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Uncatalyzed Reactions in the Classical Belousov−Zhabotinsky System. I. Reactions of Bromomalonic Acid with Acidic Bromate and with HOBr

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The uncatalyzed reactions of bromomalonic acid (BrMA) with acidic bromate and with hypobromous acid were studied in 1 M sulfuric acid, a usual medium for the oscillatory Belousov−Zhabotinsky (BZ) reaction, by following the rate of the carbon dioxide evolution associated with these reactions. In addition, the decarboxylation rate of dibromomalonic acid (Br_2MA) was also measured to determine the first-order rate constant of its decomposition (4.65×10^{-5} s^{-1} in 1 M H_2SO_4). The dependence of that rate constant on the hydrogen ion concentration suggests a carbocation formation. A slow oligomerization of BrMA observed in sulfuric acid solutions is also rationalized as a carbocationic process. The initial rate of the BrMA−BrO_3^- reaction is a bilinear function of the BrMA and BrO_3^- concentrations with a second-order rate constant of 3.8×10^{-4} M^{-1} s^{-1}. When a great excess of BrO_3^- is applied, then BrMA is oxidized mostly to CO_2. A reaction scheme compatible with the experimental finding is also given. On the other hand, when less BrO_3^- and more organic substrate − BrMA or malonic acid (MA) − is applied, then addition reactions of various carbocations with the enol form of the organic substrates should be taken into account in later stages of the reaction. It was discovered that HOBr, which brominates BrMA to Br_2MA when BrMA is in excess, can also oxidize BrMA when HOBr is in excess. As Br_2MA does not react with HOBr, it is assumed that the acyl hypobromite, formed in the first step of the HOBr and BrMA reaction, can react with an additional HOBr to give oxidation products. It was found that the initial rate of the reaction can be described by the following experimental rate law: $k_{BHOB}[BrMA]_0[HOBr]_0^2$, where $k_{BHOB} = 5$ M^{-2} s^{-1}. A reaction scheme for the oxidation of BrMA by HOBr is given for conditions where HOBr is in excess. Model calculations illustrate qualitatively that the suggested reaction schemes are able to mimic the experiments. (More quantitative simulations are prevented by kinetic data missing for the various carbocation intermediates.) Finally, the effects of these newly observed reactions on oscillatory BZ systems are discussed briefly.

1. Introduction

1.1. Motivation. The classical Belousov−Zhabotinsky (BZ) reaction,[1] the cerium ion catalyzed oxidation and bromination of malonic acid, is the most studied chemical oscillator. It is discussed in various books (see, e.g., refs 2−4) as a prime example for nonlinear dynamics in chemistry. Despite this, there are still undiscovered reactions in the organic subset when the organic substrate is malonic acid. By using oxalic acid as the simplest organic BZ substrate,[5,6] such complications of the organic chemistry can be avoided. Nevertheless, most of the interesting nonlinear phenomena were observed with malonic acid substrate; thus, it is also important to understand this classical system as well. The main steps in the development of the kinetic models suggested for the classical BZ reaction were the following: the FKN mechanism,[7] the Oregonator,[8] the Radicalator,[9] the GTF,[10,11] and most recently the MBM[12] mechanism. Even the new MBM mechanism is not free of problems, however. As emphasized already in the original MBM paper, the model predicts 2 orders of magnitude more tartronic acid (TA) than what was actually observed in the experiments. The source of TA in the MBM model is the hydrolysis of malonyl bromite. (Malonyl bromite is a recombination product of the organic malonyl and the inorganic bromine dioxide radicals. Both radicals are intermediates of the BZ reaction.[12]) There is another decomposition route for malonyl bromite leading to hypobromous and mesoxalic acids or even more probable to bromide ion and oxalic acid.[13] While these decomposition routes are more realistic than the one leading to TA, the latter route was necessary to keep in the MBM model; otherwise, the oscillations would start without an induction period, which was in sharp contrast with the experimental observations. The real reason for this is not TA itself but bromous acid which is the other product besides TA in the hypothetical hydrolysis of malonyl bromite. As it is known, bromous acid is an autocatalytic intermediate of the BZ reaction. Thus, an inflow of bromous acid can keep the system in the oxidized state for a longer time and consequently an induction period appears. Thus, if we want to eliminate the unrealistic route leading to TA and still keep an induction period in the model, then another bromous acid source is needed. The starting

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hypothesis of the present research is that uncatalyzed reactions between acidic bromate and organic substrates such as malonic acid (MA) and bromomalonic acid (BrMA) can provide a bromous acid source which is necessary to observe an induction period. Such reactions can produce bromous acid because in the first step of the oxidation an oxygen atom transfer from the acidic bromate to the organic substrate R occurs

$$H^+ + BrO_3^- + R \rightarrow HBrO_2 + RO$$

resulting in bromous acid and a short-lived organic intermediate RO, which could decompose rapidly, giving other products. If one of the products is CO_2, then its production rate can easily be measured with a technique worked out in our laboratory.[5,6,14,15] Even if RO is more stable, CO_2 will appear in later stages, when RO is oxidized further by acidic bromate.

1.2. Plan of the Research. The uncatalyzed bromate–substrate reactions of the classical BZ system are usually not discussed, as they are regarded to be very slow or negligible processes. Naturally, at the beginning of the induction period, it is only the bromate–malonic acid reaction which could play a role. One of the products of that reaction, however, is bromomalonic acid, which could also react with bromate. As this process will perturb the observation of the bromate–malonic acid reaction, we can obtain clear information about that process only if we know previously the kinetics of the bromate–bromomalonic acid. Thus, we decided to start the research with the latter especially because CO_2, what we can measure easily, should be a product here already in the first step which is not necessarily true in the case of the malonic acid substrate. The study of the more complex malonic acid–bromate reaction will be the subject of a separate publication.[16] Nevertheless, the effect of malonic acid on the BrMA–BrO_3^- reaction will be studied already here.

In preliminary experiments, we found a well measurable CO_2 evolution in the bromate–bromomalonic acid reaction. To assign a rate constant for this reaction, however, we had to study other reactions as well like the spontaneous decarboxylation of dibromomalonic acid (Br_2MA) in acidic medium and the bromate–bromomalonic acid reaction in the presence of malonic acid, etc. The results showed an unexpected complexity of these reactions. Despite that, we could reach our original aim to measure the rate constant of the title reaction in 1 M sulfuric acid.

Results of the various experiments are presented in the following order. First, we studied the spontaneous decarboxylation of dibromomalonic acid at various hydrogen ion concentrations. Then, the BrMA–BrO_3^- reaction was studied at different BrMA concentrations and also in the presence of malonic acid. Next, the BrMA–HOBr reaction was investigated in the case of an HOBr excess. Finally, we performed some model calculations to show that the experimental results can be rationalized within the reaction schemes suggested here.

2. Experimental Section

2.1. Chemicals. $NaBrO_3$ (Fluka, puriss.), H_2SO_4 (97%, Merck, p.a.), and NaBr (Merck, p.a.) were used as received. All solutions were prepared with doubly distilled water. Hypobromous acid solution was prepared freshly each week, according to the method reported by Pelle et al.,[5] and was stored in a refrigerator. Decomposition of HOBr in 1 M sulfuric acid and at 5 °C is slow: its half-life is about 2 weeks. Before a measurement, decomposition product bromine was removed by sucking air through the solution with an aspirator. The concentration of HOBr was then determined by potentiometric titration with bromide in the presence of a bromide selective electrode. Potassium salts of bromomalonic acid (K_2BrMA) and dibromomalonic acid (K_2Br_2MA) were prepared following the method of Försterling and Stuk.[17] We used freshly prepared aqueous solutions of K_2BrMA and K_2Br_2MA because acidic solutions of these salts are less stable (see later).

2.2. Preparation of Fresh Br_2MA Solution by Bromination of Malonic Acid. The simplest way to produce such a solution with an exactly known concentration would have been to dissolve a known amount of pure K_2Br_2MA in 1 M sulfuric acid. This was not possible, however, as our solid K_2Br_2MA sample contained some inert material (most probably some moisture or crystal water). To avoid such uncertainties, we prepared freshly an acidic Br_2MA solution starting from a known amount of malonic acid. To this end, two stock solutions were prepared as follows:

For solution A, a 1 mL portion of 3 M MA in 2 M H_2SO_4 and 2.2 mL of 10 M H_2SO_4 were mixed in a 10 mL flask. A 0.515 g (5 mmol) portion of NaBr was dissolved in the mixture which was diluted finally to 10 mL. After this procedure the concentrations in solution A were 0.3 M MA, 0.5 M NaBr, and 2.4 M H_2SO_4. Solution B was an aqueous solution of 0.22 M $NaBrO_3$.

A 5 mL portion of solution B was added in 0.5 mL portions to 5 mL of solution A. After each addition, a brown color, due to the bromine, appeared and disappeared after a while. After the last addition of 0.5 mL of solution B, the color was stable, indicating that the whole amount of MA was brominated to dibromomalonic acid. The excess of bromine was removed by bubbling air through the solution. To accelerate the bromate–bromide reaction and to avoid a reaction of bromate with malonic and bromomalonic acids, a slight excess of bromide was applied in the above recipe. The final concentrations in the reaction mixture were 0.15 M dibromomalonic acid and 0.03 M bromide. The sulfate concentration was 1.2 M in a mixture of sulfuric acid (0.84 M) and sodium hydrogen sulfate (0.36 M).

2.3. CO_2 Measurements. The CO_2 measurement apparatus and the reactor are described in previous publications.[5,6] The only difference is that now an additional magnetic stirring was applied in the reactor that was thermostated at 20 °C. The reactants were injected into the reactor from plastic syringes but without applying a metallic needle. (Metal ions from the needle might affect the reaction dynamics.) CO_2 was purged from the reactor with a nitrogen stream and then mixed with hydrogen. Next, CO_2 was converted to methane and measured with a flame ionization detector (FID). Further details of the method can be found in ref 14.

2.4. Determination of the Time Constants of the Apparatus. The signal (the ionization current) provided by the FID is proportional to the carbon atom current in the detector. In a steady state, the carbon atom current is equal to the CO_2 production rate in the reactor and time constants of the apparatus do not play a role. In most cases, however, the system is not in a steady state as the reaction rate is changing in time. In such cases, the measured signal versus time diagram is “smoother” than the reaction rate versus time function. This is because, first, the CO_2 produced in the liquid phase of the reactor should be transferred from the liquid to a well mixed gas phase and, then, from that gas phase, it should be transported by the carrier gas to the detector. Both processes can be simulated by first-order decays and can be modeled by the symbolic “reactions” RS1 and RS2:

$$CO_2\text{(in the liquid phase)} \rightarrow CO_2\text{(in the mixed gas phase)} \quad \text{(RS1)}$$

$$CO_2\text{(in the mixed gas phase)} \rightarrow CO_2\text{(outflow to the detector)} \quad \text{(RS2)}$$

Thus, if we want to simulate the detector signal in an experiment, we have to determine the symbolic rate constants k_{S1} and k_{S2} (the reciprocal values of these are the time constants of our apparatus). To this end, 2 mL of 2 M H_2SO_4 was added to the reactor and then a sudden increase in the liquid phase CO_2 concentration was created by injecting first 1 mL of water then 1 mL of 2×10^{-4} M Na_2CO_3. This way, at the start of the experiment, the concentration of the dissolved CO_2 was 5×10^{-5} M in 4 mL of 1 M H_2SO_4. It can be shown that in such a case the measured signal $I(t)$ can be written in the following form:

$$I(t) = A\{\exp(-k_{S1}t) - \exp(-k_{S2}t)\}$$

Thus, the symbolic rate constants can be determined by fitting exponentials to the measured $I(t)$ curve. The results are $k_{S1} = 0.03\ s^{-1}$ for a total liquid volume of 4 mL and $0.06\ s^{-1}$ when the liquid volume is 2 mL only. The other rate constant is $k_{S2} = 0.12\ s^{-1}$. All values are valid while maintaining a nitrogen gas flow of 40 mL/min and a magnetic stirring rate of 1200 rpm. The k_{S1} and k_{S2} values determined this way were applied in numerical simulations of our experiments. (Both symbolic rate constants, especially k_{S1}, are affected by the stirring rate: a faster stirring increases their values.)

2.5. CO_2 Stoichiometry in the Bromomalonic Acid−Bromate Reaction. To achieve a faster consumption of BrMA, a large excess of bromate was applied. The reactants were injected into the reactor in the following order: 1 mL of 20 mM K_2BrMA in water and then 1 mL of 4 M H_2SO_4, and the reaction was started by injecting 2 mL of 2 M $NaBrO_3$ in water. The initial concentrations were therefore 5 mM BrMA, 1 M H_2SO_4, and 1 M bromate. The stoichiometric coefficient of CO_2 was calculated from a CO_2 integral (integrating the CO_2 evolution rate between zero and infinite time). This was achieved by a numerical integration of the rate in the first 32 000 s followed by an analytical integration from 32 000 s to infinity by fitting an exponential to the experimental rate curve measured between 2800 and 32 000 s. It was found that from 1 mol of BrMA about 2.8 ± 0.2 mol of CO_2 was produced.

2.6. CO_2 Stoichiometry of the Bromomalonic Acid−Hypobromous Acid Reaction. To accelerate the consumption of BrMA, an excess of HOBr was applied. Components of the reaction were injected into the reactor in the following order: 3 mL of 23.34 mM HOBr in 1 M H_2SO_4 and then 0.5 mL of 2 M H_2SO_4, and the reaction was started by injecting 0.5 mL of 8 mM K_2BrMA in water. The initial concentrations in the reactor were therefore 17.5 mM HOBr, 1 mM BrMA, and 1 M H_2SO_4. The stoichiometric coefficient of CO_2 was calculated from the total CO_2 amount (integrating the CO_2 evolution rate between zero and infinite time). This was achieved by a numerical integration of the rate in the first 24 000 s followed by an analytical integration from 24 000 s to infinity by fitting an exponential to the experimental rate curve measured between 600 and 24 000 s. It was found that from 1 mol of BrMA about 2.7 ± 0.2 mol of CO_2 was produced.

2.7. Determination of the Initial Reaction Rate in the Bromomalonic Acid−Bromate Reaction and in Other Reactions. The initial reaction rates were calculated by extrapolating the CO_2 evolution rates to time zero. (To determine rate constants, the method of initial values was applied in all cases, as the accumulation of some intermediates could significantly contribute to the CO_2 evolution in later stages of the reaction.) The rate constants of various reactions were calculated from these initial reaction rates and the initial component concentrations.

Initial Conditions in the Bromomalonic Acid−Bromate Reaction. Two parallel measurements were performed: (a) First, 1 mL of 0.1 M K_2BrMA in water was injected, followed by 1 mL of 4 M H_2SO_4. The reaction was then started by injecting 2 mL of 0.5 M $NaBrO_3$ in water. The initial concentrations in the reactor were therefore 25 mM BrMA, 0.25 M bromate, and 1 M H_2SO_4. The total reaction volume was 4 mL. (b) Components of the reaction mixture were injected into the reactor in the following order: 1 mL of 0.1 M K_2BrMA in water and 0.5 mL of 4 M H_2SO_4. Then, the reaction was started by injecting 0.5 mL of 1 M $NaBrO_3$ in water. After mixing, the initial concentrations were 50 mM BrMA, 0.25 M bromate, and 1 M H_2SO_4. The total reaction volume was 2 mL.

Bromomalonic Acid−Bromate Reaction in the Presence of Malonic Acid. Solutions of reactants were injected into the reactor in the following order: 1 mL of 0.1 M BrMA in water, 0.5 mL of 0.8 M MA in water, and 0.5 mL of 8 M H_2SO_4. The reaction was started by injecting 2 mL of 0.5 M $NaBrO_3$ in water. The initial concentrations after mixing were therefore 25 mM BrMA, 0.1 M MA, 0.25 M bromate, and 1 M H_2SO_4. The total reaction volume was 4 mL.

Bromomalonic Acid−Hypobromous Acid Reaction. The same CO_2 measurement that was described in the paragraph of CO_2 stoichiometry of the BrMA−HOBr reaction was also used to determine the initial rate of this reaction. To determine the partial order of HOBr, however, other experiments were also performed where the initial HOBr concentrations were smaller.

Decarboxylation of Dibromomalonic Acid in 1 M H_2SO_4. The Br_2MA solution was freshly prepared as described here. Components of the reaction mixture were injected into the reactor in the following order: 1 mL of 150 mM Br_2MA in a mixture containing 0.84 M H_2SO_4 and 0.36 M $NaHSO_4$ and then 1 mL of 1 M H_2SO_4. After mixing, the initial concentrations were 75 mM Br_2MA, 0.92 M H_2SO_4, and 0.18 M $NaHSO_4$. With a second dilution by 2 mL of 1 M H_2SO_4, the final sulfuric acid concentration can be shifted even closer to 1 M (to 0.96 M) and the $NaHSO_4$ concentration can be decreased further to 0.09 M.

2.8. Decarboxylation Rate of Br_2MA as a Function of the H_2SO_4 Concentration in the Reaction Mixture. To study the hydrogen ion dependence of the rate constant, the concentration of sulfuric acid in a solution of K_2BrMA was stepwise increased starting from 0. First, 1.5 mL of 0.1 M K_2BrMA in water was injected into the reactor. Next, sulfuric acid solutions were injected, each time 0.5 mL, in the following order: 0.04 M H_2SO_4, 0.5 M H_2SO_4, 3 M H_2SO_4, 3.5 M H_2SO_4, and 4 M H_2SO_4, and two times 10 M H_2SO_4. After 2−3 min following each addition of sulfuric acid solution, a new constant level of CO_2 rate was reached. Using the constant CO_2 evolution rates and the known rate constant of the reaction in 1 M H_2SO_4, the rate constants of the decarboxylation for the other sulfuric acid concentrations could be calculated.

2.9. Measurement of Formic Acid Concentration. It is known that oxidation of malonic acid by Ce^{4+} produces some formic acid (FA). (The reaction is not quantitative, however.[18]) As formic acid production is also a possibility in the oxidations by acidic bromate, a simple and sensitive method to measure FA was developed. (FA can be oxidized further by HOBr to CO_2, but this process is very slow[19] and thus FA can be regarded as an end product which is practically inert.) To measure FA, we applied the Morgan reaction, the dehydration of FA in concentrated sulfuric acid solutions, which gives CO. We found that when H_2SO_4 is applied in high concentration the reaction is fast and quantitative. (Supersaturation of the solution by CO, which is the source of oscillations in a Morgan reaction, is not a problem here, as gas bubbling and magnetic stirring prevents that.) CO can be measured selectively with a flame ionization detector[20] applying a soda lime filter in the gas stream which removes CO_2 quantitatively.

CO Measurements. First, 1.5 mL of 97% H_2SO_4 was introduced by a pipet into the reactor through its open mouth. Then, the reactor was closed and to remove air a nitrogen carrier gas was bubbled through the sulfuric acid for 2−3 min. The Morgan reaction was started by injecting 0.25 mL of the sample into the unthermostated reactor. This way, following the injection, a sharp temperature increase helped the CO evolution. As the signal was low, an accumulation method was used to increase the sensitivity of the measurement: after the injection, the nitrogen carrier gas was switched to a bypass reactor filled with water. After a reaction-accumulation period of 5 min, the carrier nitrogen gas stream was switched back and a sharp CO peak appeared if FA was present. The amount of FA was calculated on the basis of calibration experiments with solutions of known FA concentrations.

2.10. Formic Acid Stoichiometry in the BrMA−BrO_3^- and BrMA−HOBr Reactions. Two different reaction mixtures were tested for FA:

(1) Bromomalonic Acid−Bromate Reaction. A 2 mL portion of 0.1 M BrMA in water was mixed with 4 mL of 2 M H_2SO_4 and 2 mL of 1 M $NaBrO_3$ in water. After mixing, the initial concentrations were 25 mM BrMA, 1 M H_2SO_4, and 250 mM bromate. The reaction was stopped after 16 h by adding 2.5 mL of 4 M NaBr in 1 M H_2SO_4, and the bromine was removed by sucking air through the solution with an aspirator. Applying an excess of bromide was also necessary to avoid any HOBr and bromine formation from any remaining bromate when the reaction mixture was injected into the reactor containing 97% H_2SO_4. It was found that about 5% of the BrMA was oxidized to FA. Thus, the final carbon atom stoichiometry when BrMA reacts with an excess of acidic bromate is

$$\mathrm{BrMA} \rightarrow 2.8\mathrm{CO_2} + 0.15\mathrm{FA} + 0.05\mathrm{C}$$

(C stands for the missing carbon, most probably an experimental loss.)

(2) Bromomalonic Acid−Hypobromous Acid Reaction. A 6 mL portion of 24.74 mM HOBr in 1 M H_2SO_4 was mixed with 1 mL of 2 M H_2SO_4 and 1 mL of 8 mM K_2BrMA in water. The initial concentrations after mixing were 18.56 mM HOBr, 1 mM BrMA, and 1 M H_2SO_4. As the concentration of HOBr was much higher than that of BrMA, the major reaction route was the oxidation of bromomalonic acid and its bromination to dibromomalonic acid was negligible. FA was measured in the reaction mixture 16 h after starting the reaction. The formic acid stoichiometry measured here was practically the same as in the case when the oxidant was acidic bromate: about 8.5% of the BrMA was oxidized to FA by an excess of HOBr. Thus, the carbon atom stoichiometry when BrMA reacts with an excess of HOBr is

$$\mathrm{BrMA} \rightarrow 2.7\mathrm{CO_2} + 0.26\mathrm{FA} + 0.04\mathrm{C}$$

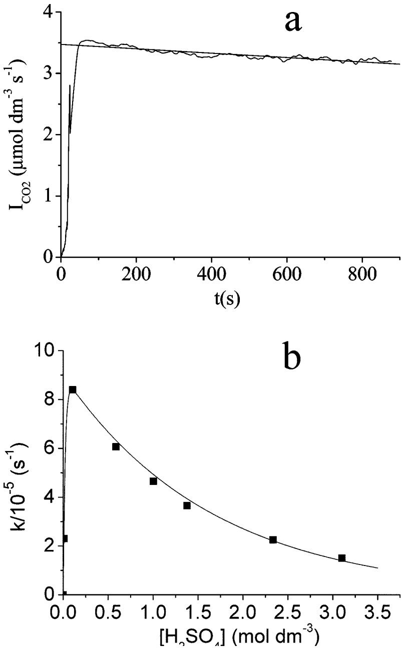


Figure 1. Decarboxylation of dibromomalonic acid in acidic media: (a) measurement of CO_2 evolution rate in 1 M H_2SO_4; (b) rate constant of the decarboxylation as a function of the H_2SO_4 concentration.

3. Results and Discussion

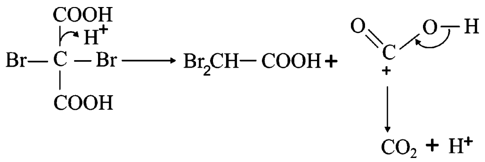
3.1. Decarboxylation of Dibromomalonic Acid. We started our investigations with this reaction because it is probably the simplest one which can be studied in separate experiments. Moreover, this reaction can contribute to the CO_2 evolution in more complex systems. (For example, dibromomalonic acid can appear in the bromomalonic acid−bromate reaction system as a bromination product of bromomalonic acid. In this case, the brominating agents Br_2 and HOBr are generated by the reduction of bromate.)

To measure the rate constant of this decarboxylation reaction in 1 M H_2SO_4, we prepared its solution freshly, as is described in the Experimental Section. CO_2 evolution rate measurement with such a solution is shown in Figure 1a. In the steady state, the CO_2 current measured in the detector is equal to the reaction rate in the reactor. The latter is normalized for a unit reactor volume (here 1 dm^3).

Due to the method of the Br_2MA preparation, the H_2SO_4 concentration was somewhat less than 1 M and it also contained some $NaHSO_4$ (see the Experimental Section). Dilution of the system with 1 M H_2SO_4, however, indicated that the error due to the different electrolyte concentrations is minimal: less than 5%.

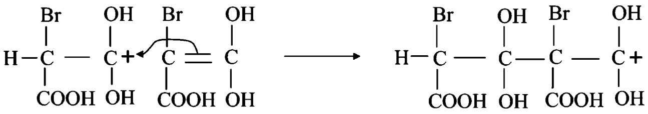
To shed light on the mechanism of the decarboxylation, we also studied the effect of the hydrogen ion concentration on the rate constant. To this end, various H_2SO_4 amounts were added to a K_2Br_2MA solution and the CO_2 evolution rate was measured after each addition (see the Experimental Section). As can be seen in Figure 1b, the rate as a function of the H_2SO_4 concentration reaches a maximum at a rather low acidity and decreases afterward. This indicates that the proton has a double role in the decarboxylation process. Probably in the first step, an electron pair from one of the C−C bonds is shifted toward the proton to form a C−H bond. A protonated CO_2 is also produced in this process which gives free CO_2 after deprotonation. Thus, the proton catalyses the decarboxylation.

At higher proton concentrations, however, it is possible that one of the carbonyl oxygens of Br_2MA is protonated and forms



a carbocation. As this positively charged ion repels the hydrogen ion necessary for the decarboxylation, the reaction slows down at higher sulfuric acid concentrations where a greater fraction of the Br_2MA is in the carbocation form.

3.2. Stability of Acidic Bromomalonic Acid Solutions. It was observed that the CO_2 evolution rate in the bromomalonic acid−bromate reaction is the highest when it is measured with freshly prepared acidic bromomalonic acid solutions. It was found that a gradual decrease in the activity of bromomalonic acid solutions occurs whenever it is prepared with sulfuric acid. Some decrease can be observed already after 1 h, and the activity of a BrMA solution kept in 2 M sulfuric acid decreases to one-third of the original value after 3 days. Aqueous solutions without sulfuric acid are more stable: their activity remains the same for a few days if the solution is stored at 5 °C. The decomposition observed in acidic medium is most probably due to a slow cationic polymerization process initiated by a reaction between the protonated form (a carbocation) and the enol form of BrMA:



In the next step, the dimer carbocation can react further with an enol molecule again and the growth of the polymer continues. Such a polymerization is probable because compounds used most frequently to initiate cationic polymerizations are mineral acids, particularly H_2SO_4 and H_3PO_4.[21,22]

On the other hand, decarboxylation of BrMA can be excluded as a decomposition process because we were able to observe only a very minor CO_2 evolution from even a rather concentrated (0.5 M) BrMA solution in 2.5 M H_2SO_4. Hydrolysis can also be excluded, as its product would be tartronic acid which can also react with bromate rapidly to give CO_2. Thus, the only remaining possibility is that two bromomalonic acid molecules react with each other to give some polymer or oligomer. This product might still react with bromate; even the rate constant of this reaction can be comparable with that of the BrMA−bromate reaction, but the rate of the reaction is much smaller because the oligomer's molar concentration is only a fraction of the original BrMA concentration. This explains the observed decrease in the rate of CO_2 evolution. As the oligomerization reaction is slow, most probably it does not play an important role in oscillatory BZ systems. Nevertheless, it is an interesting piece of information for us showing that, under certain circumstances, not only radical but also molecular or ionic organic species of the BZ system can react with each other. As will be shown later, particularly the reactions of various carbocation intermediates can be important in this respect.

3.3. Bromomalonic Acid−Bromate Reaction. To calculate the rate constant of the bromomalonic acid−bromate reaction, we had to check whether the rate of the CO_2 evolution is proportional to both the bromate and the bromomalonic acid concentration. We made this test in a series of separate experiments and found that $I_0(CO_2)$, the initial rate of the carbon dioxide evolution, is really a bilinear function of the two concentrations within the experimental error:

$$I_0(CO_2) = k_{BB}[BrMA]_0[BrO_3^-]_0$$

If we assume that in the first step of the reaction only one molecule of CO_2 is produced, then the initial rate of the reaction r_{BB} is

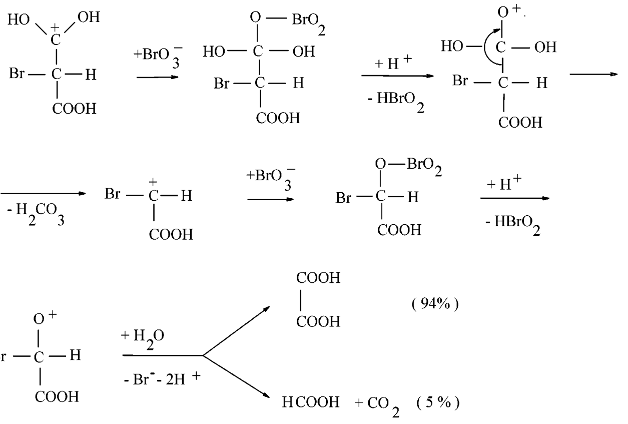
$$r_{BB} = I_0(CO_2)$$

and the rate constant k_{BB} of the bromomalonic acid−bromate reaction can be calculated from the initial values:

$$k_{BB} = I_0(CO_2)/\{[BrMA]_0[BrO_3^-]_0\}$$

On the basis of the above formula, k_{BB} was calculated based on the data of the experiment shown in Figure 2 by extrapolating back $I(CO_2)$ to zero time. The result is $k_{BB} = 3.34 \times 10^{-4}$ M^{-1} s^{-1} in the case of the experiment in Figure 2a and $k_{BB} = 4.32 \times 10^{-4}$ M^{-1} s^{-1} for the experiment shown in Figure 2b. Regarding other parallel experiments as well, the average value is 3.8×10^{-4} M^{-1} s^{-1}.

We suggest the following mechanism for the bromomalonic acid−bromate reaction for the case when acidic bromate is in a great excess:



As no mechanism was found in the literature for the acidic bromate oxidation of organic acids, the above mechanism tries to follow the reaction steps suggested recently for the acidic bromate oxidations of alcohols and aldehydes.[23,24]

The above scheme gives a fair description of the reaction when the bromate concentration is high, for example, 1 M, while at the same time the bromomalonic acid concentration is low, for example, 5 mM, like in the case of the stoichiometric experiments. In that case, we found that nearly all three carbon atoms of BrMA were oxidized to CO_2. (Reaction scheme 3 does not show the further oxidation of OA to CO_2.) After the reaction, we checked the formic acid content of the solution with the method described in the Experimental Section.

It was found that the formic acid content is about 5% of the original BrMA concentration.

In the experiments shown in Figure 2, however, the bromate concentration is 4 times lower and the BrMA concentration is 5 or 10 times higher than those in the stoichiometric experiment. Under these circumstances, the bromoacetyl carbocation has more of a chance to react not only with bromate but also with the enol form of BrMA and to start similar but faster polymerization processes which make the acidic BrMA solutions unstable. Really, if we compare parts a and b of Figure 2, it can be seen that in part b (with the 2 times higher initial BrMA concentration than that in part a) the CO_2 evolution rate decreases in the first 1000 s and starts to increase only afterward,

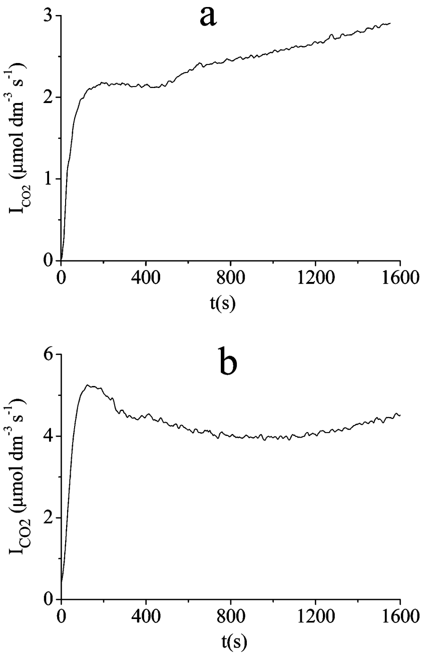


Figure 2. Determination of the initial rate of the bromomalonic acid−bromate reaction. Initial reagent concentrations (a): $[BrMA]_0 = 25$ mM, $[BrO_3^-]_0 = 0.25$ M, and $[H_2SO_4]_0 = 1$ M. In the experiment shown in part b, the initial BrMA concentration was doubled to 50 mM; the other concentrations were the same as those in part a.

while in part a the CO_2 evolution rate is practically constant in the first 500 s and starts to increase after that. This indicates that some intermediate (e.g., a carbocation) formed from BrMA can react with BrMA itself, decreasing its concentration (e.g., by polymerization). Naturally, all of the various oligomers can also react with acidic bromate and this makes the reaction system rather complex. To discover all of the possible reaction routes, however, is beyond the aim of the present work. Nevertheless, semiquantitative model calculations (see later) illustrate that our experimental observations can be rationalized by assuming polymerization reactions initiated by bromoacetyl carbocations.

3.4. Bromomalonic Acid−Bromate Reaction in the Presence of MA. When constructing a mechanism for the oxidation of an organic substrate by acidic bromate, usually it is assumed that the substrate reacts exclusively with oxybromine species (acidic bromate, bromous and hypobromous acid); moreover, it is also assumed that any organic intermediates formed in this process will react further with the oxybromine species again (like in the mechanism of the previous chapter proposed for the stoichiometric experiment where bromate was in a very high excess). Such a mechanism, however, neglects any reaction of the substrate with the organic intermediates, and as we could already see, there is an additional possibility that the substrate reacts not only with acidic bromate but also with certain carbocation intermediates, especially when the bromate concentration is lower and the organic substrate concentration is higher. To obtain more direct experimental proof for such a possibility, we repeated the experiment of Figure 2 but in the presence of 0.1 M malonic acid.

As we can see in Figure 3, the initial reaction rate is practically the same as that in Figure 2a but in later stages the evolution patterns of the two experiments are markedly different. While in the absence of malonic acid the rate of the CO_2 evolution is steady for about 500 s and even starts to grow after this time, the CO_2 evolution rate decreases in the first 1000 s in the presence of MA and a very slow growth starts only after that. The absolute values of the CO_2 evolution rates in the later stages of the experiment differ by more than a factor of 2 due to these deviations. It can also be realized that the qualitative differences between Figure 2a and Figure 3 and between parts a and b of Figure 2 are rather similar.

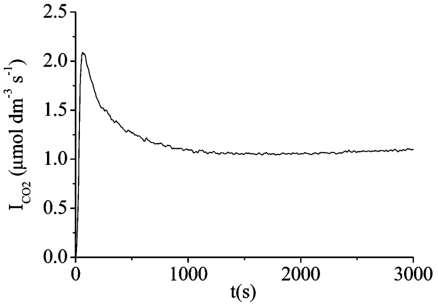
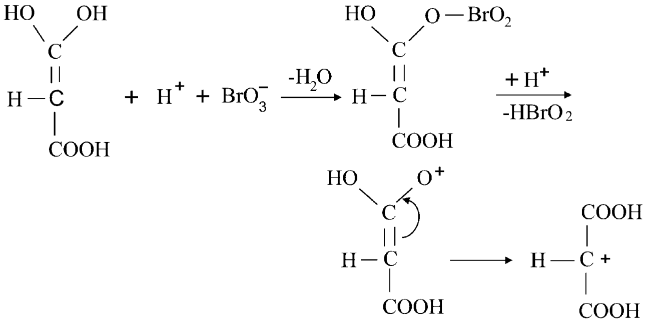


Figure 3. CO_2 evolution in the $BrMA-BrO_3^-$ reaction in the presence of malonic acid. The initial conditions are the same as those in the experiment shown in Figure 2a, but in addition, malonic acid was also present: $[MA]_0 = 0.1$ M.

How can we explain the above effect of malonic acid? First of all, we have to mention that acidic bromate can also react with malonic acid (this will be discussed in our second paper[16]) but CO_2 produced in the first stage of that reaction is minimal. Anyway, any extra CO_2 production due to the presence of malonic acid and also any bromomalonic acid produced from malonic acid can only *increase* but not *decrease* the CO_2 evolution rate. Thus, if we assume that the organic substrate and the organic intermediates can react with acidic bromate exclusively, then we are not able to explain the observed decrease of the CO_2 evolution rate displayed in Figure 3. On the other hand, if we assume that a carbocation generated in the malonic acid−bromate reaction can react with bromomalonic acid, giving a product which is less active in CO_2 generation than BrMA itself, then we can explain the observation at least qualitatively. Thus, we suggest that in the presence of malonic acid, for example, malonyl carbocations (and also other carbocations) are generated:



The malonyl and other carbocations (produced in the later stages of the reaction) can start a polymerization of the enol form of BrMA. Naturally, all carbocations can also react with acidic bromate. Again, there are too many possibilities to follow. Nevertheless, it is clear that the CO_2 evolution rate can be decreased if the original BrMA substrate is converted by malonyl or other carbocations to a less reactive substrate.

3.5. Bromomalonic Acid−HOBr Reaction. It is well-known[25] that HOBr can brominate bromomalonic acid like elementary bromine. HOBr, however, is also a strong oxidant. Thus, it was reasonable to check whether HOBr only brominates bromomalonic acid or, in a similar way as acidic bromate, it can also oxidize it. In the latter case, some CO_2 evolution could be observed. Thus, we made an experiment, the result of which is shown in Figure 4, where a great excess of HOBr was applied.

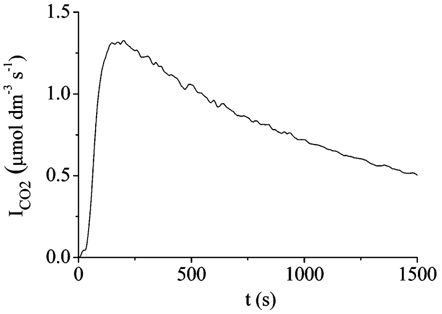
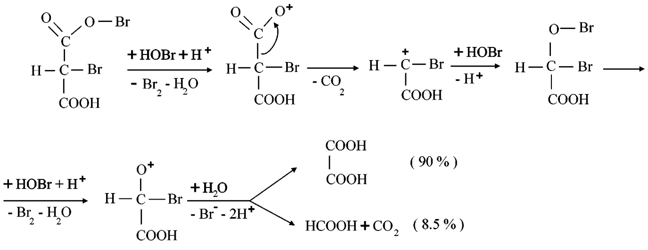


Figure 4. CO_2 evolution rate in the BrMA−HOBr reaction with an excess of HOBr. Initial conditions: $[BrMA]_0 = 1$ mM, $[HOBr]_0 = 17.5$ mM, and $[H_2SO_4]_0 = 1$ M.

In this case, a significant CO_2 evolution could be observed. The stoichiometry is close to $3CO_2$ from one BrMA, as in the case of acidic bromate oxidant. It was found in separate experiments that the CO_2 evolution rate is proportional to the square of the HOBr concentration when HOBr is in excess. On the other hand, if not HOBr but BrMA was applied in an excess, then no measurable CO_2 evolution could be observed. Finally, we checked whether dibromomalonic acid can be oxidized by HOBr in 1 M H_2SO_4. We found that this is not the case: no CO_2 evolution could be detected when Br_2MA and HOBr were mixed either in batch or in semibatch experiments. Usually, it is assumed that HOBr brominates the enol form of BrMA directly.[25] To rationalize the above experimental results, however, on the basis of that simple mechanism was not possible. Looking at the details of the bromination mechanism by HOBr published in the literature, we found that in the presence of organic acids it is an accepted mechanism[26,27] that the real brominating agent is not HOBr but a mixed anhydride (acyl hypobromite) formed from HOBr and the organic acid. Accepting the role of an acyl hypobromite intermediate, we suggest the following mechanism. In the first step, acyl hypobromite is formed from HOBr and BrMA:

$$\mathrm{HOBr + BrMA \rightarrow BrMAOBr + H_2O}$$

If BrMA is in an excess, then acyl hypobromite brominates BrMA and Br_2MA is formed as an end product. A different reaction route is opened, however, when HOBr is in an excess. In this case, decomposition of the acyl hypobromite to a carbocation, CO_2 and bromine is possible when acyl hypobromite reacts with the excess HOBr:



As was mentioned, when HOBr is in an excess, the initial CO_2 evolution rate is proportional to the square of the hypobromous acid concentration. The experimental rate law under such conditions is

$$I_0(CO_2) = k_{BHOB}[BrMA]_0([HOBr]_0)^2$$

We could even calculate a third-order rate constant of the reaction of $k_{BHOB} = 5$ M^{-2} s^{-1}. (Here, it was assumed like in the case of the BrMA−BrO_3^- reaction that in the first step 1 mol of CO_2 is produced from 1 mol of BrMA, that is, $(r_{BHOB})_0 = I_0(CO_2)$.) The above rate law can be rationalized by assuming first a fast pre-equilibrium for the acyl hypobromite production from BrMA and HOBr. In this case, the equilibrium concentration of the acyl hypobromite is proportional to the HOBr concentration. Then, in a subsequent rate determining step, HOBr reacts with the acyl hypobromite to give products. The rate of this second-order reaction is a bilinear function of the HOBr and acyl hypobromite concentrations; consequently, the overall rate of the reaction will be proportional to the BrMA concentration and the square of the HOBr concentration.

3.6. Simulations. Rate constants of the BrMA−BrO_3^- and BrMA−HOBr reactions were determined from the initial CO_2 evolution rates; thus, to understand the initial stage of these reactions, no simulations were needed. In later stages, however, the various products formed in these reactions can react further with both the oxybromine species and the BrMA substrate itself, affecting the subsequent course of the reaction. The reaction schemes suggested here for these later stages of the reaction include various carbocations and an acyl hypobromite intermediate. Presently, we have no direct information about the rates and the rate constants of reactions involving these hypothetical species. Despite that, it is reasonable to perform simulations to demonstrate that it is possible to find an appropriate set of rate constants for these hypothetical reactions which can mimic the experimental findings. Thus, the only aim of these model calculations is to show that the experimental observations can be rationalized within the reaction schemes suggested here. Reactions and rate constants applied in our computer simulations are given in Table 1.

As can be seen in our simplified mechanism, we have omitted further reactions of the "third generation" carbocations $BrC3^+$ and $C3^+$ either with bromate or with the enol form of the substrates. While these further reactions obviously occur, it was reasonable to assume that they play a less important role at least in the beginning of the reaction.

Here, we show only three simulations as illustrative examples.

As Figure 5 shows, the gradual increase of the CO_2 evolution rate in the BrMA−bromate reaction observed in the experiment is well reflected in the numerical simulation. The characteristic "shoulder" of the experiments appears on the simulated curve as well. The subsequent growth of the CO_2 evolution is more steep in the experiments, however.

Comparing Figures 3 and 6, when MA is also present, we can see again a qualitative agreement: both the experimental and simulated curves have a plateau after an initial fall in the CO_2 evolution rate. On the other hand, the plateau of the simulated curve is lower and in the experiments there is a slight increase of the CO_2 evolution during the plateau regime, a feature which cannot be seen in the simulations.

The small deviations between the experiments and the simulations of Figures 5 and 6 are most probably due to those later stage carbocationic reactions which were omitted from our mechanism.

In the case of the BrMA−HOBr reaction (Figures 4 and 7) the agreement between the experimental and simulated curves is rather good. This is because HOBr is in a great excess and BrMA and the carbocations react mainly with HOBr; consequently, the various carbocation−BrMA reactions do not play an important role here.

3.7. Conclusions and Outlook. Regarding the uncatalyzed reactions of BrMA with acidic bromate, it is a most important question whether these reactions can affect significantly the dynamics of an oscillatory BZ reaction; in other words, are they

TABLE 1: Reactions and Rate Constants Applied in the Simulations[a]

	rate constant		
reaction	forward	reverse	source
CO_2 (dissolved) → CO_2 (in the gas phase)	variable (s^{-1})	0	E
CO_2 (in the gas phase) → CO_2 (outflow to the detector)	$0.12\ s^{-1}$	0	E
Br_2 (dissolved) → Br_2 (in the gas phase)	variable (s^{-1})	0	ref 5
$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$	$8 \times 10^9\ M^{-2}\ s^{-1}$	$110\ s^{-1}$	ref 13
$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr$	$2.9 \times 10^6\ M^{-2}\ s^{-1}$	$2 \times 10^{-5}\ M^{-1}\ s^{-1}$	ref 13
$Br^- + BrO_3^- + 2H^+ \rightarrow HOBr + HBrO_2$	*	$3.2\ M^{-1}\ s^{-1}$	ref 13
$HBrO_2 + H^+ \rightarrow H_2BrO_2^+$	$2 \times 10^6\ M^{-1}\ s^{-1}$	$10^8\ s^{-1}$	ref 13
$HBrO_2 + H_2BrO_2^+ \rightarrow HOBr + BrO_3^- + 2H^+$	$1.7 \times 10^5\ M^{-1}\ s^{-1}$	0	ref 13
$OA + BrO_3^- + H^+ \rightarrow 2CO_2 + HBrO_2$	$7.47 \times 10^{-4}\ M^{-1}\ s^{-1}$	0	ref 5
$OA + HBrO_2 \rightarrow 2CO_2 + HOBr$	$4.2\ M^{-1}\ s^{-1}$	0	ref 5
$OA + HOBr \rightarrow 2CO_2 + Br^- + H^+ + H_2O$	$17\ M^{-1}\ s^{-1}$	0	ref 5
$OA + 2HOBr \rightarrow 2CO_2 + Br_2 + 2H_2O$	$1.2 \times 10^5\ M^{-2}\ s^{-1}$	0	ref 5
MA → MA(enol)	$2.6 \times 10^{-3}\ s^{-1}$	$180\ s^{-1}$	ref 13
BrMA → BrMA(enol)	$1.2 \times 10^{-2}\ s^{-1}$	$800\ s^{-1}$	ref 13
$Br_2MA \rightarrow CO_2 + Br_2AcAc$	$4.65 \times 10^{-5}\ s^{-1}$	0	E
Hypothetical Reactions			
$BrMA + BrO_3^- + 2H^+ \rightarrow CO_2 + H_2O + HBrO_2 + BrC1^+$	$3.8 \times 10^{-4}\ M^{-1}\ s^{-1}$	0	E
$BrC1^+ + BrO_3^- + H_2O \rightarrow OA + HBrO_2 + Br^- + H^+$	$7 \times 10^{-4}\ M^{-1}\ s^{-1}$	0	E + S
$BrC1^+ + BrMA(enol) \rightarrow BrC2^+$	$4 \times 10^2\ M^{-1}\ s^{-1}$	0	E + S
$BrC2^+ + BrO_3^- + H^+ \rightarrow BrC3^+ + CO_2 + H_2O + HBrO_2$	$10^{-4}\ M^{-1}\ s^{-1}$	0	E + S
$BrMA + HOBr \rightarrow BrMAOBr + H_2O$	$15\ M^{-1}\ s^{-1}$	$1.35 \times 10^{-1}\ s^{-1}$	E + S
$BrMAOBr + 3HOBr \rightarrow CO_2 + OA + 2Br_2Br^- + H^+ + H_2O$	$4.5 \times 10^{-2}\ M^{-1}\ s^{-1}$	0	E + S
$BrMAOBr + BrMA(enol) \rightarrow Br_2MA + BrMA$	$2 \times 10^3\ M^{-1}\ s^{-1}$	0	E + S
$MA(enol) + BrO_3^- + 2H^+ \rightarrow C1^+\ HBrO_2 + H_2O$	$10^5\ M^{-1}\ s^{-1}$	0	E + S
$C1^+ + BrMA(enol) \rightarrow C2^+$	$2 \times 10^4\ M^{-1}\ s^{-1}$	0	E + S
$C2^+ + BrO_3^- + H^+ \rightarrow C3^+ + CO_2 + H_2O + HBrO_2$	$10^{-4}\ M^{-1}\ s^{-1}$	0	E + S
$MA + HOBr \rightarrow MAOBr + H_2O$	$10.3\ M^{-1}\ s^{-1}$	$9.27 \times 10^{-2}\ s^{-1}$	E + S
$MAOBr + MA(enol) \rightarrow BrMA + MA$	$2 \times 10^2\ M^{-1}\ s^{-1}$	0	E + S

[a] Abbreviations: OA, oxalic acid; MA, malonic acid; BrMA, bromomalonic acid; Br_2MA, dibromomalonic acid; Br_2AcAc, dibromoacetic acid; $BrCl^+$, bromocarbocation 1; $BrC2^+$, bromocarbocation 2; $BrC3^+$, bromocarbocation 3; BrMAOBr, acyl hypobromite of BrMA; Cl^+, carbocation 1 (malonyl carbocation); $C2^+$, carbocation 2; $C3^+$, carbocation 3; MAOBr, acyl hypobromite of malonic acid; E, calculation based on experimental data; E + S, estimation based on CO_2 measurements and numerical simulations. The asterisk can be described by the following power series: $k_* = c_0 + c_1[Br^-] + c_2[Br^-]^2 + c_3[Br^-]^3$ for $[Br^-] > 2 \times 10^{-5}$ M; $k_* = 0.3$ for $[Br^-] < 2 \times 10^{-6}$ M. $c_0 = 0.487\,89\ M^{-1}\ s^{-1}$, $c_1 = 0.143\,911 \times 10^5\ M^{-1}\ s^{-1}$, $c_2 = -0.707\,695\,8 \times 10^8\ M^{-1}\ s^{-1}$, and $c_3 = 0.116\,310 \times 10^{12}\ M^{-1}\ s^{-1}$.

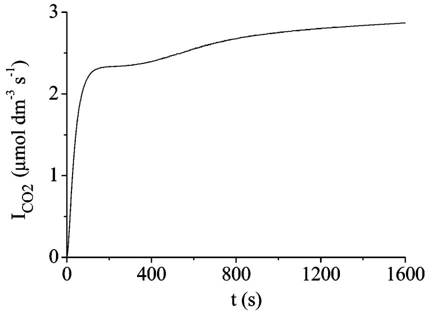


Figure 5. Simulation of the BrMA−BrO_3^- reaction with the data of Table 1. The corresponding experimental curve is shown in Figure 2a.

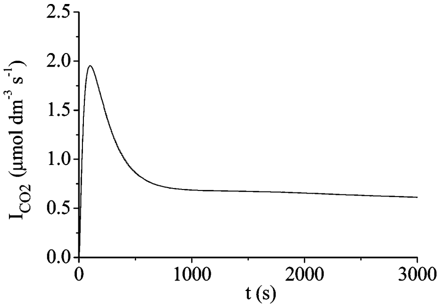


Figure 6. Simulation of the BrMA−BrO_3^- reaction in the presence of malonic acid. The corresponding experimental curve is shown in Figure 3.

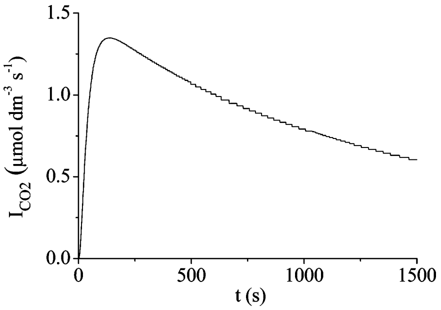


Figure 7. Simulation of the BrMA−HOBr reaction with a great excess of HOBr. The corresponding experimental curve is shown in Figure 4.

an important part of a complete BZ mechanism? This question is not easy to answer in general. Nevertheless, it is reasonable to compare the rate of the BrMA−BrO_3^- reaction with the rate of the BrMA−Ce^{4+} reaction in an oscillatory BZ system. The rate constant of the first reaction is $k_{BB} = 3.8 \times 10^{-4}\ M^{-1}\ s^{-1}$, while the latter[13] is 0.1 $M^{-1}\ s^{-1}$. Thus, the ratio R of the two rates is

$$R = 3.8 \times 10^{-3}[BrO_3^-]/[Ce^{4+}]$$

With the data of the experiment presented in the MBM paper ($[BrO_3^-] = 0.1$ M, $[Ce^{4+}] = 5 \times 10^{-4}$ M)

$$R = 0.76$$

thus the rates of the two reactions are comparable. The products of the BrMA−BrO_3^- reaction are also important components: the autocatalytic intermediate $HBrO_2$ and also the control intermediate Br^- in later stages. In this later stage, oxalic acid can also appear (see the reaction scheme in Section 3.4), which participates in various important reactions.[5,6] All of this suggests that the BrMA$-$BrO$_3^-$ reaction should be included in a realistic mechanism of the BZ reaction whenever the BrMA acid concentration is significant. On the other hand, in most cases, the oscillatory reaction mixture usually contains both BrMA and malonic acid. The possible reactions of various carbocation intermediates with the enol form of the substrates make such systems rather complex, however (see the experiment in Figure 3 as an example).

The other somewhat unexpected reaction discovered here is the oxidation of BrMA by HOBr when HOBr is in an excess. It is difficult to tell the importance of this reaction in an oscillatory BZ system. In the experimental rate law of this reaction, the partial order of HOBr is 2 and HOBr appears only periodically in the short oxidized state of the oscillatory reaction and at low (about 10^{-5} M) concentrations.[28] All of this suggests that this reaction is less important. On the other hand, just during the brief oxidized state, this newly discovered reaction reduces HOBr to bromine which in turn generates bromide by brominating malonic and bromomalonic acids. Whether this bromide source is significant or not compared to other ones should be studied in the future.

Finally, we have to remember that in a classical BZ system (at least in the beginning) the dominant substrate is malonic acid. After discovering the uncatalyzed reaction of BrMA with acidic bromate, it seemed reasonable that analogous reactions might occur between malonic acid and bromate as well. A detailed study showed that this is really the case. Results of that investigation will be published in a subsequent paper.[16] In general, while uncatalyzed bromate$-$substrate reactions were disclosed many years ago (e.g., Sevcik described[29] and studied the effect[30] of the bromate$-$oxalic acid reaction, and Field and Györgyi discovered[31] the BrMA$-$BrO$_3^-$ reaction), little attention was paid until now to their role in the mechanism of the classical BZ reaction. In the future, our laboratories are planning to study this question.

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