New Perturbant: Poly(ethylene glycol) (PEG). Recently, Cavasino et al.[19] performed preliminary experiments with PEG—another water-soluble polymer—as a perturbant of the BZ reaction. They obtained promising results: the reaction dynamics responded to the perturbation sensitively and in a way which could be characterized quantitatively. Moreover, PEG is also commercially available in various molecular weights. This polyether contains two (primary) alcoholic endgroups. We hope that perturbation of the BZ system with PEG gives a better chance to compare the polymer—monomer or the polymer backbone—end group effects with model calculations. We think so because (i) more information is available about the possible reactions of primary alcohols in a BZ system[21,22]; (ii) ethylene glycol (EG), the monomer of PEG, is a stable compound (not like vinyl alcohol in the case of PVA), thus perturbation experiments are possible with the monomer here; (iii) perturbation experiments with PEGs of various molecular weights are more informative here as the ratio of the reactive endgroups to the polymer backbone can be varied this way (in the case of PVA each repeating unit of the polymer contains a secondary alcoholic group); and finally (iv) methoxylated PEGs are also commercially available. These polymers are also water soluble and contain no alcoholic endgroups at all. Therefore the perturbation effect of the polymer backbone on the BZ reaction can be studied separately.

Methanol and Ethylene Glycol as Perturbants of the BZ Reaction. To understand the effect of the primary alcohol endgroups in the present paper, we study two primary alcohols, methanol (MeOH) and ethylene glycol, as perturbants. Methanol was chosen because its most important reactions in the BZ reaction were clarified by Försterling et al.[21] According to them, methanol reacts with acidic bromate in a rate-determining first step (R1; here we follow the notations of the cited paper):

$$\mathrm{CH_3OH + HBrO_3 \rightarrow CH_2O + HBrO_2 + H_2O} \qquad \mathrm{(R1)}$$

producing the autocatalytic intermediate bromous acid and formaldehyde. Then, in a rapid second step, formaldehyde reacts with acidic bromate to produce one more bromous acid and formic acid, which is an inert endproduct in the BZ system:

$$\mathrm{CH_2O + HBrO_3 \rightarrow HCOOH + HBrO_2} \qquad \mathrm{(R2)}$$

In the BZ system, the autocatalytic intermediate produced in R1 and R2 takes part in the autocatalytic cycle or removes the inhibitory bromide, depending on the state of the oscillatory reaction where autocatalytic and inhibitory phases follow each other alternately. In a reaction where only methanol and acidic bromate was present, Försterling et al.[21] could determine the rate constant of the following overall net process:

$$\mathrm{CH_3OH + HBrO_3 \rightarrow HCOOH + HOBr + H_2O} \qquad \mathrm{(R6)}$$

which is a sum of R1, R2, and R5, the disproportionation of bromous acid:

$$\mathrm{2HBrO_2 \rightarrow HOBr + HBrO_3} \qquad \mathrm{(R5)}$$

As R2 and R5 are fast reactions, the rate of the whole net process R6 is determined by R1. Thus, the $HBrO_2$ inflow caused by the perturbing methanol in the BZ reaction can be determined as

$$2k_6\cdot[\mathrm{CH_3OH}]\cdot[\mathrm{HBrO_3}]$$

because both R1 and R2 produce one $HBrO_2$ molecule. By following the concentration of the product HOBr with spectrophotometric measurements, Försterling et al.[21] determined a pseudo first-order rate constant k_6' where

$$k_6' = k_6 \cdot[\mathrm{HBrO_3}]$$

According to their measurements in a solution that is one molar for both sulfuric acid and sodium bromate at 20 °C, $k_6' = 3.8 \times 10^{-3}\ \mathrm{s^{-1}}$. As we will see, in our model calculations another form of the rate law was applied (see section entitled Model Calculations with the MBM Mechanism), which contains the bromate and the hydrogen ion concentration as variables directly, instead of the bromic acid. Nevertheless, as long as the hydrogen ion concentration is not varied, the two rate laws are equivalent. Most probably ethylene glycol takes part in analogous reactions, but presently no information is available about the rate of these processes. Thus, among others, it is an aim of the present paper to obtain kinetic data on the ethylene glycol—acidic bromate reaction.

Aims of the Model Calculations. The first detailed mechanism of the BZ reaction was suggested by Field, Kõrös, and Noyes (FKN) thirty years ago.[23] Its skeleton version, the Oregonator,[24] was extended and modified later by Györgyi, Turányi, and Field[25,26] mainly because of the discovery of a second negative feedback loop via organic free radicals[27,28] and other complexities in the organic subset of the reaction. That subset was the subject of a systematic research mainly by HPLC in the past years.[29−32] As a result of these investigations, a more realistic mechanism was suggested just recently,[33] the so-called Marburg-Budapest-Missoula (MBM) model. Thus it is another motivation of the present work to apply the MBM model to simulate the alcoholic perturbations of the BZ systems. Such computer simulations can show the capabilities of the new model on one hand and, on the other hand, they can help to check the proposed mechanism of the alcoholic perturbations.

Measuring the Induction Period and the Frequency of Oscillations in Batch Experiments. Both experiments and model calculations were carried out in batch conditions. It is known that the best way for mapping nonlinear behavior of a chemical system is to perform experiments in a continuously fed stirred tank reactor (CSTR), applying various parameters (such as flow rate, input reagent, or perturbant concentrations).[1−4] This way nonequilibrium phase diagrams can be produced in the parameter space giving a detailed description of the system's dynamics. Nevertheless, batch experiments can also give valuable information and they are easier to carry out. For example it is known that in the case of the BZ reaction with malonic acid substrate, a critical bromomalonic acid (BrMA) concentration should be reached before oscillations can appear. (This is because BrMA generates the inhibitory bromide which "switches off" the autocatalytic bromous acid production.) In a CSTR experiment, this means that oscillations appear only above a critical residence time (that is below a critical flow rate). In batch experiments it is the so-called induction period that plays a similar role. As an alcoholic perturbation establishes an extra bromous acid inflow, it is logical to assume that a stronger bromide source is needed now to suppress the autocatalytic process. That requires a higher BrMA concentration, which means a longer induction period. Moreover, in the oscillatory regime, the inflow of the autocatalytic intermediate shortens the oscillatory period. This is because the bromous acid inflow removes the inhibitory bromide and shortens this way the time the system spends in the reduced ("high bromide") quasi steady state. Thus measuring the induction period and the frequency of the oscillations as a function of the perturbing alcohol concentration can provide chemically significant dynamic data, which can be compared with the results of model calculations.

CO_2 Measurements. In most cases potentiometric or spectrophotometric techniques are applied to follow the dynamics of the BZ reaction. Here we have chosen a different technique developed in our laboratory:[34] it was the rate of the CO_2 evolution, which was measured and recorded in our experiments. This method was applied for two reasons. (i) Potentiometric and spectrophotometric techniques measure physical quantities that depend on the concentration of one (or more) intermediates. Those methods, however, cannot distinguish easily between different quasi steady states with high or low conversion rates or even between quasi steady states and equilibrium states because the concentration level of a single chemical species usually does not give information about the rate of the chemical processes. On the other hand, as the evolution rate of the end product CO_2 reflects the rate of the overall reaction, a high or low signal of our apparatus always indicates a proportionally high or low chemical activity of the system. We remark here that membrane inlet on line mass spectrometry is also a viable alternative for selective CO_2 measurements in BZ reactions as was shown by Degn and Lauritsen[35] and also by Schmidt and Vielstich.[36] (ii) Another motivation was to test the new MBM mechanism of the BZ reaction by comparing the measured and calculated CO_2 evolution rates. Such a comparison is all the more interesting because an early comparison made by Försterling et al.[37] gave a 2 order of magnitude disagreement between the measured and calculated values when the original FKN mechanism was applied in the model calculations.

Experimental Section

Chemicals. Malonic acid (Fluka, puriss.), $Ce(SO_4)_2 \cdot 4\ H_2O$ (Merck, p.a.), $NaBrO_3$ (Fluka, puriss), H_2SO_4 97% (J. T. Baker), methanol (Merck, for chromatography), and ethylene glycol (Reanal p.a.) were used as received. All solutions were prepared with doubly distilled water.

CO_2 Measurements on the BZ Reaction. *Preparation of the Reaction Mixture*. Components of the BZ reaction were injected into the reactor in the following order: 0.5 mL 0.4 M malonic acid solution (in 2 M sulfuric acid), 0.5 mL 0.12 M $NaBrO_3$ solution (in water) and (i) 0.5 mL water when studying the unperturbed BZ system or (ii) 0.5 mL aqueous solution containing the perturbant in various concentrations for perturbation experiments. The latter solutions were diluted from 0.15 M MeOH or 0.15 M ethylene glycol stock solutions. The mixture was bubbled with the carrier nitrogen gas for 0.5 min. Then the reaction was started by injecting the catalyst, 0.5 mL 1.6×10^{-3} M $Ce(SO_4)_2$ solution (in 2 M sulfuric acid). Thus, after mixing, the initial concentrations of the main reactants were: 0.1 M malonic acid, 0.03 M bromate, 4×10^{-4} M Ce^{4+}, and 1 M sulfuric acid in a total volume of 2 mL.

Injecting the reactants into the reactor. *Role of the carrier gas*. A plexiglass injector similar to the ones applied in gas chromatography was constructed. The reaction components were injected via the silicon rubber septum of that injector by a syringe into a constant nitrogen gas stream (40 cm^3/min). The gas stream played multiple roles here. First it carried the liquid reactants to the reactor and created anaerobic conditions there for the reaction. It also provided a constant stirring of the reactor by bubbling through the reaction mixture continuously. Most importantly, however, the gas stream striped the evolving CO_2 from the reaction mixture and carried it to the measuring system.

Reactor. A double walled glass test tube (inner diameter: 7 mm, total volume: 3 cm^3) was applied as a reactor. It was thermostated to 20 °C. The carrier gas was introduced via a narrow Teflon tubing (outer diameter: 1.7 mm, inner diameter: 0.8 mm) at the bottom of the reactor.

Apparatus. The CO_2 measuring instrument was similar to the one applied in one of our previous experiments.[34] Here the nitrogen carrier gas containing the CO_2 was mixed directly with a hydrogen gas flow (flow rate: 40 cm^3/min), then it was converted to methane on a nickel catalyst. Finally the methane content of the gas mixture was measured by a flame ionization detector (FID). Further details of the method and the apparatus can be found in ref 34.

Spectrophotometric Measurements on the Acidic Bromate−Alcohol Reactions. *Preparation of the Reaction Mixture*. Sodium bromate, methanol, ethylene glycol, and sulfuric acid were of commercial analytical quality (Fluka) and used without further purification. Deionized water from reverse osmosis (Elga, model Option 3), having a resistivity higher than 1 MΩ cm, was used to prepare all solutions. Solutions were prepared directly in the cuvette adding 0.6 mL H_2O + 0.6 mL 5 M H_2SO_4 + 1.5 mL 2 M $NaBrO_3$ + 0.3 mL 0.1 M MeOH/ethylene glycol.

Instrument. Measurements have been carried out following HOBr absorbance in a quartz cuvette ($d = 1$ cm) at 330 nm with a computer-controlled Beckman model DU-640 spectrophotometer, equipped with thermostated compartments and stirring apparatus. The temperature of all the experiments was regulated to 20.0 ± 0.1 °C with a thermostat HAAKE model D8.

Results

CO_2 Evolution in the Unperturbed BZ System. Figure 1 shows the behavior of the unperturbed BZ system. The recording of the FID signal displayed in Figure 1 starts with the injection peak. This peak is due to the variable atmospheric CO_2 content of the Ce^{4+} solution injected to the reactor at the start of the reaction; consequently its height does not provide any relevant information. The position of this peak is important, however, as it marks the effective start of the measurement. (All events are delayed in the diagram because a certain time (about 30 s) is necessary for the carrier gas to elute the CO_2 formed in the reactor to the catalytic converter and then carry the methane

TABLE 1: Induction Period, Period (τ), and Amplitude (A) of Oscillations of the Test BZ System as a Function of the Initial Methanol (MeOH) and Ethylene Glycol (EG) Concentration[a]

perturbant↓	concentrated/mM →	0 (Figure 1)	3.75 (a)	9.38 (b)	18.75 (c)	28.13 (d)
MeOH Figure 2	ind per/s	(140)+1150	(20)+1150	1500	2120	2290
	τ (osc per)/s	124	55	39	29	27
	A (amplitude) μmol/(s·dm^3)	3.1	1.9	1.1	0.7	0.5
EG Figure 3	ind per/s	(140)+1150	1230	1350	1580	no oscillations
	τ (osc per)/s	124	64	42	20	
	A (amplitude) μmol/(s·dm^3)	3.1	2.2	1.3	0.4	

[a] Whenever it was possible, the total induction period was split to a preinduction and a real induction period. (The former is given in parentheses.) As the preinduction time was practically zero for the perturbed systems with 9.38 mm or larger alcohol concentrations, such separation was not possible there. τ and A are averages of the first five oscillations.

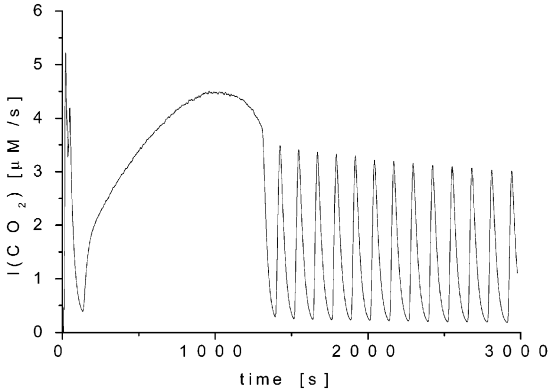

Figure 1. Reaction dynamics of the BZ system without any perturbant. CO_2 evolution rate measured in a batch reactor as a function of time. The unit of that rate is μmol/s·dm^3. Initial concentrations: malonic acid $[MA]_0 = 0.1$ M, $[NaBrO_3]_0 = 0.03$ M, $[Ce^{4+}]_0 = 4 \times 10^{-4}$ M, and $[H_2SO_4]_0 = 1$ M. The length of the induction period is 1250 s. The time period of the oscillations $\tau = 124$ s (an average of the first 5 oscillations).

further to the detector. Any calculation with this time delay can be omitted, however, if the time of the injection peak maximum is regarded as an actual zero time.) Right after the injection peak there is a second peak partially merged with the first one. This peak is due to the CO_2 produced in the Ce^{4+}−malonic acid reaction caused by the high initial Ce^{4+} content of the reaction mixture right after the injection. Because the autocatalytic reaction starts only later, the Ce^{4+} concentration and the rate of the CO_2 evolution fall to a minimum. The time interval between the injection peak and this minimum is the so-called preinduction period.

After this short period, the start of the real induction period is marked by a sharp increase in the CO_2 evolution due to the start of the autocatalytic reaction. As can be seen in the real induction period, the rate of the CO_2 evolution first grows and, after reaching a flat maximum, declines gradually. The end of the induction period, which is the start of the oscillatory regime, is indicated by the sharp fall in the CO_2 evolution due to a temporary halt of the autocatalytic processes. The oscillatory regime is in fact a series of such temporary halts and restarts of the CO_2 evolution. It is interesting to observe that the minimum of the oscillations is close to zero in Figure 1, thus the temporary halt is nearly complete in that experiment.

CO_2 Evolution in the Methanol and Ethylene Glycol Perturbed BZ Systems. Next the experiment shown in Figure 1 was repeated with various initial methanol concentrations. The results are depicted in Figure 2. As Figure 2 shows, the alcohol has four characteristic effects: (i) the methanol shortens or eliminates the short preinduction period; (ii) increases the length of the real induction period; (iii) decreases the period; and (iv) decreases the amplitude of the oscillations. Quantitative data on these effects are given in Table 1.

For comparison, experiments were performed with ethylene glycol as a perturbant instead of methanol but applying the same concentrations. The results of these experiments are shown in Figure 3 and in Table 1 as well.

Qualitatively, ethylene glycol has the same effect on the BZ reaction as methanol: it eliminates the preinduction period and increases the time of the real induction period; moreover, decreases the time period and the amplitude of the oscillations. Even the concentration range where the two different perturbants are effective is rather close. Nevertheless, there are also some quantitative differences between the effect of MeOH and ethylene glycol, as Table 1 indicates.

It seems that at low concentrations it is the methanol that is more effective in lengthening the induction time and also in shortening the time period and the amplitude of the oscillations. At higher perturbant concentrations, however, the methanol remains superior only in lengthening the induction time, and ethylene glycol decreases the time period and the amplitude of the oscillations more effectively. In case of the highest concentrations of Table 1, ethylene glycol is able to eliminate oscillations while this level of MeOH still allows oscillations.

Results of the Spectrophotometric Experiments on the Methanol−Bromate and Ethylene Glycol−Bromate Reactions. When acidic bromate reacts with methanol the main product is HOBr according to reaction R6. If any further reaction of HOBr with the methanol is neglected and the relative changes in the bromate concentration are small then the rate law according to Försterling et al.[21] is

$$d[HOBr]/dt = k_6' \, [MeOH]$$

Under these ideal conditions the amount of HOBr produced after infinite time is equal to the initial methanol content:

$$[MeOH]_0 = [HOBr]_\infty$$

and the following balance equation holds:

$$[MeOH] = [MeOH]_0 - [HOBr]$$

Thus, if the hypobromous acid concentration is denoted by c, the following differential equation holds:

$$dc/dt = k_6' \, (c_\infty - c)$$

Consequently for $A(t)$, the absorbance measured by the spectrophotometer as a function of time, the following relationship can be derived:

$$\ln\{[A_\infty - A(t)]/A_\infty\} = -\, k_6' t$$

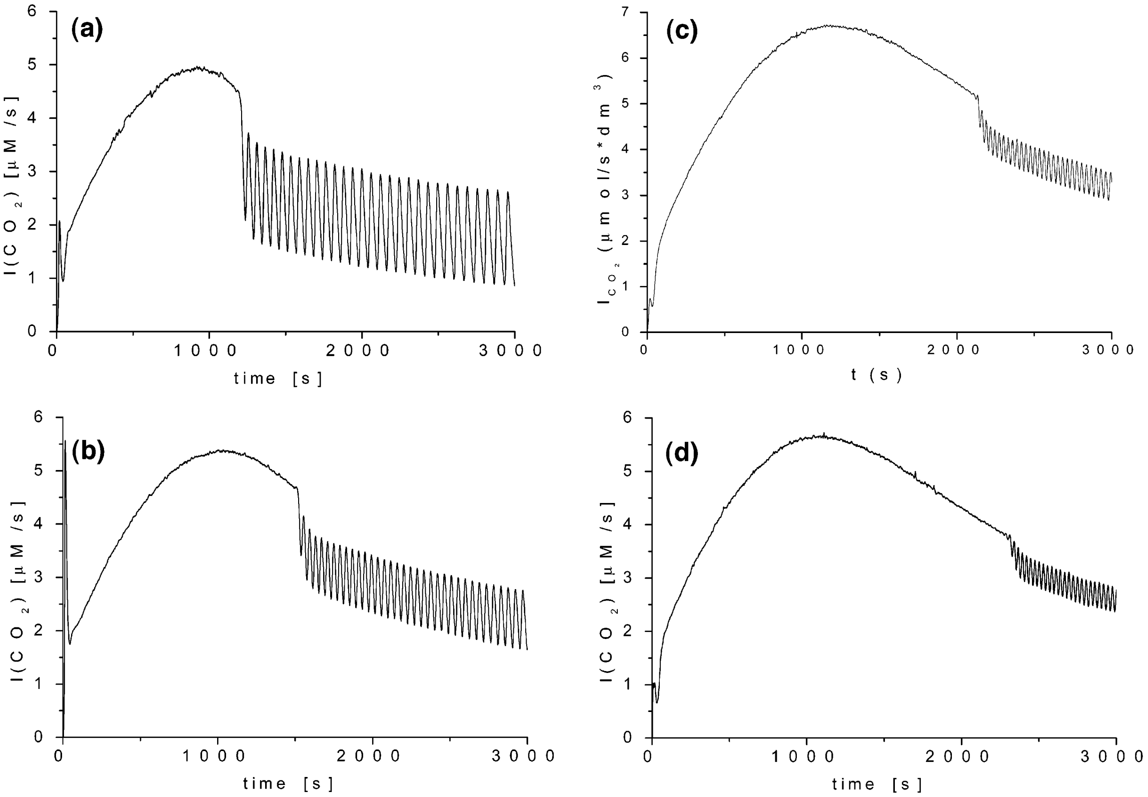

Figure 2. Dynamics of the BZ system perturbed with methanol. Initial perturbant concentrations: $[\text{MeOH}]_0$ = (a) 3.75 mM, (b) 9.38 mM, (c) 18.75 mM, and (d) 28.13 mM. The perturbing methanol concentration range was chosen to obtain characteristic stages of the perturbation. Observe that the highest methanol concentration applied here does not extinguish oscillations yet. All other concentrations are given in figure caption 1.

and depicting $\ln\{[A_\infty - A(t)]/A_\infty\}$ versus time should give a straight line, the slope of which is the rate constant k_6'. According to Försterling et al.,[21] for HOBr at 330 nm $\epsilon = 32$ M^{-1} cm^{-1}.

The curve shown in Figure 4 a) exhibits a maximum between 2000 and 3000 s. This observation suggests that the reaction is more complex than it was assumed, and a further reaction of HOBr with methanol also proceeds on the time scale of the experiment. That reaction was already observed by Försterling et al.,[21] who found that in addition to HOBr, some Br_2 also appeared among the products of the reaction, and the final HOBr yield of reaction R6 was only 86%. Their initial methanol concentration was around 10^{-3} M. In our experiments the methanol concentration was much higher (as our cuvette was 10 times shorter we had to apply a higher methanol concentration), consequently the maximum HOBr yield was even lower (around 60%). All of these can lead to complications when calculating k_6' from the linearized diagram.

To avoid these problems (i) A_∞ was not determined from the experiments but it was calculated from the initial alcohol concentration and the extinction coefficient of HOBr. Thus the value of $A_\infty = (32\ \text{M}^{-1}\ \text{cm}^{-1}) \times (0.01\ \text{M}) \times (1\ \text{cm}) = 0.32$ was applied in the calculations. (ii) Only the first 200 s of the measurements were selected to determine the initial slope of the linearized diagram from which k_6' was determined. According to our measurements performed in 1 M sulfuric acid and in 1, 0.3, and 0.15 M bromate solutions, $k_6'(\text{MeOH}) = (3.6 \pm 0.6) \times 10^{-3}\ \text{M}^{-1}[\text{BrO}_3^-]\ \text{s}^{-1}$. This is in good agreement with the value $k_6'(\text{MeOH}) = 3.8 \times 10^{-3}\ \text{s}^{-1}$ found by Försterling et al.[21] in a 1 M bromate solution, thus we have used their result in the calculations. Actually, one reason to repeat the determination of k_6'(MeOH) was to check the method itself, which method, in the next step, was applied to determine k_6'(EG) as well. The other reason was to check whether k_6'(MeOH) is really linearly dependent on the bromate concentration. Our results justify the expectation that k_6'(MeOH) is a linear function of the bromate concentration under the conditions applied in our experiments.

The rate constant k_6'(EG) can be determined analogously to k_6'(MeOH). Figure 4b shows the absorbance−time diagram recorded in the course of the ethylene glycol−acidic bromate reaction. To evaluate this curve in a manner similar to the case of methanol, we can regard the analogous oxidation steps (E1) and (E2):

$$\text{HOCH}_2\text{CH}_2\text{OH} + \text{HBrO}_3 \rightarrow \text{HOCH}_2\text{CHO} + \text{HBrO}_2 + \text{H}_2\text{O} \quad \text{(E1)}$$

$$\text{HOCH}_2\text{CHO} + \text{HBrO}_3 \rightarrow \text{HOCH}_2\text{COOH} + \text{HBrO}_2 \quad \text{(E2)}$$

Again, E1 is a rate-determining slow reaction while E2 is much faster, as in the case of R1 and R2, and the net process in an analogy to R6 is

$$\text{HOCH}_2\text{CH}_2\text{OH} + \text{HBrO}_3 \rightarrow \text{HOCH}_2\text{COOH} + \text{HOBr} + \text{H}_2\text{O} \quad \text{(E6)}$$

and k_6'(EG) can be determined from the initial slope of the $\ln\{[A_\infty - A(t)]/A_\infty\}$ versus time diagram. Based on experimental results, $k_6'(\text{EG}) = (2.7 \pm 0.3) \times 10^{-3}\ \text{M}^{-1}\ \text{s}^{-1}$.

Regarding the initial reaction rates, the above calculation is correct but on a longer time scale a new problem appears. In R6 the end product was formic acid while in E6 it is glycolic (hydroxy acetic acid). It is known that formic acid is an inert end product in the BZ reaction,[38] but glycolic acid is not completely inert. According to Ruoff et al.,[39] in the BZ reaction

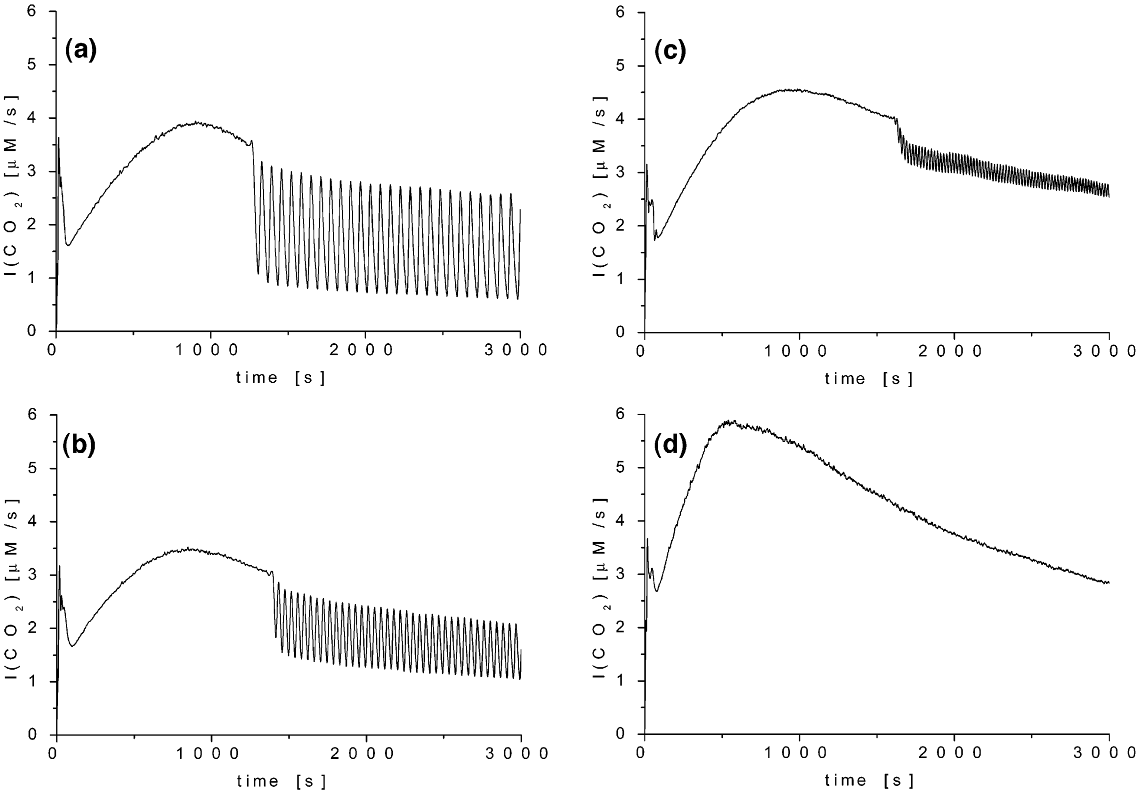

Figure 3. Dynamics of the BZ system perturbed with ethylene glycol. Initial perturbant concentrations: $[EG]_0$ = (a) 3.75 mM, (b) 9.38 mM, (c) 18.75 mM, and (d) 28.13 mM. The perturbing ethylene glycol concentrations were the same as for the methanol. Here the highest ethylene glycol concentration already extinguishes oscillations. All other concentrations are given in figure caption 1.

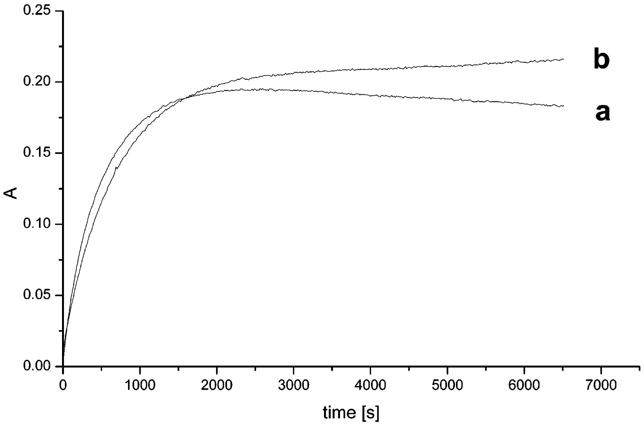

Figure 4. Reaction of MeOH (a) and ethylene glycol (b) with acidic bromate. Absorbance of the product HOBr at 330 nm as a function of time. Initial concentrations $[H_2SO_4]$ = 1 M, $[NaBrO_3]$ = 0.3 M, [MeOH] = 0.01 M (a), [EG] = 0.01 M (b). Cuvette thickness: 1 cm.

glycolic acid reacts slowly first to give glyoxylic acid which is oxidized further rapidly to formic acid:

$$HOCH_2COOH + HBrO_3 \rightarrow OCHCOOH + HBrO_2 + H_2O \quad (G1)$$

$$OCHCOOH + HBrO_3 \rightarrow HCOOH + HBrO_2 + CO_2 + H_2O \quad (G2)$$

In addition to the G1−G2 sequence, they also found evidence for another reaction pathway where glyoxylic acid is oxidized completely to CO_2.

Really, observing Figure 4b it can be seen that, unlike the curve in Figure 4a, this one does not reach a maximum within 6000 s, indicating a slow consecutive reaction that is able even to counterbalance the HOBr consumption, which would lead a decrease of the absorbance otherwise.

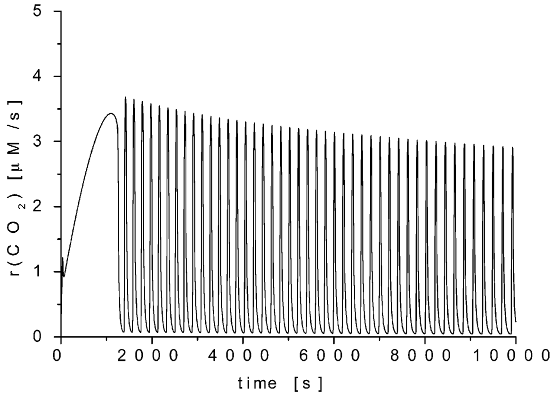

Figure 5. CO_2 evolution rate as a function of time calculated with the MBM mechanism for the unperturbed BZ system. The length of the induction period is 1250 s, τ = 190 s, A = 3.7 μmol/(s·dm^3).

Model Calculations with the MBM Mechanism

Application of the MBM Mechanism for the Unperturbed BZ System. The MBM mechanism[33] reproduces very well the oscillations in a BZ system where the substrate is bromomalonic acid. However, when the substrate is malonic acid, some characteristic deviations between the experimental and simulated curves were observed already in ref 33, and these problems appear here in Figure 5 as well.

Comparing Figures 1 and 5 it can be seen that the CO_2 evolution rate and the induction time agree well, but the simulated time period is too long by a factor of 1.7 and there is

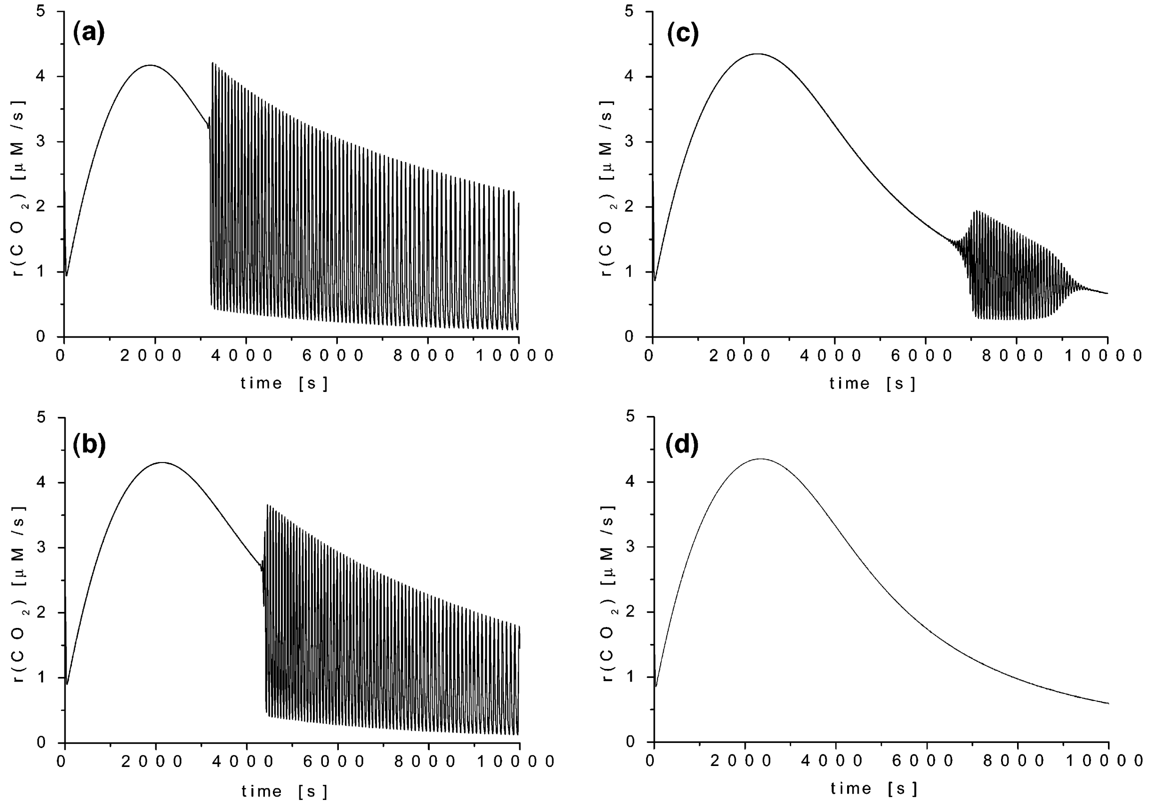

Figure 6. Calculated CO_2 evolution curves for the following initial methanol concentrations: (a) 3.75, (b) 6, (c) 8.5. and (d) 9.38 mM. The lowest (3.75 mM) and the highest values (9.38 mM) are identical with the ones applied in the perturbation experiments shown Figure 2 (a and b). No oscillations were detected in calculations when the initial methanol concentration was above 8.6 mM. Calculated dynamic parameters: length of the induction period: (a) 3200, (b) 4000, (c) ~6500 s; τ (time period of oscillations): (a) 70, (b) 64, (c) 60 s; A (maximal amplitude): (a) 3.8, (b) 3.3, (c) 1.7 μmol/(s·dm^3).

no preinduction period in the model calculations. Obviously, the MBM mechanism is far from being perfect, nevertheless it gives a qualitatively fair description of the observed dynamical phenomena except the preinduction period. Now let us see the effect of the alcohol perturbation as simulated by MBM mechanism.

Insertion of the Perturbing Reaction to the MBM Mechanism. It is a slight problem that in the paper of Försterling et al.[21] the rate law for the oxidation of methanol by acidic bromate calculates with bromic acid ($HBrO_3$) concentration, but in our BZ/MBM model the only variable containing Br(V) is not $HBrO_3$ but bromate ion. (This is because the Br(V) occurs mostly in this form.) Natarayan and Venkatasubramanian[40] studied the oxidation of various secondary alcohols by bromate in acidic media and they found the following rate law:

$$k_4[\mathrm{Br(V)}][\mathrm{ROH}][\mathrm{H}^+]^2$$

where Br(V) stands for BrO_3^-. They argue that it is the protonated bromic acid that is the active reagent, and this explains the second-order dependence on the hydrogen ion concentration. In our calculations we used this rate law, but k_4 is denoted here by k_{ROH}. As the two different rate laws should give the same reaction rate, the following equation holds:

$$k_{\mathrm{ROH}}[\mathrm{BrO_3}^-][\mathrm{ROH}][\mathrm{H}^+]^2 = k_6'[\mathrm{ROH}]$$

Thus k_{ROH} was calculated as

$$k_{\mathrm{ROH}} = k_6'/[\mathrm{BrO_3}^-][\mathrm{H}^+]^2 = 3.8 \times 10^{-3}/1.29^2 = 2.28 \times 10^{-3}\ \mathrm{s}^{-1}\ \mathrm{M}^{-3}$$

With this value the rate of the $HBrO_2$ production is

$$2k_{\mathrm{ROH}}[\mathrm{BrO_3}^-][\mathrm{ROH}][\mathrm{H}^+]^2$$

as two molecules of $HBrO_2$ are produced in the course of the oxidation of each methanol molecule. In the BZ simulations the above second-order dependence on the hydrogen ion concentration is not so important, however, as the hydrogen ion concentration does not change too much in the course of the reaction.

Simulation of the Methanol Perturbed BZ Systems. After including the perturbation reaction to the MBM mechanism, we performed model calculations applying four different methanol concentrations. The results are shown in Figure 6.

Comparing Figures 2 and 6, a rather good qualitative agreement can be observed between experiments and calculations. An increasing amount of methanol increases the induction period and decreases the amplitude and the time period of the oscillations both in the experiments and in the calculations. On a quantitative level, however, there is a disagreement: the perturbations predicted by the model calculations are too strong. For example, in the calculations 8.7 mM methanol is already able to eliminate oscillations completely while in real experiments this occurs only well above 40 mM. Also, the calculated induction period of the perturbed systems is too long by a factor of 2 or 3. On the other hand, the frequency of the methanol perturbed system increases less in the calculations than in the real experiments.

Simulation of the Ethylene Glycol Perturbed BZ Systems. The following two net processes were used as perturbing reactions of the MBM mechanism:

$$HOCH_2CH_2OH + 2HBrO_3 \rightarrow HOCH_2COOH + 2HBrO_2 + H_2O \quad (E6')$$

and

$$HOCH_2COOH + 2HBrO_3 \rightarrow HCOOH + 2HBrO_2 + H_2O + CO_2 \quad (G6')$$

While the rate constant value $k_6'(EG) = 2.7 \times 10^{-3}$ M^{-1} s^{-1} was known from our experiments, no data were available for $k_6'(GA)$ (here GA denotes glycolic acid). Regarding Figure 4b, it is reasonable to assume that $k_6'(GA) < k_6'(EG)$. Thus, just to see the qualitative behavior of such a model, we performed illustrative calculations assuming $k_6'(GA) = 1.9 \times 10^{-3}$ M^{-1} s^{-1}. The aim of those calculations was to show that the experimentally observed differences between the methanol and ethylene glycol perturbed systems can be simulated qualitatively regarding the different perturbation schemes for MeOH and ethylene glycol. The results are shown in Figure 7.

Comparing the dynamical parameters of Figures 6 and 7 it is clear that when the perturbant is applied in a low concentration (3.75 mM) methanol is a stronger perturbant than ethylene glycol, but with a higher ethylene glycol concentration this order is reversed. A similar change in the order was observed in the experiments (see Figures 2 and 3).

Discussion

As it was shown in the previous paragraph, the simulations are successful qualitatively but there is a disagreement on a quantitative level. This suggests that at some point the model calculations are not realistic enough and should be modified if that is possible. There are two possibilities: (a) the rate and/or the mechanism of the alcoholic perturbation is different from the assumed one (and this way the alcohol can produce only a weaker perturbation in the BZ; and (b) the perturbation is not weaker but the BZ oscillator is more robust and can survive stronger perturbations. In this case it is the mechanism of the unperturbed system that should be modified.

Possibility (a) will be analyzed first. (As we can see, the mechanism of the ethylene glycol oxidation is rather complex thus this discussion focuses mainly on the perturbation with methanol where the mechanism is simple and well discovered.) We see two different ways in which the effect of the alcohol in the BZ system would be weakened. (i) The rate of the perturbing reaction (the production of the autocatalytic intermediate bromous acid from the alcohol and acidic bromate) was determined originally[21] in a separate spectrophotometric experiment applying the same sulfuric acid concentration as in the BZ solution but a much higher (1 M) bromate concentration. Thus, if the rate law is not linear in the bromate concentration, then the perturbation in the BZ system can be overestimated. We checked this possibility by spectrophotometric measurements on the perturbing reaction applying much lower (0.3 and even 0.15 M) bromate concentrations, and no measurable deviation from the linear rate law was found either in the case of MeOH or for ethylene glycol. This is in agreement with the results of Natarayan and Venkatasubramanian[40] who found, in the case of secondary alcohols, that the rate law is linear for bromate at low bromate concentrations. Thus nonlinearity cannot be the reason for the weaker perturbation found in the experiments. (ii) The alcoholic perturbation can be also weaker than expected if the alcohol takes part not only in the production but also in the consumption reactions of the bromous acid. We have carried out further model calculations for methanol (including all possible reactions of the intermediate formaldehyde as well) which show, however, that the simulation results are affected significantly only if the rate constants of these additional reactions are set to unusually high values. When applying such high rate constants, however, other nonrealistic phenomena appear while the magnitude of the predicted alcoholic perturbation is still too high.

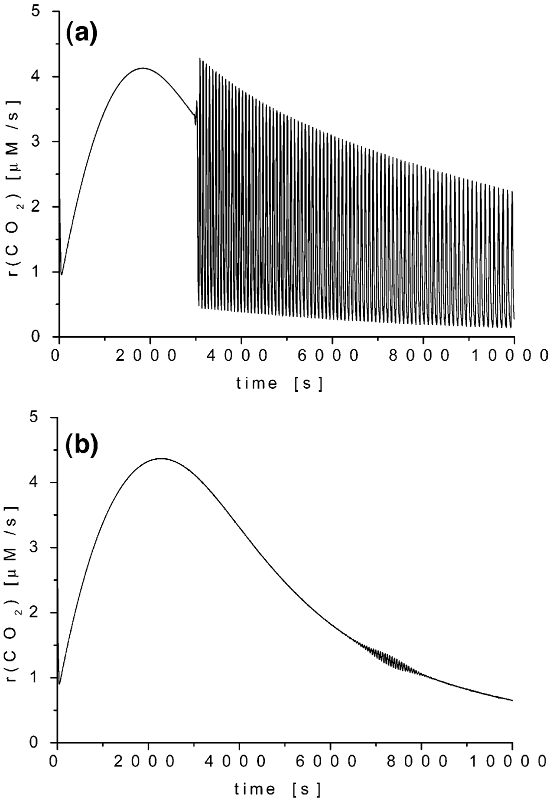

Figure 7. Calculated CO_2 evolution curves for the following initial ethylene glycol concentrations: (a) 3.75, (b) 8.5 mM. Dynamic parameters: length of the induction period (a) 3050, (b) ~6200 s; τ, (a) 70, (b) 25 s, *A*, 3.9; (b) 0.2 μmol/(s·dm³).

Thus, most probably, it is not the mechanism of the alcoholic perturbation but the MBM mechanism itself that should be modified slightly. One possibility is that organic free radicals, especially carboxyl radicals,[33] play a more important role in the mechanism. Development of such a modified MBM mechanism is in progress.

Conclusions

(1) The MBM mechanism is able to model the unperturbed BZ system studied here. It is especially successful in predicting the rate of the CO_2 evolution in this system: calculated and measured values agree within 20−30%. (This is an improvement compared to the 2 orders of magnitude disagreement found earlier[37] between experiments and other model calculations.) The time period of the calculated oscillations (190 s), however, is longer than that of the experimental ones (124 s).

(2) Simulation of the alcoholic perturbations of the BZ system with the MBM mechanism gives qualitatively correct results: the alcoholic perturbation increases the induction period and decreases the amplitude and the time period of the oscillations. The calculated perturbation is stronger, however, by a factor of 4 or 5 compared to the experiments.

(3) The small differences observed experimentally between methanol and ethylene glycol perturbed systems can be explained by the different rate constants of the reactions of these

alcohols with acidic bromate (k_6'(MeOH) = 3.8×10^{-3} M^{-1} [BrO_3^-] s^{-1}, k_6'(EG) = 2.7×10^{-3} M^{-1}·[BrO_3^-] s^{-1} in 1 M sulfuric acid medium).

(4) Points 2 and 3 support that the mechanism of the alcoholic perturbation (generation of the autocatalytic intermediate bromous acid in oxygen atom transfer reactions) is basically correct. Quantitative differences between the calculated and the experimentally found alcohol effects suggest, however, that the MBM mechanism should be modified at some points to achieve a better agreement.

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