Uncatalyzed Reactions in the Classical Belousov−Zhabotinsky System. 2. The Malonic Acid−Bromate Reaction in Acidic Media

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The title reaction was studied with various techniques in 1 M sulfuric acid, a usual medium for the oscillatory Belousov−Zhabotinsky (BZ) reaction. It was found to be a more complex process than the bromomalonic acid (BrMA)−BrO_3^- reaction studied previously in the first part of this work. Malonic acid (MA) can react with acidic bromate by two parallel mechanisms. The main aim of the present research was to determine the mechanisms, the rate laws, and the rate constants for these parallel channels. In one reaction channel the first molecular products are glyoxalic acid (GOA) and CO_2 while in the other channel mesoxalic acid (MOA) is the first molecular intermediate, that is, no CO_2 is formed in this step. To prove these two independent routes specific colorimetric techniques were developed to determine GOA and MOA selectively. The rate of the GOA channel was determined by following the rate of the carbon dioxide evolution characteristic for this reaction route. In this step, regarding it as an overall process, one MA is oxidized to GOA and CO_2 and one BrO_3^- is reduced to HOBr, which forms BrMA with another MA. The initial rate of the GOA channel is a bilinear function of the initial MA and BrO_3^- concentrations with a second-order rate constant $k_{GOA} = 2.4 \times 10^{-7}$ M^{-1} s^{-1}. The rate of the other channel was calculated from the rate of the BrO_3^- consumption measured in separate experiments, assuming that the measured depletion is a sum of two separate terms reflecting the consumptions due to the two independent channels. In the MOA channel one MA is oxidized to MOA and one BrO_3^- is consumed while another MA is brominated as in the GOA channel. It was found that the initial rate of the MOA channel is also a bilinear function of the MA and BrO_3^- concentrations with a second-order rate constant $k_{MOA} = 2.46 \times 10^{-6}$ M^{-1} s^{-1}. Separate chemical mechanisms are suggested for both channels. In all of the various bromate−substrate reactions of these mechanisms oxygen atom transfer from the bromate to the substrate occurs generating bromous acid intermediate. This can be of high importance in BZ systems as bromous acid is the autocatalytic intermediate there. GOA and MOA also can be oxidized by acidic bromate but a study of these reactions will be published later.

1. Introduction

The classical Belousov−Zhabotinsky (BZ) reaction is the cerium ion catalyzed oscillatory oxidation and bromination of malonic acid by acidic bromate.[1−4] Usually it is assumed that oxidation of malonic and bromomalonic acid (MA and BrMA) is caused exclusively by the Ce^{4+} ions and a direct oxidation of these organic substrates by oxybromine species is not significant. Nevertheless, in our previous paper[5] it was found that oxidation of BrMA by acidic bromate and also by HOBr are well measurable processes, the rate of the BrMA−BrO_3^- reaction can be even comparable with that of the BrMA−Ce^{4+} reaction. In the present paper we study the analogous MA−BrO_3^- reaction. As both malonic acid and bromate are main components of the classical BZ system a direct MA−BrO_3^- reaction where acidic bromate is reduced to bromous acid ($HBrO_2$) can be of prime importance as $HBrO_2$ is an autocatalytic intermediate of the BZ reaction. Such a steady inflow should affect both the induction and the time period of the chemical oscillations.

This way the MA−BrO_3^- reaction can be even more important in the BZ chemistry than the BrMA−BrO_3^- reaction especially in the initial phase when the BrMA concentration is low. Despite this consideration we started the study of the uncatalyzed reactions with the BrMA−BrO_3^- system for the following three main reasons:

(i) The BrMA−BrO_3^- reaction is simpler than the MA−BrO_3^- reaction. As we are going to show the latter has two parallel oxidation pathways characterized with two different intermediates: glyoxalic acid (GOA) and mesoxalic acid (MOA).

(ii) Our sensitive carbon dioxide measuring method cannot be applied to follow the rate of oxidation of MA to MOA as there is no CO_2 formation in this step. Thus we had to develop different techniques to measure the rate of this process.

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(iii) BrMA reacts much faster with acidic bromate than MA. Thus in later stages of the MA−BrO_3^- reaction, where BrMA is also produced, a contribution of the BrMA−BrO_3^- reaction to the total rate of the CO_2 evolution should be taken into account.

In the present work first a colorimetric method known from the literature was applied in a modified form to determine the sum of GOA and MOA production in the title reaction. It was necessary to develop an entirely new colorimetric method, however, for a selective determination of these compounds. The rate constant of the GOA channel was determined by CO_2 evolution rate measurements. Potentiometric titration was applied to measure the bromate concentration and its rate of consumption in the MA−BrO_3^- reaction, which is the sum of the rates of the separate GOA and MOA channels. A rate constant for the MOA channel was calculated from this sum, knowing already the net rate of the GOA channel.

When calculating the rate constants from the initial reaction rates subsequent reactions, including the GOA−BrO_3^- and the MOA−BrO_3^- reactions, were neglected. The study of these two processes will be the subject of a subsequent paper with the aim to present a realistic model valid not only for the initial but also for later stages of the MA−BrO_3^- reaction.

2. Experimental Section

2.1. Chemicals. Malonic acid (MA; Fluka, puriss.), $NaBrO_3$ (Fluka, purum p.a.), H_2SO_4 (Merck, p.a.), NaBr (Merck, suprapur), KBr (Reanal, analytical grade), $AgNO_3$ (Reanal, purum), KOH (Reanal, purum), $NiSO_4 \cdot 7H_2O$ (Reanal, purum), NH_4OH (Interkémia, 25%), 2-thiobarbituric acid (Fluka, purum), resorcinol (Fluka, purum), 2,4-dinitrophenylhydrazine (Fluka, puriss. p.a.; moistened with 50% water), the sodium salt of glyoxalic acid (NaGOA; Fluka, purum), and the disodium salt of mesoxalic acid monohydrate ($Na_2MOA \cdot H_2O$; Fluka purum) were used as received. All solutions were prepared with doubly distilled water. We used freshly prepared acidic solutions of MA as the activity of MA in the MA−BrO_3^- reaction changes slowly in time when MA is kept under acidic conditions. In our previous paper[5] we found a similar behavior in the case of bromomalonic acid (BrMA), which was explained by a carbocationic oligomerization. While the mechanism of the observed activity changes is probably the same, the rate of change is orders of magnitude slower in the case of MA: it can be observed only on the time scale of weeks. We found that the rate of the initial CO_2 evolution is higher, e.g., by a factor of 3.6, after keeping 3 M malonic acid in 2 M H_2SO_4 for 6 months. This can be rationalized if we assume that the oligomer reacts faster with bromate than malonic acid to yield CO_2 instantaneously in a mechanism that is similar to that of the GOA channel.

2.2. Qualitative Test for Oxalic Acid (OA) in a Sample Containing Reaction Products of the MA−BrO_3^- Reaction. *2.2.1. Preparation of the Sample*. The reagents were introduced in a 10 mL flask in the following order: 4 mL of 2 M MA in 2 M H_2SO_4, 1 mL of 2 M H_2SO_4, and 1 mL of 2 M $NaBrO_3$ in water. The mixture was diluted finally to 10 mL. The initial concentrations after mixing were 0.8 M MA, 0.2 M bromate, and 1 M H_2SO_4. The reaction mixture was kept at room temperature for 24 h. Then, 7 mL of 5 M KOH was added dropwise to reach a pH 5−6 and stop the MA−bromate reaction.

To 5 mL of the above mixture, 1 mL of 0.5 M $NiSO_4$ and a few drops of 5 M KOH were added to precipitate Ni^{2+} salts. At neutral pH, a green precipitate appeared. Then to obtain an optimum yield of Ni-oxalate in the precipitate, a few more drops of 5 M KOH were added. The final pH was 13.5. The precipitate was settled in a centrifuge and washed with 0.01 M $NiSO_4$ in water three times. Each time, the presence of bromate in the clear solution above the precipitate was checked. On a watch glass one drop of the tested solution was mixed with one drop of acidic KI solution, which also contained some starch. A dark blue color indicated the presence of bromate. After the third washing of the precipitate, there was no bromate in the solution. Next, to remove the Ni^{2+} ions, the whole precipitate was mixed with 4 g of Varion KS cationic exchanger resin in hydrogen form and 3 mL of distilled water until the whole precipitate disappeared. The solution, which contained various carboxylic acids, was separated from the resin beads and was mixed with 0.2 mL of 25% NH_4OH solution and concentrated by evaporation at 80 °C. When the volume was reduced to 1 mL, the sample was cooled.

2.2.2. Qualitative Test ("*Spot Reaction*"[6,7]). The sample, together with 0.3 mL of 25% NH_4OH, was evaporated to dryness in a test tube, over a free flame. At that point about 5 mg of 2-thiobarbituric acid was added and carefully heated over the free flame. A characteristic brick-red color indicated the presence of oxalic acid in the sample.

2.3. Colorimetric Determination of the Intermediates GOA and MOA in the MA−Bromate Reaction. Two different colorimetric reactions were used: a specific reaction of GOA and MOA with resorcinol and a nonspecific reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine (2,4-DNPhydrazine). It was discovered, however, that GOA and MOA hydrazons have a strong characteristic color in alkaline solutions, which can be different for the GOA and MOA hydrazones depending on the pH.

2.3.1. Instrument for Spectrophotometric Measurements. The absorbance has been monitored in the range 190−820 nm with a computer-controlled Hewlett-Packard model 8452A diode array spectrophotometer.

2.3.2. Preparation of the Reaction Mixture. MA (40 mL, 5 M) in 1 M H_2SO_4 and 5 mL of 2 M H_2SO_4 were introduced into a 50 mL volumetric flask. The reaction was started by adding 2.5 mL of 2 M $NaBrO_3$ in water. Then, the solution was diluted with distilled water to 50 mL. The initial concentrations after mixing were therefore 4 M MA, 0.1 M $NaBrO_3$, and 1 M H_2SO_4. The volumetric flask with the reaction mixture was kept in a thermostating bath at 20 °C.

2.3.3. Preparation of the Samples for the Colorimetric Reactions. Four 10 mL samples were taken 0.5, 2.33, 5, and 9 h after the start of the reaction. The samples were mixed with 0.55 mL of 4 M NaBr in 1 M H_2SO_4. This way the MA−bromate reaction was stopped as the bromate reacted fast with the excess bromide. HOBr and bromine formed in the reaction brominated the malonic acid present in high amounts. The H_2SO_4 concentration of a sample was between 0.9 and 0.7 M, depending on the moment when the reaction between MA and bromate was stopped. After the reaction was stopped, the mixtures were kept at 4 °C and were analyzed within 1 day.

2.3.4. Colorimetric Determination of the Sum of GOA and MOA with Resorcinol. The details of the method are given in the Supporting Information.

2.3.5. Colorimetric Determination of GOA and MOA with 2,4-Dinitrophenylhydrazine. Reaction with 2,4-DNPhydrazine. One milliliter of the sample was mixed with 1 mL of distilled water in a test tube. To this mixture 2 mL of 0.05% 2,4-DNPhydrazine in 0.5 M H_2SO_4 was added. (After mixing the initial H_2SO_4 concentration was between 0.425 and 0.475 M, depending on the sample.) As a next step the tube was heated

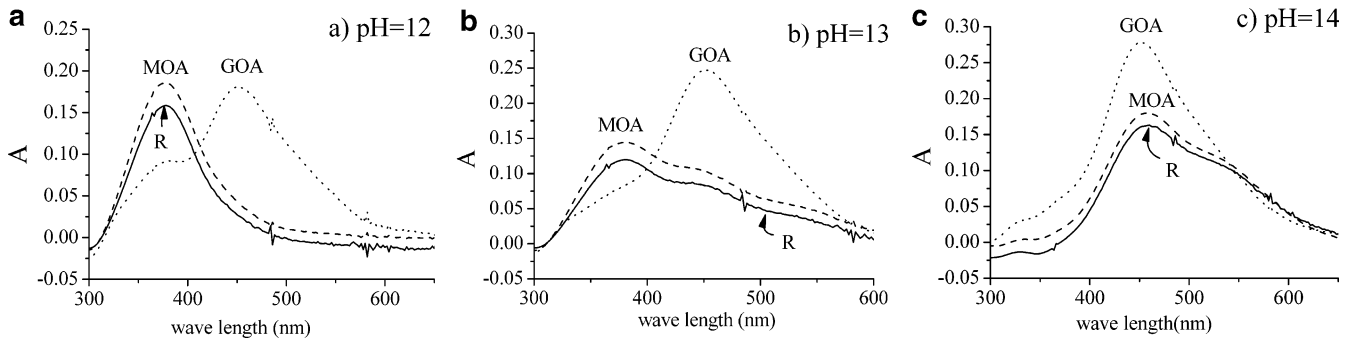


Figure 1. Visible absorption spectra of 2,4-DNPhydrazone derivatives of GOA, MOA, and the reaction mixture at pH (a) 12, (b) 13, and (c) 14. The MA−BrO_3^- reaction mixture was tested after 5 h of reaction. Initial concentrations: $[MA]_0 = 4$ M, $[BrO_3^-]_0 = 0.1$ M in 1 M H_2SO_4. Cuvette thickness: 1 mm.

and kept at 65 °C for 10 min. After cooling, the absorption spectrum of the sample was measured at different pH values.

Absorbance Measurements in the UV−Visible Range at pH 12, 13, and 14. At acidic pH values it is difficult to observe the light orange color of the 2,4-DNPhydrazones of GOA and MOA without separating them from the unreacted reagent of the similar color. It was realized, however, that these hydrazones have a characteristic deep red color in alkaline solutions at pH 14. Moreover, it was also found that while their absorption spectra are similar at this pH these spectra differ from each other at pH 13 and even more at pH 12. To establish these different pH values the following processes were applied. *pH 12*: To 1 mL of solution a 1.8 M KOH solution was added dropwise until pH ∼8. The pH was checked by indicator paper. Since besides sulfuric acid a large amount of malonic and other organic acids were present with a considerable buffer capacity, to reach pH ∼8, addition of about 1.85 mL of 1.8 M KOH was necessary. (This amount varied a little depending on the reaction time. The present numerical example assumes that the total volume after reaching pH ∼8 is 1 + 1.85 = 2.85 mL.) Next 0.15 mL of 0.2 M KOH was added. As the buffer capacity of the organic acids in the alkaline pH region is negligible the final pH should be around 12. *pH 13*: In the same way as for pH 12, first the pH ∼8 state was reached. Then 0.15 mL of 2 M KOH was added. *pH 14*: First to reach the pH ∼8 state, 0.5 mL of 7 M KOH was added dropwise to 1 mL of solution after the reaction with 2,4-DNPhydrazine. Next 1.5 mL of 2 M KOH was added.

Calibration measurements were made at the above three pH values with GOA and MOA solutions of known concentrations. These calibrating solutions including the blank also contained 2 M MA and all went through the same procedures as the samples. This way errors due to any contamination with the carbonyl group in the MA sample were eliminated.

Spectra measured for 2,4-DNPhydrazones of GOA, MOA, and the reaction mixture at different pH values are shown in Figure 1.

Comparing these spectra suggests that the majority of the carbonyl compounds found in the reaction mixture should be MOA, and GOA is a minor component. Such a conclusion can be drawn even without a spectrophotometer, observing the color of the various 2,4-DNPhydrazones at different pH values as displayed in Table 1.

A Characteristic Difference between the Stability of 2,4-DNPhydrazones of GOA and MOA at pH 14. The protocol described in the previous section, to give 2,4-DNPhydrazones in aqueous solution, at pH 14, was applied also in this study. As we already mentioned, at pH 14, the 2,4-DNPhydrazone derivatives of both GOA and MOA have absorption maxima at $\lambda = 450$ nm. However, the color of the solution of GOA's

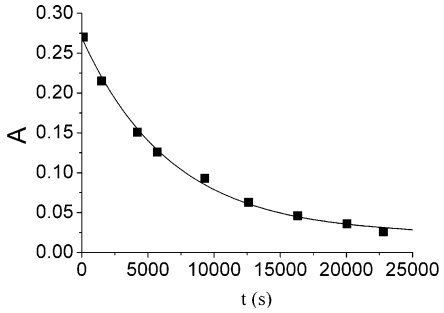


Figure 2. Plot of maximum absorbance (at $\lambda = 450$ nm) of GOA 2,4-DNPhydrazone in aqueous solution at pH 14 vs time. Cuvette thickness: 1 mm.

TABLE 1: Colors of 2,4-DNPhydrazones at Different pH Values in Alkaline Medium

	pH 12	pH 13	pH 14
2,4-DNPhydrazone of GOA	red	red	red
2,4- DNPhydrazone of MOA	yellow	brick-red	red
2,4-DNPhydrazones formed by the reaction mixture	yellow	brick-red	red

derivative changes gradually in time. The color, originally deep red, becomes yellow after 24 h. After 6 h the absorbance of the 2,4-DNPhydrazone of GOA is only 10% of the original value (Figure 2). In sharp contrast, the red color and the absorbance of MOA 2,4-DNPhydrazone solution does not change during this time.

When measuring the maximum absorbance of the 2,4-DNPhydrazones of the reaction mixture at pH 14 it decreased during the first few hours. After that, however, the absorbance remained constant. It could be assumed that while the initial absorbance is due to both MOA and GOA hydrazones, the final one is due to the remaining MOA hydrazone only. Thus we can conclude that MOA and GOA concentrations can be measured separately with this method.

2.4. CO_2 Measurements. The same CO_2 measuring apparatus, reactor, and method were applied as in our previous publication.[5] Details of the method can be found there.[5,8] Prior to the experiments atmospheric CO_2 dissolved in the reactant solutions was removed by bubbling nitrogen through them.

2.4.1. Instantaneous CO_2 Production in the GOA Channel of the Malonic Acid−Bromate Reaction. As we shall show acidic bromate can react with malonic acid in two different ways. In one way an instantaneous decarboxylation occurs and GOA appears as an intermediate. The rate of this reaction channel, the corresponding rate constant, and the partial reaction order for the main reactants were determined in the following way.

2.4.2. Determination of the Rate Constant k_{GOA}. First 2 mL of 3 M MA in 2 M H_2SO_4 was injected into the reactor. The

reaction was started by injection of 2 mL of 2 M $NaBrO_3$ in water. The initial concentrations after mixing were therefore 1.5 M MA, 1 M bromate, and 1 M H_2SO_4. The initial reaction rate was calculated by extrapolating the CO_2 evolution rate to time zero (see Figure 4 in the Discussion). Then, the rate constant for the instantaneous CO_2 evolution in the MA−BrO_3^- reaction could be calculated from the initial reaction rate and the initial concentrations of the reactants.

2.4.3. Determination of the Partial Reaction Order for Malonic Acid. Separate CO_2 measurements were performed with solutions of various concentrations of MA in sulfuric acid, every time using the same initial concentrations of bromate and sulfuric acid in the reaction mixture: 1 M $NaBrO_3$ and 1 M H_2SO_4. The partial reaction order for MA was calculated from the initial CO_2 evolution rates.

2.4.4. Determination of the Partial Reaction Order for Bromate. A series of separate CO_2 measurements were made using different initial $NaBrO_3$ and the same MA (1.5 M) and H_2SO_4 (1 M) concentrations in the reaction mixture. The partial reaction order for bromate was calculated from the initial CO_2 evolution rates.

2.4.5. Determination of the Partial Reaction Order for the Hydrogen Ion. Separate CO_2 measurements were performed with different initial H_2SO_4 and the same MA (1.5 M) and bromate (1 M) concentrations in the reaction mixture. The partial reaction order for hydrogen was calculated in the same way as for MA and bromate.

2.5. Determination of the Bromate Consumption in the MA−Bromate Reaction.

2.5.1. Preparation of Reaction Mixtures. To check the reaction order for MA in the reaction two different reaction mixtures were prepared.

Reaction Mixture A. Initial concentrations: 4 M MA, 0.1 M $NaBrO_3$, 1 M H_2SO_4. MA (8 mL, 5 M) in 1 M H_2SO_4 and 1 mL of 2 M H_2SO_4 were mixed in a 10 mL flask. The reaction was started by adding 0.5 mL of 2 M $NaBrO_3$ in water and the volumetric flask was filled with distilled water to 10 mL. After a careful mixing the flask was placed into a water bath thermostated to 20 °C.

Reaction Mixture B. Initial concentrations: 2 M MA, 0.1 M $NaBrO_3$, 1 M H_2SO_4. MA (4 mL, 5 M) in 1 M H_2SO_4 was introduced into a 10 mL flask together with 3 mL of 2 M H_2SO_4. The reaction was started by adding 0.5 mL of 2 M $NaBrO_3$ in water and the mixture was diluted to 10 mL. After mixing the flask was thermostated to 20 °C.

2.5.2. Preparation of Samples for Titration. One milliliter samples were taken from the reaction mixtures at different times in the course of the MA−bromate reaction. Each sample was mixed with 2 mL of 0.11 M NaBr in 1 M H_2SO_4. This way the MA−bromate reaction was stopped as bromate reacted rapidly with the added bromide in the acidic medium. Products of the BrO_3^-−Br^- reaction (HOBr and Br_2) react with MA to form bromomalonic (BrMA) and some dibromomalonic acid (Br_2MA). The bromide was applied in 10% excess compared to the initial amount of bromate. That is 10% of the bromide remains unreacted if it is added to the reaction mixture at the start of the experiment. As more and more bromate is consumed in the course of the MA−BrO_3^- reaction the excess of bromide compared to the remaining bromate increases gradually. The unreacted bromide in the 3 mL sample was determined with potentiometric titration.

2.5.3. Potentiometric Titration of the Excess of Bromide in the Samples with Silver Nitrate. A magnetically stirred 50 mL beaker with a thermostated jacket was used as a reactor. The bromide concentration was monitored by a homemade Ag/AgBr electrode (silver wire electrode coated with AgBr melt[9]). An Ag/AgCl reference electrode was used in a solution of 1 M KCl in 1 M H_2SO_4. The reference electrode was connected to the reactor by a salt bridge filled with 1 M H_2SO_4.

First, 17 mL of 1 M H_2SO_4 was pipetted into the reactor and then the 3 mL sample containing the excess of bromide was added under continuous stirring. After 5 min, when the measured potential reached a steady value, a steady inflow of an aqueous $AgNO_3$ solution (concentration: around 0.1 M) was started. The inflow rate was 139 μL/min maintained by a peristaltic pump. The bromide concentration was calculated from the inflection point of the electrode potential versus time diagram. To find the factor of the $AgNO_3$ solution, calibration was performed by potentiometric titration of 20 mL of 0.01 M KBr in 1 M H_2SO_4 with the $AgNO_3$ solution.

According to the stoichiometry of the BrO_3^-−Br^- reaction in the presence of MA, the bromate consumption due to the MA−BrO_3^- reaction is half of the increment of the bromide excess measured by the potentiometric titration.

3. Results and Discussion

3.1. Colorimetric Determination of Organic Acid Intermediates in the MA−Bromate Reaction.

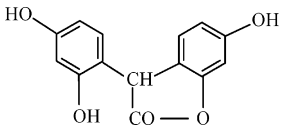
3.1.1. Possible Organic Acid Intermediates of the MA−BrO_3^- Reaction. In the course of the MA−BrO_3^- reaction subsequent oxygen atom transfer reactions occur from the acidic bromate first to MA then to the various organic intermediates produced in these oxygen atom transfers. On the basis of mechanistic considerations (see later), two different oxidation pathways seemed reasonable. In the first one oxidation and decarboxylation first lead to glyoxalic acid (GOA), which is oxidized further to oxalic acid (OA) and finally to carbon dioxide. In the other pathway the first molecular intermediate is mesoxalic acid (MOA), which is also oxidized to OA and then to CO_2. Our plan here was a qualitative identification of the three organic acid intermediates (GOA, MOA, and OA) with sensitive and specific colorimetric tests. Moreover we also wanted to measure the MOA and GOA intermediates quantitatively to see the relative importance of the two different oxidation pathways in the complete mechanism. To this end it was necessary to develop and combine two different colorimetric methods with two different reagents: the resorcinol and the 2,4-dinitrophenyl hydrazine.

We have to mention that besides GOA, MOA, and OA, bromomalonic and dibromomalonic acid can also appear as additional organic acid intermediates of the reaction. This is because the reduction of acidic bromate leads to bromous acid, which disproportionates rapidly to bromate and to hypobromous acid, and the latter brominates malonic acid. Reactions of BrMA produced this way with acidic bromate and HOBr are discussed in our previous paper.[5]

3.1.2. Qualitative Test for Oxalic Acid. Application of the thiobarbituric acid test (as it is described in the Experimental Section) proved that the MA−bromate reaction really produces oxalic acid. OA is only an intermediate, however, as it reacts further with acidic bromate[10] producing carbon dioxide.

3.1.3. GOA and MOA Determination by a Reaction with Resorcinol. Pesez[11] discovered that heating a mixture of glyoxalic acid with resorcinol in an acidic medium leads to the

lactone of tetrahydroxy-2,2′,4,4′-diphenylacetic acid:



A solution of this lactone becomes violet when mixed with sodium ethylate with an absorption maximum at 560 nm.[12] For the formation of such a five-membered lactone ring the carbon atom of the carbonyl group and the carbon atom of the carboxyl group should be connected. As glyoxalic acid is the only aldehyde where this condition is satisfied, the resorcinol test is specific for glyoxalic acid among all aldehydes.[13] Carboxylic acids with ketonic carbonyl groups were not tested, however. To do this test we substituted GOA with MOA in the same procedure and in the final step we could observe the same violet color as in the case of GOA. (The molar extinction coefficient was smaller by a factor of 2, however.) Obviously, as MOA has the same functional groups as GOA it can form a similar lactone with resorcinol. Thus a positive resorcinol test is specific proof for the presence of a carboxylic acid with an α-carbonyl group but it cannot differentiate between glyoxalic and mesoxalic acids.

The resorcinol method proved that either GOA or MOA or maybe both can be intermediates in the MA−BrO_3^- reaction. Applying this method we were even able to calculate the weighed sum of the two concentrations $S = [MOA] + 2[GOA]$ at different times in the course of the MA−bromate reaction (see the formula in the Supporting Information) to obtain well reproducible *S* vs time diagrams. Nevertheless, to calculate individual MOA and GOA concentrations was not possible with this method.

3.1.4. Selective Determination of MOA and GOA with 2,4-DNPhydrazine. Evolution of MOA and GOA Concentrations during the MA−Bromate Reaction. To measure separately the concentrations of GOA and MOA intermediates in the course of the MA−bromate reaction, we used the colorimetric reaction of carbonyl compounds with 2,4-DNPhydrazine[14,15] in acidic solutions. It was discovered that the hydrazones of GOA and MOA can be measured sensitively and selectively by absorption spectrophotometry in alkaline solutions. Figure 1 presents such a measurement as an illustration.

Regarding the absorption spectra of Figure 1, it is rather obvious that MOA is the main carbonyl compound in the reaction mixture. That is, the MOA channel is the dominant one in the MA−BrO_3^- reaction. In theory the different spectra of the hydrazones could be a basis of their selective determination. The relative error of the GOA concentration would be high in this case, however, as GOA is a minor component. Thus for a quantitative determination of GOA we made use of the great difference between the stability of the two hydrazones at pH 14. The absorbance of the hydrazones' mixture was measured at its maximum ($\lambda = 450$ nm) and the decrease observed after 6 h was attributed to the hydrazone of GOA, which, within experimental error, decomposed during this time completely. The remaining absorbance was attributed to the much more stable MOA hydrazone, which showed no decomposition during 6 h in a separate experiment. This way it was possible to calculate the ratio $\eta = [GOA]/[MOA]$ of the two components. (Naturally, the absolute values of the concentrations can be determined by applying the 2,4-DNPhydrazine method only. Nevertheless, we found that the *S* value measured with the resorcinol method was somewhat more reliable. Thus to calculate the concentrations we combined the results measured with the two different methods. The deviation between the *S* values determined with the two methods is not dramatic, however, about 15−20% as a maximum.) If η is known from the hydrazine method and *S* from the resorcinol method, then the MOA and GOA concentrations can be calculated by the following formula:

$$[MOA] = S/(1 + 2\eta) \quad [GOA] = \eta[MOA]$$

Results of these calculations can be seen in Figure 3.

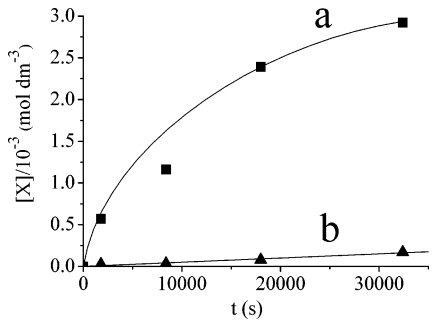


Figure 3. Time evolution of the intermediate concentrations in the MA−bromate reaction: (a) mesoxalic and (b) glyoxalic acid. Initial concentrations: $[MA]_0 = 4$ M, $[BrO_3^-]_0 = 0.1$ M in 1 M H_2SO_4.

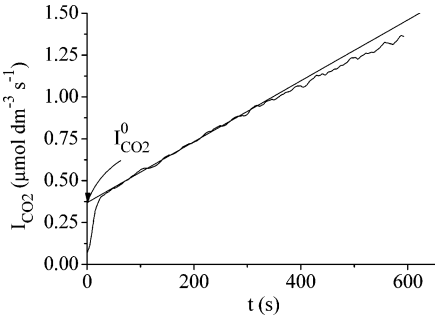


Figure 4. Determination of the initial rate of that channel in the malonic acid−bromate reaction that produces GOA and CO_2. Initial reagent concentrations: $[MA]_0 = 1.5$ M, $[BrO_3^-]_0 = 1$ M in 1 M H_2SO_4.

3.2. Rate Constant and Mechanism of the GOA Producing Reaction Channel in the MA−Bromate Reaction. Figure 4 depicts the result of an experiment performed to determine the initial rate of the CO_2 evolution in the MA−BrO_3^- reaction. From a series of separate CO_2 measurements (see the Experimental Section for the details) we found that the partial reaction order for both MA and BrO_3^- is 1 in this reaction channel of instantaneous CO_2 production. The initial rate of carbon dioxide evolution, $I^0_{CO_2}$, is therefore a bilinear function of the two concentrations within the experimental error:

$$I^0_{CO_2} = k_{GOA}[MA]_0[BrO_3^-]_0$$

In the above formula the hydrogen ion concentration was included in the rate constant k_{GOA} as in all of the above experiments we used the same concentration of sulfuric acid, 1 M, as in the BZ reaction.[16] However, in another series of experiments we changed the sulfuric acid concentration and found that the partial reaction order for the hydrogen ion is 2 (see section S2 in the Supporting Information). This piece of information will be applied later in mechanistic considerations.

It is reasonable to assume that in the first step of the reaction only one molecule of CO_2 is produced. In this case the initial

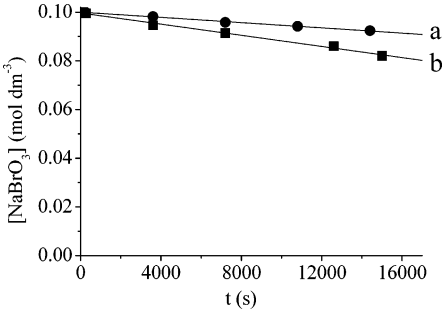
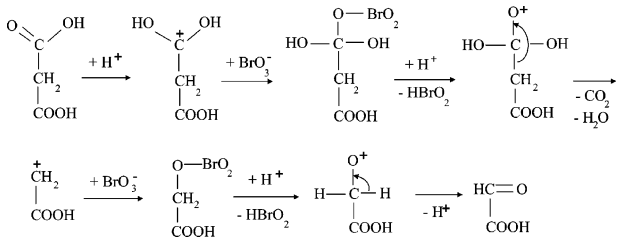


Figure 5. Bromate concentration as a function of time in the malonic acid−bromate reaction. Initial concentrations of the components: (a) $[MA]_0 = 2$ M, $[BrO_3^-]_0 = 0.1$ M in 1 M H_2SO_4; (b) $[MA]_0 = 4$ M, $[BrO_3^-]_0 = 0.1$ in 1 M H_2SO_4.

SCHEME 1: The GOA Channel



rate of the reaction $r^0_{GOA} = I^0_{CO_2}$. Then the rate constant of this channel k_{GOA} can be calculated with the following formula:

$$k_{GOA} = I^0_{CO_2}/\{[MA]_0[BrO_3^-]_0\}$$

On the basis of the experiment shown in Figure 4 and also on various other CO_2 measurements, the result is $k_{GOA} = 2.4 \times 10^{-7}$ M^{-1} s^{-1}.

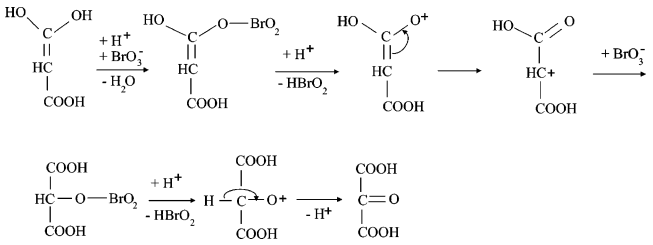
We suggest the mechanism in Scheme 1 for this channel of the malonic acid−bromate reaction where an instantaneous CO_2 production occurs and the first molecular intermediate is glyoxylic acid.

If we assume that the rate determining step in the decarboxylation is the hydrogen ion catalyzed decomposition of the organobromate intermediate (formed in the second step of the reaction in Scheme 1) then even the experimentally observed second-order kinetics for the hydrogen ion can be rationalized. This is because the concentration of the organobromate intermediate should be proportional with the hydrogen ion concentration—assuming a fast preequilibrium—and the rate of its decomposition should be proportional with the hydrogen ion concentration again. Thus the rate of the overall reaction should be proportional with the square of the hydrogen ion concentration in accordance with the experiments.

3.3. Rate Constant and Mechanism of the MOA Producing Reaction Channel in the MA−Bromate Reaction. Figure 5 shows the results of two different experiments conducted to follow the bromate concentration, which is decreasing gradually in the course of the MA−BrO_3^- reaction. Bromate concentrations were measured by potentiometric titrations as described in the Experimental Section.

As we can see in Figure 5a,b, the bromate concentration decreases slowly and the rate of its consumption is practically constant in the first 5 h of the MA−BrO_3^- reaction. Thus we applied a linear fit for these data. The initial bromate consumption rates, $I^0_{BrO_3^-}$, in Figure 5, are equal to the slopes of the fitted straight lines. On the basis of the experimental result displayed in Figure 5, and also on other parallel measurements, it becomes clear that the $I^0_{BrO_3^-}$ values are more than 10 times

SCHEME 2: The MOA Channel



higher than the $I^0_{CO_2}$ values which are the initial carbon dioxide evolution rates calculated for the same experimental conditions. In the GOA channel, consumption of 1 BrO_3^- would result in the production of 1 CO_2 (including the disproportionation of the bromous acid). The fact that the bromate consumption is much higher than the CO_2 production indicates the presence of another channel where the bromate can be consumed by malonic acid without CO_2 production. As we shall see this is the MOA channel.

Already the first step of the MOA channel should be different from that of the GOA channel. It is known that in aqueous solutions malonic acid also is present in the form of enol,[16] and there are reports in the literature about the oxidations of alcohols by acidic bromate.[17] It is reasonable to propose a reaction between the enol form of MA and bromate. As this reaction channel produces MOA first (see the mechanism later), no carbon dioxide is formed in this first step. (The next step, which is an oxidation of MOA by acidic bromate, is not discussed here.)

Thus the initial bromate consumption is due to two parallel reaction channels:

$$I^0_{BrO_3^-} = r^0_{GOA} + r^0_{MOA}$$

According to the experimentally found rate law $I^0_{BrO_3^-}$ is again a bilinear function of the malonic acid and bromate concentrations:

$$I^0_{BrO_3^-} = (k_{GOA} + k_{MOA})[MA]_0[BrO_3^-]_0$$

thus we can write the rate law valid for the MOA channel r^0_{MOA}

$$r^0_{MOA} = k_{MOA}[MA]_0[BrO_3^-]_0$$

in a similar form as in the case of the GOA channel.

Using the above formula, and the already known value of the rate constant k_{GOA} and the initial concentrations, we calculated that $k_{MOA} = 2.46 \times 10^{-6}$ M^{-1} s^{-1}.

We propose the mechanism in Scheme 2 for the MA(enol)−BrO_3^- reaction leading to MOA as a first molecular intermediate. The experimentally found rate law can be rationalized based on Scheme 2 if we assume a preequilibrium in the first step, in the formation of the bromic acid ester of the enol, and a rate determining second step, the decomposition of that enol ester. The equilibrium concentration of this ester, consequently the rate of the MOA channel, will be proportional with both the malonic acid and the bromate concentrations. It is interesting to remark that the above assumption (preequilibrium + rate determining second step) predicts a second-order kinetics for the hydrogen ion as in the case of the GOA channel. A direct experimental study of the pH dependence in the MOA channel is more difficult, however, as its initial step does not generate CO_2.

4. Conclusions and Outlook

4.1. Comparison of the MA−BrO_3^- and the BrMA−BrO_3^- Reactions. When the substrate is BrMA[5] the first step of the reaction always involves a decarboxylation. MA, on the other hand, is oxidized mainly to MOA in the first step without any carbon dioxide production, only the less important GOA channel generates CO_2. The BrMA−BrO_3^- reaction is also faster: its rate constant is 3.8×10^{-4} M^{-1} s^{-1}, which is more than 2 or 3 orders of magnitude higher than that of the MOA ($k_{MOA} = 2.46 \times 10^{-6}$ M^{-1} s^{-1}) or the GOA ($k_{GOA} = 2.4 \times 10^{-7}$ M^{-1} s^{-1}) channel, respectively. The first molecular intermediate is oxalic acid (OA) in the case of BrMA. Kinetics and mechanism of the further oxidation of OA by acidic bromate and also by HOBr in 1 M sulfuric acid are well-known as these were already studied by Ševčik and co-workers[18,19] and also in our laboratory.[10] With MA substrate the first molecular intermediates are GOA and MOA; however, the kinetics and the mechanism of further oxidation of these organic acids by acidic bromate is not known. Thus an experimental study on the GOA−BrO_3^-, MOA−BrO_3^-, GOA−HOBr, and MOA−HOBr reactions is necessary and it is planned to be the subject of a subsequent publication.[20]

4.2. On the MA−HOBr Reaction. In our previous study[5] it was discovered that in the course of the BrMA−HOBr reaction not only the well-known bromination but an unexpected oxidation of BrMA can also occur. This was indicated by a CO_2 evolution, which was detected whenever HOBr was applied in excess. It is reasonable to assume that an analogous oxidation of MA by HOBr can also occur. Research is in progress to prove the above hypothesis.

4.3. Model Calculations. Presently only initial rates of the two reaction channels were measured when accumulation of the intermediates could be neglected. Later stages of the reaction could be modeled only when the mechanism and the kinetics of the GOA−BrO_3^- and especially the MOA−BrO_3^- reactions are known. Thus a reliable modeling of later stages of the MA−BrO_3^- reaction will be published later, together with the detailed study of the above-mentioned two reactions.[20]

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Supporting Information Available: Details of the colorimetric determination of the sum of GOA and MOA with resorcinol, absorption spectra, and a graph of the initial CO_2 evolution rate as a function of the initial H_2SO_4 concentration in the malonic acid−bromine reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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