Ce^{4+}−Malonic Acid Reaction in the Presence of O_2. Reaction Channels Leading to Tartronic and Oxalic Acid Intermediates

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Received: March 16, 2000; In Final Form: August 14, 2000

The effect of oxygen on the Ce^{4+}−malonic acid reaction was studied in a semibatch reactor. That effect is important for the Belousov−Zhabotinsky (BZ) chemical oscillator. The Ce^{4+} reagent inflow and consequently the rate of the reaction itself was controlled by a peristaltic pump. The reaction products were analyzed by HPLC. With this technique two major oxidation pathways were identified. One is significant at high Ce^{4+} inflow rates only; the product of this channel is tartronic acid. The other pathway leading to oxalic acid is active at all flow rates but dominant when the feed is slow. A great part of oxalic acid is oxidized further to carbon dioxide and water. A reaction mechanism compatible with these findings is presented. A key step of this mechanism is the fate of the peroxymalonyl radical which is the first intermediate for both channels. It is proposed that at high Ce^{4+} concentrations a fast reaction of this intermediate with Ce^{4+} leads to tartronic acid. At low Ce^{4+} concentrations, however, the peroxymalonyl radical has a longer lifetime to decarboxylate before reacting with a second Ce^{4+} and giving oxalic acid this way. Two mechanistic schemes proposed for this low Ce^{4+} channel were tested with further HPLC and kinetic experiments. From the high and low Ce^{4+} channels it is only the low one which plays a significant role in oxygen-perturbed BZ systems. The effect of that channel and its intermediates on BZ oscillators is discussed briefly.

Introduction

The Ce^{4+}−malonic acid (MA) reaction is an important part of the Belousov−Zhabotinsky (BZ) reaction which is a classical system used to study oscillations and chemical waves.[1,2] It is well-known that oxygen can have a strong effect on both oscillations[3−7] and traveling waves[8−10] in various BZ systems. Despite these studies the chemical background of the oxygen effect is still poorly understood. Only the first step of the mechanism, the peroxymalonyl radical formation, was confirmed directly by Neumann and co-workers.[11,12] The aim of this work is to learn more about that mechanism by identifying the molecular intermediates of the aerobic Ce^{4+}−malonic acid reaction.

It is known that in nitrogen atmosphere the primary malonyl radicals (MA•) react with each other to form 1,1,2,2-ethane tetracarboxylic acid (ETA)[13] and monomalonyl malonate (MAMA).[14] Under aerobic conditions malonyl radicals can react not only with each other but also with oxygen. Both reactions are fast but at high enough O_2 concentrations the recombination of the malonyl radicals becomes insignificant compared to their reaction with O_2. The first intermediate of the latter reaction, as Neumann et al. proved by ESR measurements,[11] is a peroxymalonyl radical (MAOO•):

$$\mathrm{MA\bullet} + \mathrm{O_2} \rightarrow \mathrm{MAOO\bullet} \qquad \text{(N1)}$$

They also made suggestions on some disproportionation products of the peroxymalonyl radicals. First they proposed that the products were tartronic acid (TA) and mesoxalic acid (MOA):[11]

$$2\mathrm{MAOO\bullet} \rightarrow \mathrm{TA} + \mathrm{MOA} + \mathrm{O_2} \qquad \text{(N2)}$$

Later on, based on stoichiometric considerations mesoxalic acid was changed to glyoxylic acid (GOA):[12]

$$2\mathrm{MAOO\bullet} \rightarrow \mathrm{TA} + \mathrm{GOA} + \mathrm{CO_2} + \mathrm{O_2} \qquad \text{(N3)}$$

Although their chemical model worked rather well in simulating the stoichiometry of the Ce^{4+} consumption, they had no direct experimental evidence about the appearance of these organic acids. In this study our aim was to get more information about these processes by identifying the products using HPLC.

Experimental Section

Materials. *Commercial Products.* Malonic acid (Fluka, puriss.), tartronic acid (Heraeus), $Ce(SO_4)_2 \cdot 4H_2O$ (Merck, pro analysi), oxalic acid (Merck, pro analysi), mesoxalic acid (Sigma, pro analysi), PbO_2 (pure), 0.025 M ferroin solution (Fluka, pro analysi), $Ce_2(SO_4)_3$ (Fluka, purum), 2-thiobarbituric acid (Fluka, purum), ortho-phosphoric acid 85% (Merck, pro analysi), NH_4OH 25% (J. T. Baker), and H_2SO_4 (J. T. Baker) were used as received. All solutions were prepared with doubly distilled water.

Ferriin solution was freshly prepared from ferroin solution as follows: 7.5 mL of 1.66 M H_2SO_4 solution and 0.035 g of PbO_2 powder were added into 5 mL of ferroin solution then stirred for 1 h in an ice bath. The freshly prepared 0.01 M ferriin (in 1 M H_2SO_4) solution was used immediately.

Ce^{4+}−Malonic Acid Reaction in a Semibatch Reactor. A 30 mL three-necked vessel was used as a semibatch reactor.

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10.1021/jp001005l CCC: $19.00

One neck was used for the gas inlet, another for the reactant inlet, and the third one for the gas outlet. A continuous inflow of the reactant was established by a peristaltic pump. Backward diffusion of air was prevented by bubbling the gas through water after leaving the reactor.

The reaction of malonic acid with Ce^{4+} was examined in 1 M sulfuric acid medium at room temperature (22 ± 2 °C). We used two solutions containing malonic acid and Ce^{4+}, respectively. Both reagents were dissolved in 1 M sulfuric acid. In all experiments 5 mL of 0.1 M Ce^{4+} solution was added continuously into 5 mL of 1 M malonic acid solution with a peristaltic pump applying various pumping rates. The feed times were 1, 8, 30, 60, and 90 min, respectively. As malonic acid was in great excess a steady-state Ce^{4+} concentration was reached rapidly. In this state the rate of the reaction was determined exclusively by the Ce^{4+} inflow. Consequently different steady-state Ce^{4+} and malonyl radical concentrations could be established by varying the Ce^{4+} input rate.

The reaction mixture and the reagent was bubbled continuously with N_2 or O_2 according to the anaerobic or aerobic conditions.

Ce^{4+}−Malonic Acid Reaction with Added Oxalic or Mesoxalic Acid. The reactions with added organic substrates were performed as those with malonic acid except the malonic acid solution contained oxalic or mesoxalic acid as well.

Rate Constant Measurements. The experiments were carried out in 1 M H_2SO_4 medium. Two solutions were used: one contained the organic acid and the other the Ce^{4+} reagent. Ce^{4+} reagent (1 mL) was injected into 140 mL substrate solution. The temperature was controlled at 20 ± 0.05 °C in a thermostated vessel with an optical path length of 10.8 cm. The reaction was followed with a sensitive spectrophotometer[15] measuring the Ce^{4+} absorbance at 400 nm. The substrate solutions were bubbled for half an hour with N_2 or O_2 before mixing the reagents and the bubbling was continued during the reaction. The applied concentrations (after mixing): 5×10^{-2} M malonic acid + 10^{-4} M Ce^{4+}; 10^{-3} M oxalic acid + 10^{-4} M Ce^{4+}; 5×10^{-5} M mesoxalic acid + 5×10^{-6} M Ce^{4+}.

Ferriin−Malonic Acid Reaction in N_2 and O_2 Atmosphere. The ferriin−MA reactions were performed in a similar way as with Ce^{4+}. The only difference was that the reaction was carried out as a batch experiment. A 5 mL volume of 1 M MA in 1 M H_2SO_4 was added to 5 mL of 0.01 M ferriin solution while bubbled with O_2 or N_2 gas stream continuously. The samples were analyzed with HPLC after 20 min reaction time.

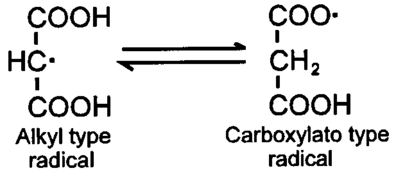
Analytical Methods

HPLC. HPLC experiments were performed with a Shimadzu equipment (LC-10AS pump, CTO-10A column oven, SPD-10A dual wavelength UV-detector, 8 nm bandwidth, 1 cm path length, 8 μL sample volume). The sample was injected using a Rheodyne 7010 injector with a 20 μL sample loop. The ion-exchange column[16] was working at 45 °C and a UV detector at 220 nm. All organic acids can be detected at this wavelength. The eluent was 0.01 M H_2SO_4, flow rate 0.40 mL/min. As the sulfuric acid concentration in the reaction medium (1 M) was 100 times more concentrated than in the eluent (0.01 M), samples were diluted 100 times prior to the HPLC analysis. The organic acid concentrations given in captions of Figures 1, 4, and 6 are for the original reaction mixture (that is, before the 100 times dilution for HPLC). The same HPLC conditions have already been applied successfully in a series of previous investigations to separate various organic acid intermediates of the BZ reaction. No decomposition of these acids was observed under these conditions. For further details see refs 13, 14, 17, and 18.

Oxalic Acid Test. The 2 mL sample solution to be tested was mixed first with 1 mL of 0.02 M $Ce_2(SO_4)_3$ then with 1 mL of 25% NH_4OH solution. The white precipitate (mixture of Ce(III) hydroxide and Ce(III) oxalate) was centrifuged, isolated, and washed with 0.005 M $Ce_2(SO_4)_3$ solution twice. The precipitate was dried at 100 °C. To liberate oxalic acid we added 0.1 mL of 1 M H_3PO_4 solution and the mixture was boiled over a free flame for half a minute. After cooling we added 0.2 mL of 25% NH_4OH and evaporated the solution. Under these conditions, oxalic acid forms ammonium oxalate which on dry heating yields water and oxamide. In the last step approximately 0.1 g of 2-thiobarbituric acid was added to the sample and the mixture was heated to 140−150 °C. If oxamide was present, a brick-red condensation product resulted. This spot test is specific for oxalic acid without any interference.[19]

Results and Discussion

Analytical Results for the Ce^{4+}−Malonic Acid Reaction. *Semibatch Experiments in N_2 Atmosphere*. First, as a control, the anaerobic reaction of Ce^{4+} with malonic acid[13,14] was repeated (Figure 1a) in the semibatch reactor. Independently of the input rate only the recombination products of the malonyl radicals, ETA and MAMA, appeared and their ratio was also constant within the experimental error. The first step in the anaerobic (and also in the aerobic) Ce^{4+}−malonic acid reaction is the formation of malonyl radicals. Malonyl radicals exist in two forms: alkyl and carboxylato type radicals. These two types are assumed to be in a fast equilibrium:



ETA is formed when two alkyl malonyl radicals recombine, while MAMA is formed from one alkyl and one carboxylato type radical. As in our experiments the ratio of the recombination products ETA and MAMA was always constant, this supports the assumption of the fast equilibrium between the two radical species.

We remark that in Figure 1a most of the Ce^{4+} (about 84%) produced ETA and MAMA but this is not the only sink of Ce^{4+}. The remaining 16% is used in another reaction route[20] leading to formic acid and CO_2 via carbene intermediates.

Semibatch Experiments in O_2 Atmosphere. Next the Ce^{4+}−malonic acid reaction was investigated in the presence of oxygen. The reaction was performed at various steady-state Ce^{4+} concentrations in the semibatch reactor. Figure 1b shows the chromatogram of the reaction products in the case of relatively high Ce^{4+} concentration (feed rate: 5 mL/1 min). Here, two changes can be observed compared to the oxygen-free experiment: (i) an additional peak appeared at $t_{ret} = 804$ s and (ii) the ratio of the peaks at 570 and 602 s ("MAMA and ETA peaks") has been changed. The peak at 804 s retention time could be easily identified as tartronic acid as there is no possible interference at that retention time. At the retention times of mesoxalic and glyoxylic acids, the products of (N2) and (N3) (638 and 968 s, respectively) no peak appeared. On the other hand, as the ratio of the recombination products ETA and

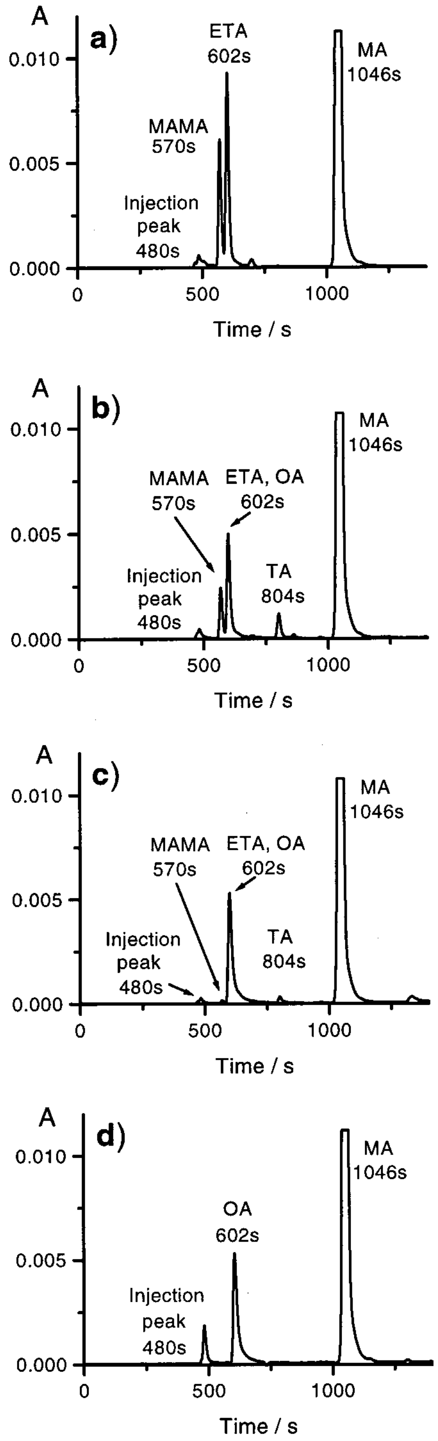


Figure 1. HPLC chromatograms of the products of the Ce^{4+}−MA reaction in N_2 or O_2 atmospheres. A volume of 5 mL 0.1 M Ce^{4+} solution was added to 5 mL of 1 M MA solution with various feed rates. (a) N_2 atmosphere, feed rate: 5 mL of Ce^{4+} solution/1 min. The products are ETA (1.47×10^{-2} M) and MAMA (6.30×10^{-3} M). (b) O_2 atmosphere with high feed rate: 5 mL/1 min. The “ETA” and “MAMA” peaks can still be detected but they are smaller and their ratio has been changed. A new peak has also appeared at $t_{ret} = 804$ s which corresponds to tartronic acid (TA) (3.42×10^{-3} M). (c) O_2 atmosphere with an intermediate feed rate: 5 mL/8 min. Observe the decrease in the tartronic acid (9.64×10^{-4} M) and MAMA peaks. (d) O_2 atmosphere with low feed rate: 5 mL/30 min. MAMA and tartronic acid peaks have disappeared. The remaining peak at $t_{ret} = 602$ s (at the former place of ETA) is identified as oxalic acid (OA) (6.20×10^{-3} M).

MAMA was always constant in all anaerobic measurements, the peak ratio change is probably due to the appearance of some new product increasing the “ETA” peak at 602 s. Neither this product nor the tartronic acid is present in the anaerobic experiments showing that new reaction channels were opened which can start with the reaction of malonyl radicals with O_2. To examine the products of these channels the reaction conditions should be chosen such that the O_2−malonyl radical reaction be dominant. If there is enough oxygen in the reaction mixture this prerequisite is not a problem as malonyl radicals form peroxymalonyl radicals with free oxygen rapidly.[21] At higher Ce^{4+}−MA reaction rates, however, the rapid oxygen consumption can drive the steady-state oxygen concentration to a very low level and such conditions, together with the increased malonyl radical concentration, favor the unwanted radical−radical recombination reactions. This unwanted reaction channel can be suppressed by decreasing the reaction rate, i.e., by adding the Ce^{4+} solution more slowly.

Figures 1c and 1d show the products of the Ce^{4+}−malonic acid reaction at lower reaction rates. In Figure 1c the flow rate was 5 mL/8 min, and in Figure 1d it was 5 mL/30 min. Further increase of the feed time had no effect, experiments with 30, 60, and 90 min feed times gave the same results. In Figure 1c all the peaks appear that were present in Figure 1b, but their heights have drastically changed. In Figure 1d the peak at 804 s disappeared, that is, no tartronic acid had been formed here. Moreover, the peak of MAMA also disappeared, but the peak at 602 s remained there. This peak cannot be ETA, however, as the other recombination product is absent. The most likely candidate is oxalic acid (OA) as its retention time is the same as that of ETA. To check this hypothesis we performed additional tests.

Qualitative Tests for Oxalic Acid. We found that while ETA decomposes readily on heating, oxalic acid is rather stable against it. Thus we kept the sample at 90 °C for 20 min and then analyzed with HPLC again. We have performed this test for all samples of anaerobic reactions and also of the aerobic ones. Samples produced in N_2 atmosphere, containing MAMA and “real” ETA peaks, behaved as expected. After heating, the real ETA peak nearly disappeared and peaks of its decomposition products (1,1,2-ethanetricarboxylic acid (ETRA) at 840 s and succinic acid (SA) at 1240 s) appeared. The MAMA peak also disappeared as at this temperature malonyl malonate hydrolyses completely to tartronic and malonic acids. On the other hand, in the aerobic case in samples produced with low Ce^{4+} inflow (like Figure 1d) the peak at 602 s did not change at all. This clearly shows that the product formed in the presence of oxygen cannot be ETA but some more stable compound.

To get final evidence that this stable compound is oxalic acid we have performed a color test which is specific for oxalic acid with no interference (details are given in the Experimental Section). This test was positive for the aerobic reactions and negative for the anaerobic one. The conclusion is that at low reaction rates the product of the Ce^{4+}−malonic acid reaction in the presence of oxygen is mainly oxalic acid.

Mechanistic Proposals. Before presenting the actual mechanistic schemes it is useful to summarize the experimental observations briefly. As Figure 1 shows, the product distribution depends not only on the atmosphere but in the case of O_2 atmosphere it also depends on the rate of the reaction. At high reaction rates (e.g., in the case of batch experiments), a part of the malonyl radicals might remove most of the oxygen creating anaerobic conditions for the remaining ones. In this case the already known anaerobic recombination channel leading to ETA and MAMA can be also active. In the presence of oxygen, however, two new reaction channels appear. One is active at

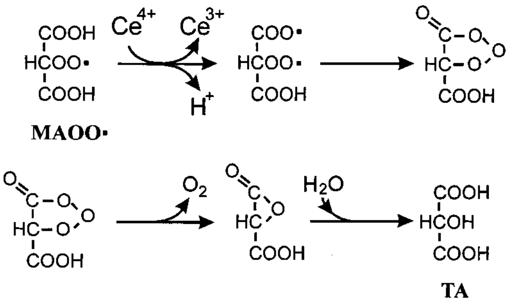


Figure 2. Mechanism of tartronic acid production from peroxymalonyl radicals at high Ce^{4+} concentrations.

high Ce^{4+} inflow rates and leads to tartronic acid. The other is active at all flow rates but it becomes dominant at lower steady-state Ce^{4+} concentrations and gives oxalic acid. Below, we present mechanistic proposals for these two new channels.

*The High Ce^{4+} Reaction Channe*l. This aerobic channel leads to tartronic acid which should be formed in a reaction between a peroxymalonyl radical and a Ce^{4+}. The proposed mechanism is shown in Figure 2.

Actually, the scheme assumes two consecutive reactions with Ce^{4+}: the first one (not shown in the figure) generates the peroxymalonyl radical, then the second one gives the tartronic acid. This pathway is preferred by high enough Ce^{4+} concentrations when other reactions of the peroxymalonyl radical (like decarboxylation or chain transfer to malonic acid) are partially suppressed by the Ce^{4+}−peroxymalonyl radical reaction. These suppressed reactions, however, are always present but they dominate only at low Ce^{4+} concentrations.

The Low Ce^{4+} Reaction Channel. Routes (a) and (b). Decreasing the Ce^{4+} input rate lowers the steady-state Ce^{4+} concentration in the semibatch reactor and the probability of the Ce^{4+}−peroxymalonyl radical reaction decreases accordingly. Under these conditions the role of the slower, Ce^{4+} independent decomposition routes of the peroxymalonyl radical becomes more pronounced. As our experiments show, the low Ce^{4+} channel should lead to oxalic acid production. Two possible routes lead to oxalic acid: routes (a) and (b) (see Figures 3a and 3b).

In route (a) decarboxylation of the peroxymalonyl radical takes place before the reaction with a second Ce^{4+}. In the last step a H^+ ion promoted rearrangement of the peroxide bond gives oxalic acid. Route (b) starts with a radical transfer reaction: the attack of a peroxymalonyl radical results in a malonyl radical and a hydroperoxy malonic acid molecule. As the malonyl radical forms a new peroxymalonyl radical with oxygen the process is a chain reaction producing hydroperoxy malonic acid from oxygen and malonic acid. After a H^+ ion catalyzed rearrangement, hydroperoxy malonic acid is transformed to mesoxalic acid which is oxidized by two Ce^{4+} to oxalic acid.

We were not able to find mesoxalic acid in our HPLC experiments. However, this does not exclude the possibility of route (b) as the Ce^{4+}−MOA reaction is probably very fast. To check this and to decide whether route (a) or (b) is the dominant one further experiments were necessary.

Further Experiments Checking Routes (a) and (b). *Semibatch Experiments with Mixed Substrates*. First to test the role of oxalic and mesoxalic acids in the mechanism of the Ce^{4+}−malonic acid reaction we added these assumed intermediates to the initial reagent mixture both in N_2 and in O_2 atmosphere experiments. The products were analyzed by HPLC and the results are displayed in Figure 4.

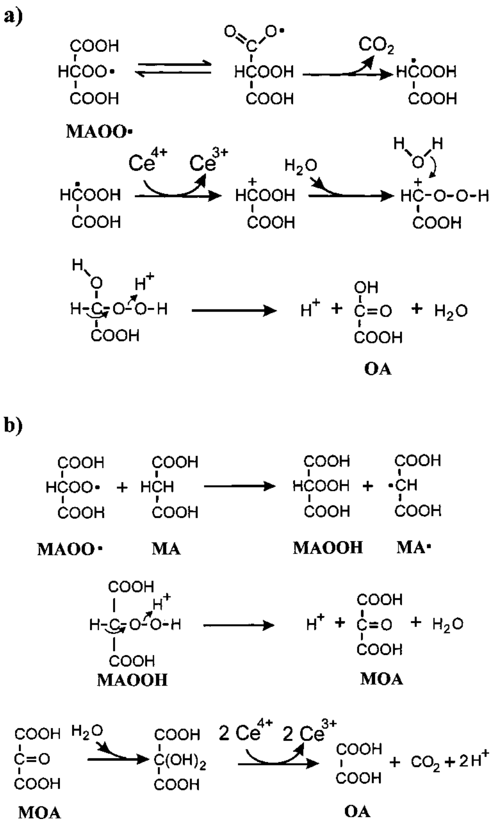


Figure 3. Two possible versions of the oxalic acid production from a peroxymalonyl radical at low Ce^{4+} concentrations: (a) decarboxylation route, (b) route starting with a radical transfer reaction producing mesoxalic acid intermediate in a chain reaction.

Interpretation of the experiments in N_2 atmosphere (Figure 4a−c) is rather straightforward: the more reactive substrates (oxalic and mesoxalic acids) reduce a close to stoichiometric part of Ce^{4+} and only the excess Ce^{4+} reacts with malonic acid. The extent of the Ce^{4+}−malonic acid reaction can be estimated from the double peak of MAMA and ETA.

In Figure 4a, the initial Ce^{4+} concentration was 5×10^{-2} M after mixing the reagents. In Figure 4b,c the Ce^{4+} concentration available for malonic acid should be reduced to 3×10^{-2} M and 10^{-2} M, respectively, assuming a stoichiometric reaction with 10^{-2} M oxalic acid (Figure 4b) or 10^{-2} M mesoxalic acid (Figure 4c). Thus the ratio of the double peaks should be 5:3:1 if in the oxalic acid−malonic acid and the mesoxalic acid−malonic acid mixtures the more reactive substrates are oxidized quantitatively to CO_2 and water and only the remaining Ce^{4+} is used to oxidize the malonic acid. Really the experimental ratio is very close to this theoretical prediction. A small deviation from that can be detected in Figure 4c only, where some remaining oxalic acid traces increase the ETA peak slightly.

Figure 4d−f shows analogous experiments such as in Figure 4a−c, but here in O_2 atmosphere instead of N_2. Now the results are completely different. The main product of the reaction is always oxalic acid. An initial addition of oxalic or mesoxalic acid to the reaction mixture increases the final oxalic acid concentration. Thus in the presence of oxygen the Ce^{4+} does not consume all the initial oxalic acid indicating that O_2 accelerates the overall Ce^{4+}−malonic acid reaction which produces oxalic acid. (Another possibility would be that O_2 could slow somehow the Ce^{4+}−oxalic acid reaction but according to our experiments O_2 has no effect on the rate of this reaction.) Both routes (a) and (b) would be able to accelerate the reaction but obviously route (b) should have a stronger effect.

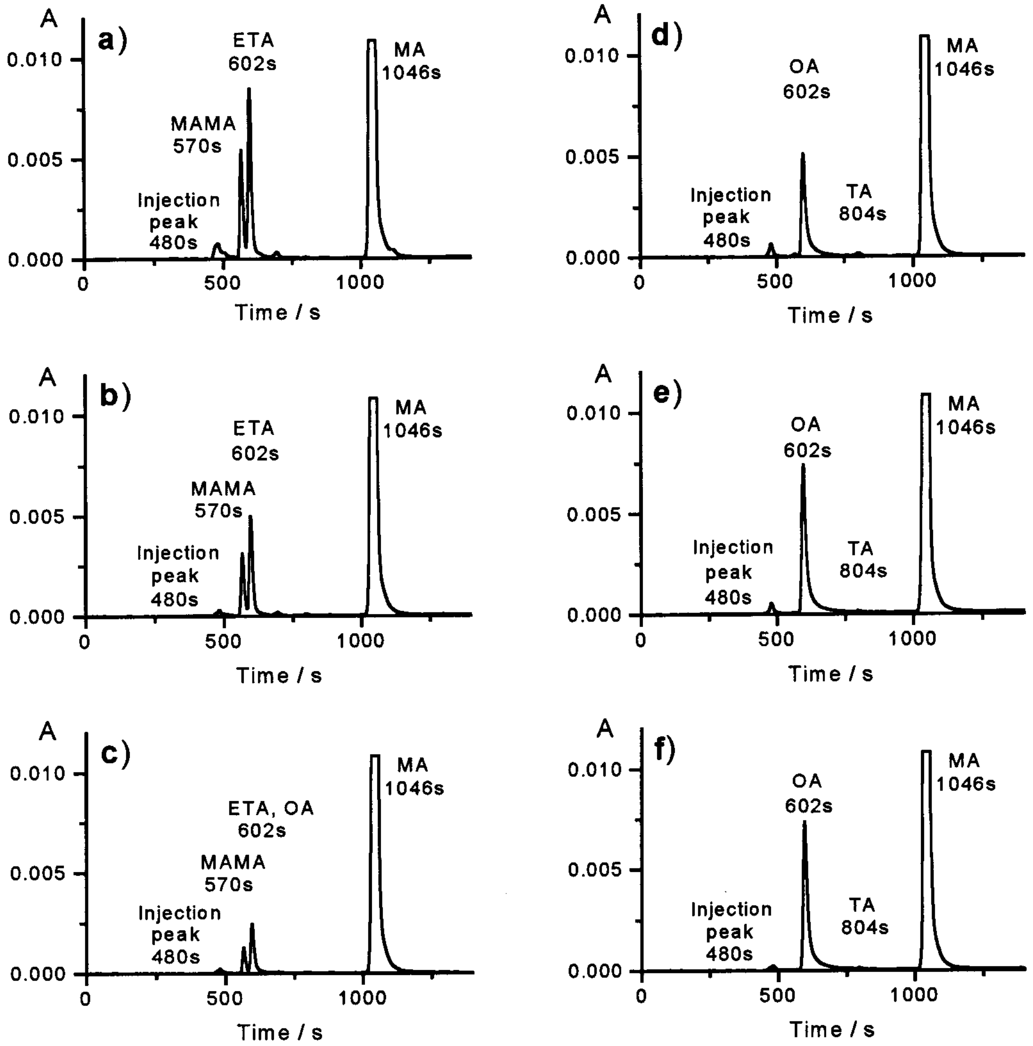


Figure 4. HPLC of the products of the Ce^{4}−malonic acid reaction (a−c) in N_2 and (d−f) in O_2 atmosphere. Other experimental conditions were like those in Figure 1d, except that beside malonic acid an initial oxalic acid concentration of 2×10^{-2} M was established in (b) and (e) or an initial mesoxalic acid concentration of 2×10^{-2} M was applied in (c) and (f).

TABLE 1: Second-Order Rate Constant of the Reactions of Different Organic Acids with Ce^{4+} in 1 M Sulfuric Acid Solution at 20 °C

	rate constant k ($M^{-1}\,s^{-1}$)	
organic substrate	N_2 atmosphere	O_2 atmosphere
malonic acid	0.24	0.46
oxalic acid	53	53
mesoxalic acid	$\sim 10^4$	$\sim 10^4$

Moreover the experiments also show clearly that even if mesoxalic acid were an intermediate it could not be detected in the reaction mixture due to its very fast reaction with Ce^{4+}. Thus while our experiments with mixed substrates gave some information on the behavior of oxalic and mesoxalic acids in the reaction system they did not clarify whether route (a) or (b) is the dominant one. To answer that question we performed kinetic experiments to determine the rate of the relevant Ce^{4+}−organic acid reactions quantitatively.

Rate Constant Measurements. The second-order rate constant of the Ce^{4+}−organic acid substrate reaction was determined for three substrates: malonic, oxalic, and mesoxalic acids both in N_2 and O_2 atmosphere. The results are shown in Table 1. In all experiments a great excess of the organic substrate was applied and the pseudo first-order rate constant of the Ce^{4+} consumption was measured. For further details see the Experimental Section.

Experiments made with malonic acid are depicted in Figure 5. It can be seen that the logarithmic plot is not a straight line in either O_2 or N_2. In the case of N_2 this is due to the not perfectly anaerobic conditions at the beginning. This increases the reaction rate until the radicals remove the last traces of oxygen. In O_2 atmosphere the slope of the line is increasing slightly because oxidation of oxalic acid (produced from malonic acid) increases the reaction rate.

We can conclude that the slope of the logarithmic plot in O_2 is about two times higher than in N_2 atmosphere, i.e., the reaction proceeds approximately two times faster in O_2 than in N_2 atmosphere.[22] This result suggests that route (a) should be the dominant one and route (b) cannot be significant in the low Ce^{4+} reaction channel. We present the following arguments to support the above conclusion. The rate-determining step in the Ce^{4+}−malonic acid reaction is the first one which produces a malonyl radical. In N_2 atmosphere these radicals mainly recombine to form ETA and MAMA. This way these radicals do not consume additional Ce^{4+}, while in O_2 atmosphere they are transformed to peroxymalonyl radicals which in route (a) consume a second Ce^{4+} after decarboxylation. Thus route (a) can explain the observed 2-fold acceleration[22] in O_2 atmosphere.

On the other hand, route (b) predicts a more dramatic acceleration in O_2 atmosphere. For example, if each malonyl radical would participate in only one chain transfer reaction

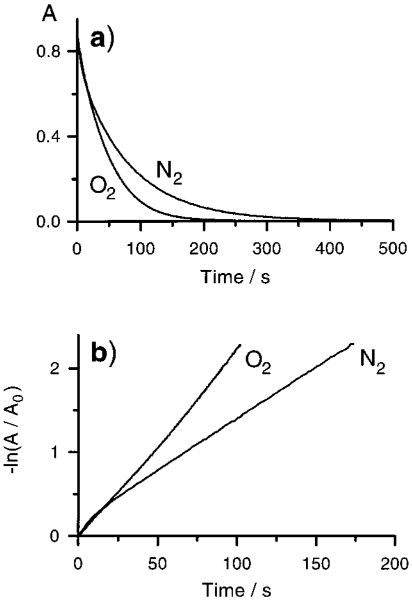


Figure 5. Spectrophotometric traces of the Ce^{4+}−malonic acid reaction in oxygen and nitrogen atmosphere. "A" is the Ce^{4+} absorbance measured at 400 nm. Initial conditions: [MA] = 0.05 M, $[Ce^{4+}] = 10^{-4}$ M, $[H_2SO_4] = 1$ M. (a) Linear, (b) logarithmic plots.

before termination then the emerging mesoxalic acid would consume two additional Ce^{4+} to form oxalic acid. Thus a 3-fold acceleration would be expected and in the case of longer chains this acceleration would be proportionally higher. The experimentally found 2-fold acceleration suggests that route (b) cannot play an important role here.

Oxygen and BZ Oscillators. *The Role of "High" and "Low" Ce^{4+} Reaction Channels in Oxygen-Perturbed BZ Systems.* BZ experiments are usually performed in batch or continuously fed stirred tank reactors (CSTRs) where Ce^{4+} is generated in the course of the reaction. How can we decide in this case whether the "high" or the "low" Ce^{4+} channel is the dominant one? To answer this question we first have to estimate the steady-state Ce^{4+} concentrations in the semibatch experiments favoring the high and low channels. The steady-state Ce^{4+} concentration in the semibatch reactor $[Ce^{4+}]_{ss}$ can be calculated from the following component balance:

$$\frac{w_F}{V}[Ce^{4+}]_F = [Ce^{4+}]_{ss} \cdot k[MA]$$

where w_F is the volumetric flow rate of the feed, $[Ce^{4+}]_F$ is the Ce^{4+} concentration in the feed, V is the actual volume of the liquid in the reactor, k is the second-order rate constant of the Ce^{4+}−MA reaction in the presence of O_2, and [MA] is the actual malonic acid concentration in the reactor:

$$[MA] = [MA]_0 \cdot \frac{V_0}{V}$$

where $[MA]_0$ is initial malonic acid concentration, and V_0 is initial volume of liquid in the reactor. (As the malonic acid is in a high excess its consumption can be neglected.) Thus,

$$[Ce^{4+}]_{ss} = \frac{w_F}{V_0} \cdot \frac{[Ce^{4+}]_F}{k[MA]_0}$$

With our experimental data the steady-state Ce^{4+} concentrations calculated for Figures 1b and 1c are 3.2×10^{-3} M and 4×10^{-4} M, respectively. This answers our question about the high and low Ce^{4+} concentrations: the borderline should be somewhere between these concentrations that is around 10^{-3} M.

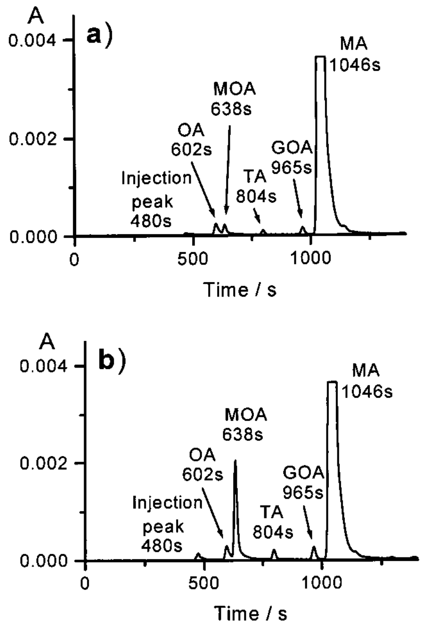


Figure 6. HPLC of the products of the ferriin−malonic acid reaction (a) in N_2 and (b) in O_2 atmosphere. Initial conditions: [MA] = 0.5 M, [ferriin] = 5×10^{-3} M, $[H_2SO_4] = 1$ M. The products of the reactions: (a) OA (3.10×10^{-4} M), MOA (4.46×10^{-4} M), TA (3.05×10^{-4} M), GOA (2.80×10^{-3} M); (b) OA (3.75×10^{-4} M), MOA (4.05×10^{-3} M), TA (6.22×10^{-4} M), GOA (4.64×10^{-3} M).

In BZ oscillators the Ce^{4+} concentration is usually below 10^{-3} M most of the time, thus the low Ce^{4+} channel is the only important one in these systems. Furthermore tartronic acid, the product of the high Ce^{4+} channel is much less reactive than oxalic acid. Regarding these facts we conclude that it is the low Ce^{4+} channel which is responsible for the oxygen effects in the BZ oscillators.

The Ferriin−Malonic Acid Reaction in N_2 and O_2 Atmosphere. As we could see in the low Ce^{4+} channel, route (b) can play only a minor role. A direct evidence for the route (b) mechanism would be the identification of its characteristic intermediate mesoxalic acid. However, the extremely fast Ce^{4+}−mesoxalic acid reaction prevents the identification of mesoxalic acid traces in the reaction mixture. On the other hand we could hope to find mesoxalic acid if ferriin is applied in the experiments instead of Ce^{4+} because the oxidation of organic substrates by ferriin is usually slow. Thus if the primary malonyl radicals are generated with ferriin we can expect similar initial reactions but further oxidation of the intermediates such as mesoxalic acid can be avoided this way. Figure 6 shows HPLC analysis of the products of the ferriin−malonic acid reaction in N_2 and in O_2 atmosphere.

In N_2 atmosphere the reaction is very slow; only traces of various acids were found after 20 min reaction time. In O_2 atmosphere, however, the reaction proceeds faster and the mesoxalic acid (MOA) peak is 1 order of magnitude higher than in N_2. The peak of tartronic acid (TA) and glyoxylic acid (GOA) also grows somewhat (about a factor of 2) in O_2 atmosphere. Glyoxylic acid indicates that probably route (a) also plays a role here. (Glyoxylic acid can be produced when a decarboxylated peroxymalonyl radical reacts in a chain transfer reaction with malonic acid. The resulting peroxide type molecule can give glyoxylic acid after a H^+ ion-assisted rearrangement of the chemical bonds.)

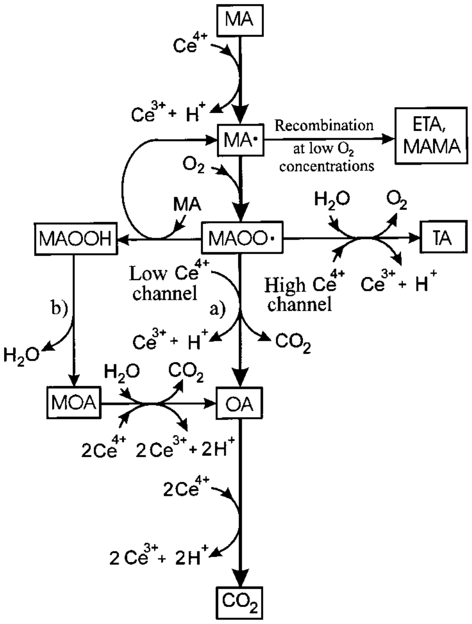


Figure 7. Skeleton mechanism of the oxygen-mediated Ce^{4+} oxidation of malonic acid. The "high" Ce^{4+} channel leading to tartronic acid is on the right-hand side, while the other pathways leading to oxalic acid and CO_2 represent the "low" Ce^{4+} channel with two parallel routes—routes (a) and (b).

To present detailed mechanistic proposals for the ferriin–malonic acid reaction would be too early at this stage, however. Our aim here was only to show that the products and consequently also the mechanism can be different for Ce^{4+} and ferriin oxidants.

Summary and Conclusions for O_2-Perturbed BZ Oscillators.

As a summary Figure 7 presents an integrated picture showing all possible routes of the reaction mechanism. For oxygen-perturbed Ce^{4+} oscillators the main stream is the vertical one flowing through the oxalic acid intermediate via route (a). In these oscillators— when the autocatalytic reaction is "switched off"—the main stream produces oxalic acid affecting strongly the reaction dynamics. That effect is probably due to the oxalic acid–hypobromous acid reaction[23] generating some inhibitory bromide. This could also explain the somewhat surprising observation that oxygen can keep a BZ oscillator in its reduced steady state.[4] In oxygen-perturbed ferroin catalyzed systems mesoxalic acid can play a similar role. It was observed that in these systems mesoxalic acid has a strong effect on oscillations and chemical waves.[24]

Acknowledgment. This work was partially supported by OTKA (T-030110), FKFP (0287/1997) grants, by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the ESF Program: "Reactor". M.W. acknowledges the support of the Bolyai Research Stipendium. The authors thank V. Farkas for help in the experiments, E. Kókai, G. Taba, and M. Kozák for developing the details of the oxalic acid test, J. Nyitrai for discussions, and especially a Referee who made helpful mechanistic suggestions.

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(22) Note: In our explanation we neglect further reaction of Ce^{4+} with the oxalic acid product. As the initial concentration of Ce^{4+} is 10^{-4} M the maximum oxalic acid concentration would be 5×10^{-5} M. Regarding the rate constant in Table 1 and the malonic acid concentration which is 0.05 M in this case, the rate of the Ce^{4+}–oxalic acid reaction can be maximum 30% of the rate of the Ce^{4+}–malonic acid reaction. Thus in O_2 atmosphere roughly 20% of the Ce^{4+} consumption is due to another reaction. But the same is true in N_2 atmosphere: about 16% of the Ce^{4+} is consumed in nonrecombinative but CO_2-producing reactions.[20] Thus a theoretical 1:2 ratio for the rates in N_2 and O_2 atmosphere is still an acceptable estimation.

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