Ph.D. THESIS
Abstract

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The Marburg-Budapest-Missoula (MBM) model of the oscillatory Belousov-Zhabotinsky reaction and the experimental research leading to this model

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Foreword, the aim of this work:

The Belousov-Zhabotinsky (BZ) reaction -the oxidation of malonic acid by acidic bromate in the presence of Ce^{4+} catalyst and related reactions- is in the focus of interest in the last decades because of its interesting dynamics. Presently its chemical mechanism, the reaction steps and rate constants are elaborated so that kinetic simulations show a rather good agreement with various types of the observed dynamical phenomena. In spite of that many important details in the organic chemistry of the reaction are still unknown. This lack of information is due to the fact that appropriate analytical techniques (like NMR and HPLC) were missing or not generally available at the time when the reaction was discovered. Though these mechanisms give a detailed description of the inorganic subset including elementary steps, they involve hypothetical composite reactions in the organic subset of the whole BZ reaction. It would be important to understand more details of the latter reactions because these are crucial ones in the negative feedback loop of the autocatalytic process.

The first step in investigating the organic steps of the whole BZ reaction is to examine the reaction of the catalyst -say Ce^{4+} ions- with malonic acid (MA) and bromomalonic acid (BrMA), respectively. Recently a series of papers has identified some primary products of these reactions using HPLC technique. These were 1,1,2,2-ethanetetracarboxylic acid (ETA) and malonyl monomalonate (MAMA) in the Ce^{4+} - malonic acid reaction and bromoethenetricarboxylic acid (BrEETRA) in the Ce^{4+} - bromomalonic acid reaction. It was assumed that these products emerge in the recombination of the primarily formed malonyl or bromomalonyl radicals.

In this study my aim was to get a better insight into these processes by various experimental techniques. In 1994 a program started in Marburg applying mostly high performance liquid chromatography (HPLC) to identify various organic products and intermediates of the BZ reaction. I joined to this program at the end of nineties.

The first step in investigating the organic steps of the whole BZ reaction is to examine the CO_2 evolution from the reaction of the catalyst -say Ce^{4+} ions- with malonic acid [1]. The effect of oxygen on the Ce^{4+} - malonic acid reaction was studied in a semibatch reactor [2]. The next step

was the examination the reaction of the catalyst -say Ce^{4+} ions- with bromomalonic acid [1]. I studied analogous reactions between ferriin and the same two organic substrates, namely malonic and bromomalonic acids [3]. Finally I started to study the products of whole BZ systems by HPLC.

First HPLC and CO_2 measurements were performed in the induction period of the classical BZ reaction (malonic acid - bromate - cerium catalyst in sulfuric acid medium) [4]. With the aid of the HPLC technique I followed the evolution of the main chemical components in a cerium and in a ferroin catalysed full BZ system [5]. After collecting all the available experimental data for the Ce^{4+} catalysed system, with help of our coworkers we performed calculations with a revised and updated GTF model which will be referred to as Marburg-Budapest-Missoula (MBM) model [5].

Methods

Measuring CO_2 evolution

A constant fraction of the CO_2 was permeated via a silicone rubber membrane into to a gas H_2 stream where CO_2 was converted to methane on Ni catalyst. Methane was detected by a flame ionization detector.

HPLC measurements

HPLC experiments were performed with a Shimadzu equipment using an ion exchange column (separation principle: ion exclusion chromatography) at 45 °C and a UV detector working at 220 nm. All organic acids can be detected at this wavelength. No decomposition of these acids was observed under these conditions.

Spectrophotometric (UV-VIS) measurements

Rate constant measurements: The reaction was followed with a sensitive double wavelength spectrophotometer measuring the Ce^{4+} absorbance at 400 nm (reference 650 nm). During the measurements the substrate solutions were bubbled for half an hour with N_2 (or with O_2 in the case of aerobic measurements) before injecting the reagent solution at 20 ± 0.05 °C into a thermostated

vessel with an optical pathlength of 10.8 cm. At the start of the pre-experimental kinetic measurements the reagent solution was injected into the substrate solution in a cell with an optical pathlength of 2 cm. The Ce^{4+} absorbance was followed with the spectrophotometer.

Potentiometric measurements

Electric potential was measured between a bromide selective electrode (Radiometer type) and a Ag/AgCl electrode in saturated KCl as a reference (Metrohm type) via a salt bridge containing 0.5 molar sulfuric acid. The measurement was performed with a high imput impedance voltmeter and registered with a computer.

New results

1.) Based on the results of the CO_2 measurements in the Ce^{4+} - MA reaction two new decarboxylation route of the primarily formed malonyl radicals were confirmed beside the already known recombination pathway. One of them is active when the Ce^{4+} concentration is low and the endproduct of this decarboxylation route is acetic acid. The other is dominant at high Ce^{4+} concentrations the products of which are different and highly reactive intermediers: ions radicals, carbenes and radical ions but the final product is carbon dioxide [1].

Obviously, we have to apply different parameters in a semibatch experiment if we want to study one or the other channel. To explain this result the following scheme (Figure 1) is suggested for the low Ce^{4+} decarboxylation channel.

Low Ce^{4+} decarboxylation channel

The first step in this channel -after the production of a malonyl radical- is a monomolecular decomposition of this species into an alkyl acetyl radical and a CO_2.

A possible next step could be the recombination of the various radicals. Nevertheless, in a semibatch experiment with low input rate, the radical concentration is relatively low thus there is time enough even for a less reactive reaction partner to compete for radicals before they recombine. Especially malonic acid molecule can be such a reaction partner because it is in a high excess. Naturally, a reaction between malonic acid and malonyl radical does not give a net chemical

change. On the other hand, a reaction between malonic acid and acetyl radical gives acetic acid and a new malonyl radical. This chain reaction could produce several CO_2 molecules per Ce^{4+} depending on the fate of the produced new malonyl radical. Anyway, the chain reaction finally terminates with a recombination even in a semibatch experiment to give mainly ETA and MAMA. Production of some ethane tricarboxylic acid (ETRA) and succinic acid (SA) is also possible, what shows the presence of acetyl radicals.

High Ce^{4+} decarboxylation channel

Applying a low malonic acid inflow into the reactor where the Ce^{4+} concentration was high (0.2 M) also gave a high CO_2 yield. The decarboxylation mechanism detailed in Figure 1 cannot explain these results. Consequently another mechanism is necessary to explain the observations at high Ce^{4+} concentrations.

The possible and conventionally supposed molecular intermediates in the decarboxylation channel would be too stable against further oxidation by Ce^{4+}, thus they would be end products. Here, and also in the complete scheme of the high Ce^{4+} decarboxylation channel shown in Figure 2 carbenes as new reactive intermediates are proposed.

However, glycolic acid was not detected in the reaction mixture in quantities according to an end product, furthermore our experiments prove that oxidation proceeds to CO_2 or at least to formic acid on all the three carbon atoms of malonic acid. This excludes the possibility that such molecular intermediates are involved in the oxidation process. Consequently the decarboxylation reaction has to proceed through more reactive species: ions, radicals, carbenes and radical-ions.

It is clear that the very labile radical and carbene intermediates of the main line cannot be detected by conventional analytical techniques. However, if more stable molecular by-products appear these can be detected with sensitive analytical methods.
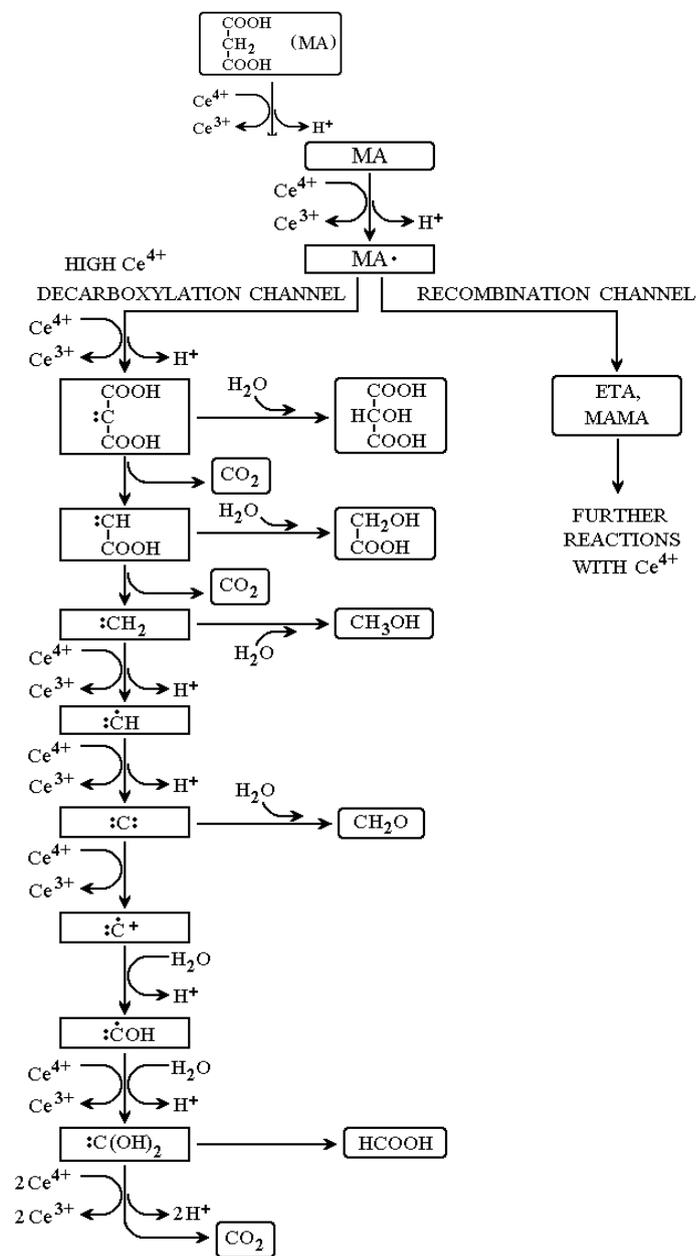
COOH
CH₂ (MA)
COOH

Ce^{4+}
Ce^{3+} → H⁺

MA

Ce^{4+}
Ce^{3+} → H⁺

MA·

HIGH Ce^{4+}

DECARBOXYLATION CHANNEL   RECOMBINATION CHANNEL

Ce^{4+}
Ce^{3+} → H⁺

COOH
:C H_2O →   COOH
COOH   HĊOH
                           COOH

ETA,
MAMA

→ CO_2

:CH H_2O → CH_2OH
COOH   COOH

FURTHER
REACTIONS
WITH Ce^{4+}

→ CO_2

:CH_2 → CH_3OH
             H_2O

Ce^{4+}
Ce^{3+} → H⁺

:ĊH

Ce^{4+}
Ce^{3+} → H⁺

:C: H_2O → CH_2O

Ce^{4+}
Ce^{3+}

:Ċ⁺

H_2O
→ H⁺

:ĊOH

Ce^{4+} H_2O
Ce^{3+} → H⁺

:C(OH)₂   →   HCOOH

$2Ce^{4+}$
$2Ce^{3+}$ → 2H⁺

→ CO_2

Figure 2
The high Ce^{4+} decarboxylation channel of the Ce^{4+} - malonic acid reaction

Figure 1
Mechanistic scheme of the low Ce^{4+} decarboxylation channel in the Ce^{4+} - malonic acid reaction

2) Based on the CO_2 measurements in the Ce^{4+} - BrMA reaction the decarboxylation of the bromomalonyl radical was proposed beside the already known recombination route. The decarboxylation pathways are analogous to the two different mechanisms assumed in the case of the Ce^{4+} - MA reaction [1].

A reaction scheme proposed for this reaction is shown in Fig. 3. Reaction steps of the decarboxylation channel are analogous to that of malonic acid (compare with Figs. 1 and 2) but the low and high Ce^{4+} decarboxylation channels are integrated into one scheme. This modification is due to the fact that the CO_2 evolution is usually one order of magnitude higher with bromomalonic acid substrate compared to malonic acid and considerable CO_2 evolution occurs even at high substrate concentrations.

A carbene intermediate analogous to the first carbene intermediate of malonic acid cannot be formed in the case of bromomalonic acid. This does not mean, however, that the bromomalonyl radical cannot react with Ce^{4+} but a carbene intermediate can be formed only after loosing a CO_2. Obviously decarboxylation of bromomalonyl radicals is faster than that of malonyl radicals.

The first step is a one-electron oxidation of the enol form of BrMA by cerium followed by the decarboxylation of the bromomalonyl radical in the acidic medium:
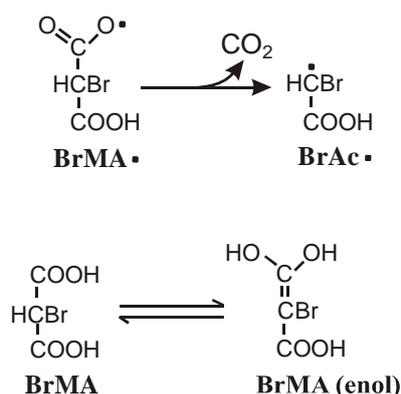
In the next step the bromoacetyl radical reacts with the double bond of the enol form of BrMA. The next step is the loss of an HBr molecule from hydrated acyl radical. This new radical can be oxidized further by cerium to bromo-ethene-tricarboxylic acid (BrEETRA).
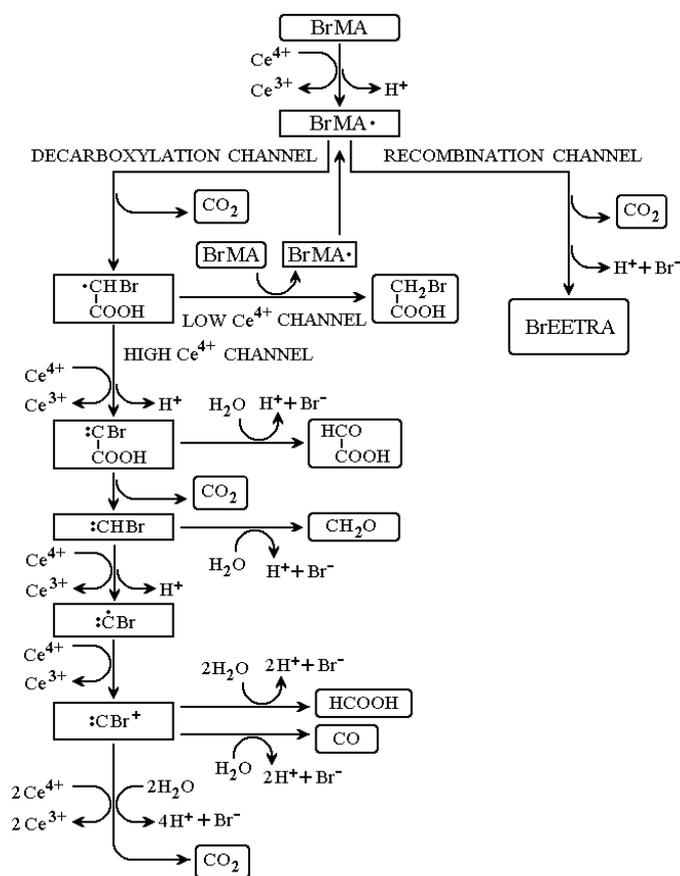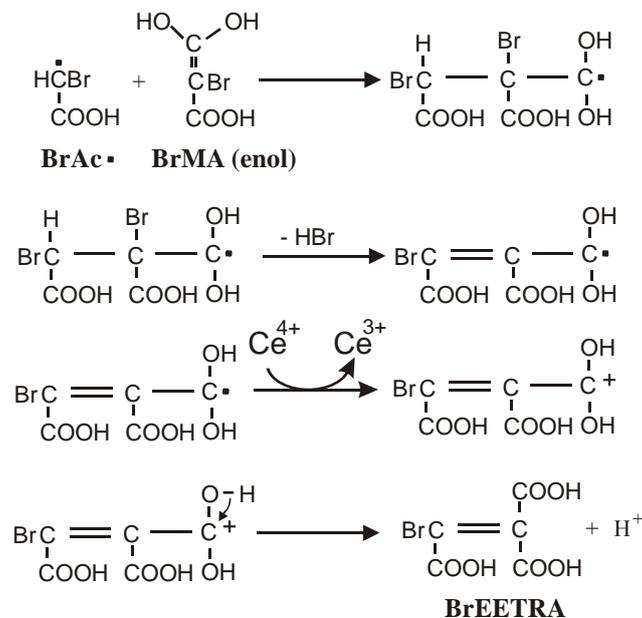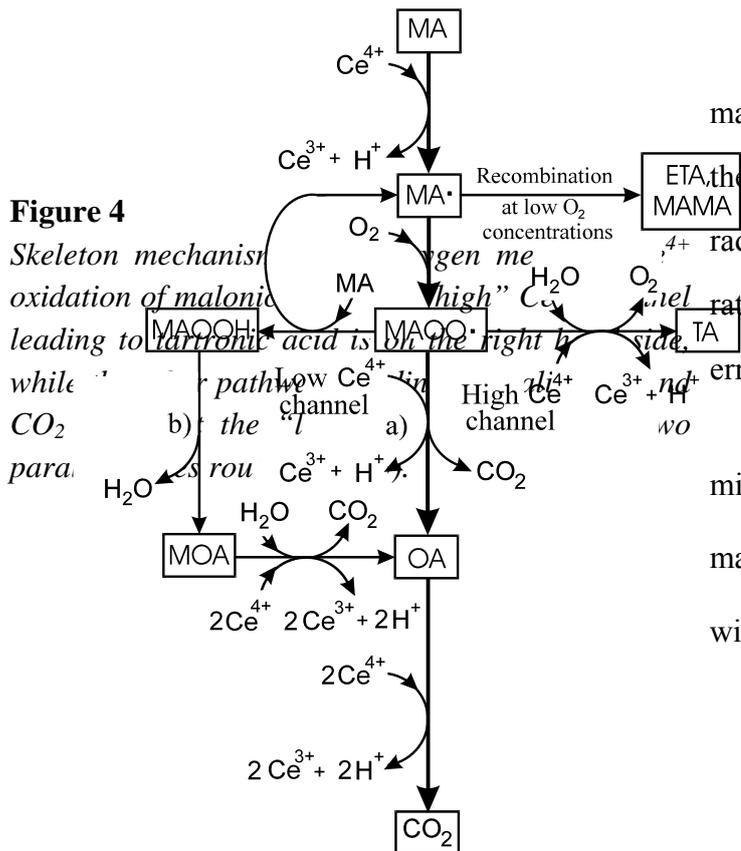
BrAc•   BrMA (enol)

− HBr

Ce^{4+} Ce^{3+}

BrEETRA

BrMA

Ce^{4+}
Ce^{3+} H^+

BrMA•

DECARBOXYLATION CHANNEL   RECOMBINATION CHANNEL

CO_2

CO_2

BrMA   BrMA•

$H^+ + Br^-$

•CHBr
COOH   LOW Ce^{4+} CHANNEL CH_2Br
COOH   BrEETRA

HIGH Ce^{4+} CHANNEL

Ce^{4+}
Ce^{3+} H^+ H_2O $H^+ + Br^-$

:CBr
COOH   HCO
COOH

CO_2

:CHBr CH_2O

H_2O $H^+ + Br^-$

Ce^{4+}
Ce^{3+} H^+

:ĊBr

Ce^{4+}
Ce^{3+} $2H_2O$ $2H^+ + Br^-$

:CBr$^+$ HCOOH
CO

H_2O $2H^+ + Br^-$

$2Ce^{4+}$ $2H_2O$
$2Ce^{3+}$ $4H^+ + Br^-$

CO_2

Figure 3
Decarboxylation channels in the Ce^{4+} - bromomalonic acid reaction

Another possibility that the hydrated acyl radical decarboxylates first and reacts with cerium in the next step (formes dibromoethane tricarboxylic acid, Br_2ETRA) and after reacts looses HBr to yield

BrEETRA.

At low Ce^{4+} concentrations, the decarboxylation of the radical seems to be the dominant reaction. The proposed mechanism is supported by the fact that when Ce^{4+} is in excess then more than 2 carbon atoms of the substrate is oxidized to CO_2 as an average. To collect some more direct evidence for the scheme the products of the side reactions will be further investigated with HPLC and other measurements.

3.) While studying intermediates of the Ce^{4+} - MA reaction under aerobic (O_2) conditions two new reaction routes were found. One of them is active at high Ce^{4+} feeding rates of the semibatch reactor (at high steady state Ce^{4+} concentrations) and its endproduct is tartronic acid (TA). The other one is always active but become dominant only at low steady state Ce^{4+} concentrations. The endproduct of the latter is oxalic acid (OA) [2].

Figure 4
Skeleton mechanism ... oxidation of malonic ... leading to tartronic acid is on the right ... side. while ... pathway ... CO_2 ... b) the "l ... a) para ... rou ...

In the anaerobic reaction of Ce^{4+} with malonic acid 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.

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. In the presence of

oxygen, however, two new reaction channels appear. One is active at 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. I present mechanistic proposals for these two new channels. There are two possible routes leading to oxalic acid: route a) and b). In route a) decarboxylation of the peroxymalonyl radical takes place before the reaction with a second Ce^{4+}.
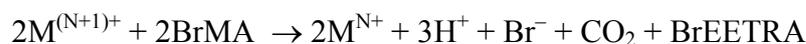
In the last step a H^+ ion promoted rearrangement of the peroxide bond gives oxalic acid. Route b) starts with a radical transfer reaction: the attack of a peroxymalonyl radical results in a malonyl radical and a hydroperoxy malonic acid molecule. As the malonyl radical forms a new peroxymalonyl radical with

oxygen the process is a chain reaction producing hydroperoxy malonic acid from oxygen and malonic acid. After a H^+ ion catalysed rearrangement hydroperoxy malonic acid is transformed to mesoxalic acid which is oxidized by two Ce^{4+} to oxalic acid. As a summary Figure 4. 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).

4.) The ferriin-BrMA and the ferriin-MA reactions were studied under anaerobic conditions. Based on the experimental results an analogy was found between the ferriin-BrMA and the Ce^{4+}-BrMA reactions. Instead of the radical-radical reactions proposed earlier a more realistic mechanism was suggested. It was found, however, that there is no analogy between the ferriin-MA and the Ce^{4+}-MA reactions as ferriin is not able to oxidize malonic acid. In this case ferriin is reduced most probably by water and malonic acid plays the role of the catalyst only in this reaction [3].

i) There is an analogy between the ferriin – bromomalonic acid and the Ce^{4+} – bromomalonic acid reactions.

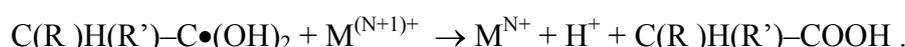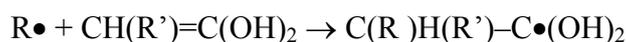The experiments support that a combination of the following two stoichiometries

$$2M^{(N+1)+} + 2BrMA \rightarrow 2M^{N+} + 3H^+ + Br^- + CO_2 + BrEETRA$$

$$2M^{(N+1)+} + 3BrMA \rightarrow 2M^{N+} + 3H^+ + Br^- + CO_2 + EETRA + Br_2MA$$

can describe the overall processes if bromomalonic acid is oxidized by Ce^{4+} or by ferriin. Here $M^{(N+1)+}$ and M^{N+} denote the oxidized and the reduced form of the catalyst, respectively. The mechanism suggests a fast decarboxylation of the bromomalonyl radical and also a fast consumption of the subsequent radicals. This predicts a low organic radical concentration. Really, while in the Ce^{4+}– MA reaction the malonyl radical concentration is high, in the case of the Ce^{4+} – BrMA reaction the organic free radical concentration is low.

ii) A more realistic mechanism for the above processes avoids the radical – radical reactions assumed in the earlier mechanisms.

In the present new mechanism the organic radical R• produced in the

$$M^{(N+1)+} + RH \rightarrow M^{N+} + H^+ + R\bullet$$
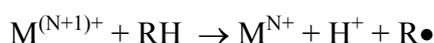
reaction does not recombine with another radical as was proposed earlier, but it reacts with a double-bound containing compound (here this is the enol form of BrMA) and the new radical formed this way reacts again with the oxidized form of the catalyst

$$R\bullet + CH(R')=C(OH)_2 \rightarrow C(R)H(R')-C\bullet(OH)_2$$

$$C(R)H(R')-C\bullet(OH)_2 + M^{(N+1)+} \rightarrow M^{N+} + H^+ + C(R)H(R')-COOH \ .$$

A similar mechanism can be given for the ETA and MAMA formation in the Ce^{4+} – MA reaction as well.

iii) No analogy exists between the ferriin – malonic acid and the Ce^{4+} – malonic acid reactions.

It is known that in the Ce^{4+} – MA reaction in the first step malonyl radicals are produced which form the products ETA and MAMA. Neither ETA nor MAMA or any other oxidation product of malonic acid was found in the ferriin – malonic acid reaction. Consequently ferriin – unlike Ce^{4+} – does not oxidize malonic acid.

5.) While studying the induction period of the Ce^{4+} catalyzed BZ reaction it was possible to clarify the mechanism of certain radical reactions. It was found that oxalic (OA) and mesoxalic (MOA) acids are important intermediate both in the bromide ion and the radical controlled negative feedback loops. Moreover oxidation products of ethane tetracarboxylic acid (ETA) ethenetertarcarboxylic (EETA) acid and its decomposition products, namely maleic and fumaric acids (EETRA, MaleA, FuA) were identified [4].

The first negative feedback loop via bromide was known from the beginnings. While the control role of bromide was clear the source of this bromide was more problematic. One source is the Ce^{4+}-bromomalonic acid reaction the mechanism and the products of which were clarified just recently.

The second negative feedback loop was discovered later, about 15 years ago. Here organic free radicals play the control role as they react with bromine dioxide, the second autocatalytic intermediate. In this loop the source of both the organic and the inorganic radicals was clear but there was no information about the products of these radical-radical reactions.

These observations strongly support the conclusion that both CO_2 and oxalic acid are products of the radical-radical reactions. Moreover, as in the beginning of the induction period the majority of the organic radicals are malonyl radicals, CO_2 and oxalic acid should be decomposition products of malonyl bromite. Most probably this decomposition route gives mesoxalic and
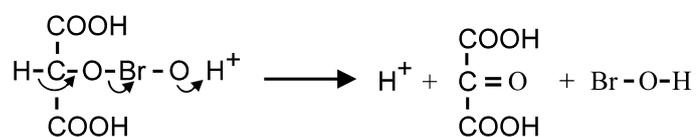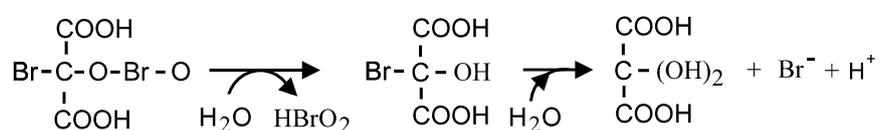

hypobromous acids.

Nevertheless, identification of the characteristic first intermediate mesoxalic acid in this reaction mixture was not possible due to the fact that the oxidation of mesoxalic acid by Ce^{4+} is very fast (more than two orders of magnitude faster than that of oxalic acid).

Another possibility would be some complex rearrangement reaction giving directly oxalic acid, CO_2 and bromide ions:
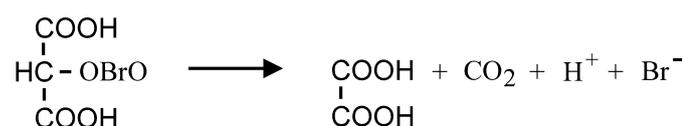
While we cannot exclude this route completely its contribution cannot be significant because this would eliminate the possibility of the so - called "non-bromide controlled" oscillations. On the other hand, it can play a role as an additional bromide source.

In later stages of the induction period the situation becomes more complex as bromo- and dibromomalonic acids and their radicals can appear in the reaction mixture. Hydrolysis should play a major role here. Hydrolysis of bromomalonyl malonate in the first step yields bromotartronic acid beside bromous acid and in the next step bromotartronic acid hydrolyses rapidly yielding mesoxalic acid and bromide:

$$
\begin{array}{ccc}
\text{COOH} & \text{COOH} & \text{COOH} \\
| & | & | \\
\text{Br--C--O--Br--O} \xrightarrow[\text{H}_2\text{O} \quad \text{HBrO}_2]{} & \text{Br--C--OH} \xrightarrow[\text{H}_2\text{O}]{} & \text{C--(OH)}_2 \; + \; \text{Br}^- + \text{H}^+ \\
| & | & | \\
\text{COOH} & \text{COOH} & \text{COOH}
\end{array}
$$

Thus, as we can see, with the appearance of bromomalonic acid the bromide controlled and the radical controlled feedback loops become mixed: the radical-radical reaction finally produces a bromide ion, and this connects the two different loops.

Finally it is interesting to mention that oxalic acid itself is a substrate of the BZ reaction and that the hypobromous acid-oxalic acid reaction also provides an additional bromide source. It is probable that mesoxalic acid can play a similar role. Thus we can conclude that oxalic and mesoxalic acids can be important intermediates of both the bromide and the radical controlled feedback loops.

A method to accumulate multivalent organic acids present in very low concentrations in the BZ reaction was also developed. Applying this and a thermal decomposition method ethenetetracarboxylic acid (EETA) was identified as an oxidation product of ethanetetracarboxylic acid (ETA).

6.) HPLC analysis of a complete BZ system catalyzed by cerium was performed under anaerobic conditions [5]. This was the first HPLC study on a complete BZ system and the concentration of the following components was measured in the course of the reaction:

a) major components: acidic bromate (BrO₃⁻), malonic acid (MA), bromomalonic acid (BrMA),

b)radical recombination products: Bromoethene tricarboxylic acid (BrEETRA), malonyl malonate (MAMA), ethane tetracarboxylic acid (ETAA),

c)oxidized intermediates: oxalic (OA) and tartronic (TA) acids,

d)brominated products: dibromo- (Br₂AcA) and tribromo (Br₃AcA) acetic acids.

First the oscillatory behaviour of the system was recorded with a bromide selective electrode (Figure 5 a)). In Fig. 5 b) the complete oscillatory regime is depicted indicating the potential minima and maxima and the time period in the oscillatory regime. As the diagram shows, oscillations appear and disappear with finite amplitude in this batch experiment.
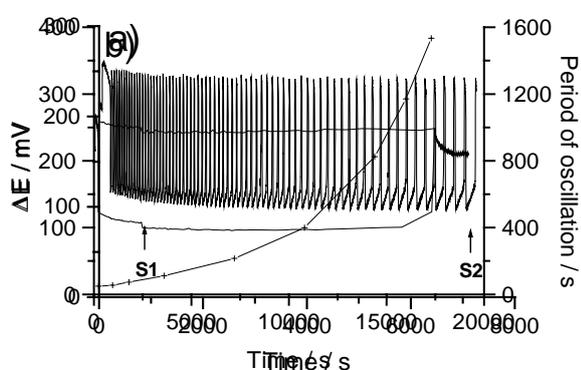
Figure 5.
Evolution of Ce-catalysed BZ oscillations in batch. $[MA]_0 = 0.1$ M, $[NaBrO_3]_0 = 0.1$ M, $[Ce^{4+}]_0 = 5\times10^{-3}$ M, $[H_2SO_4] = 1$ M.
a) Potential oscillations of a bromide selective electrode. Arrows indicate times when HPLC samples (S1, S2) were taken. The corresponding chromatograms are shown in Fig 6 (S1, 15 min) and Fig. 7 (S2, 2 hours).
b) Evolution of bromide electrode potential minima and maxima and the time period of the oscillations.

Fig. 6 a) and b) shows the same chromatogram recorded in the beginning of oscillatory regime (15 minutes after start) with a lower and a higher sensitivity simultaneously. The strong tailing of the bromate peak hides any small peaks of dibromomalonic (Br₂MA) or ethenetetracarboxylic acids both of them having a retention time of 500 s.
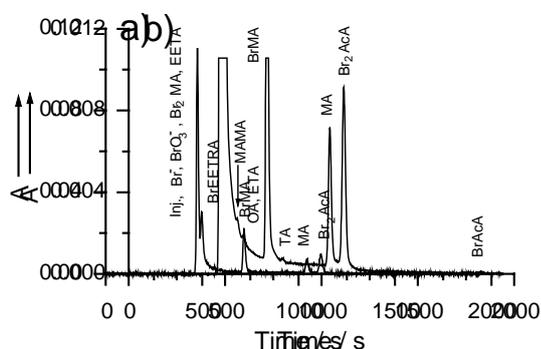
Figure 6
HPLC chromatogram of sample S1
a) Low and b) high sensitivity record.

At higher sensitivity as shown in Fig. 6 b) further components can be discovered: malonyl malonate (MAMA, $t_r = 570$ s), oxalic (OA, $t_r = 600$ s), ethanetetracarboxylic (ETA, $t_r = 600$ s), tartronic (TA, $t_r = 800$ s) and bromoacetic (BrAcA, $t_r = 1810$ s) acids. At even higher sensitivity (not shown here) these minor peaks are well separated and sharp ones which can be easily utilized for concentration determinations. There is an interference, however, between OA and ETA what was resolve with independent experiments. Contribution of ETA to the peak at 600 s can be calculated from the MAMA peak as the ETA/MAMA peak ratio is a stable value of 1.6. OA concentrations can be calculated from the remaining absorbance.
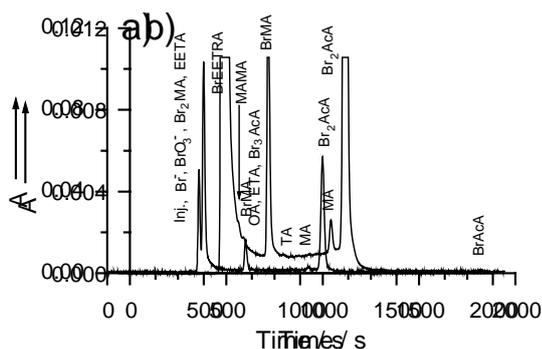

Figure 7
*HPLC chromatogram of sample S1*
a) Low and b) high sensitivity record.

Figure 7 shows similar chromatograms of a second sample taken in a later stage of the reaction (2 hours after start). Time evolution of the various components is clear when Fig. 6 and 7 are compared. For example bromate, BrMA and MA peaks decreased while BrEETRA and Br_2AcA peaks have grown during this period.

Evolution of chemical concentrations as measured by HPLC

Figure 8 displays the concentrations of the various components as a function of the reaction time. Concentrations were calculated from HPLC chromatograms similar to the ones shown in Figs. 6
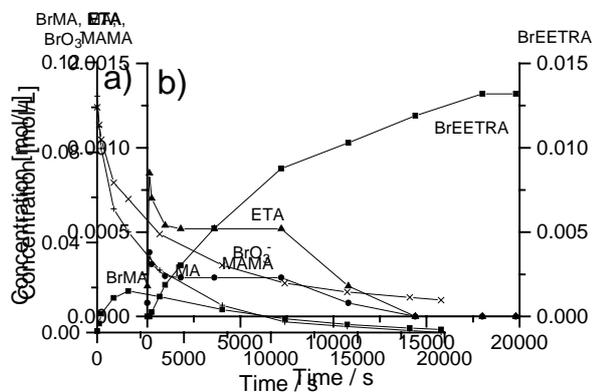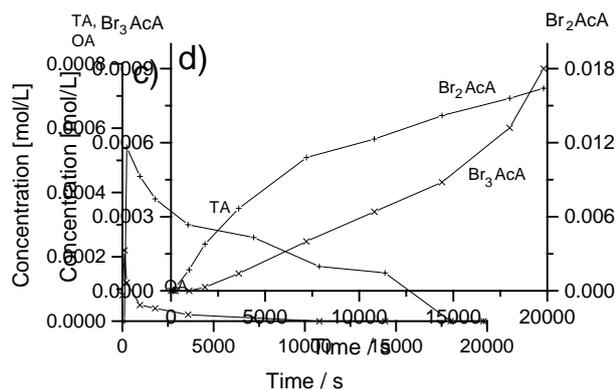

and 7.

Figure 8

Concentration evolution of bromate and various organic components in the course of the Ce-catalysed batch reaction.
a) Main components: acidic bromate, malonic and bromomalonic acids.
b) Radical recombination products: bromoethenetricarboxylic acid (right scale), malonyl malonate and ethanetetracarboxylic acid (left scale).
c) Oxidized intermediates: oxalic and tartronic acids.
d) Brominated products: Br₂AcA (right scale) and Br₃AcA (left scale).

7.) HPLC analysis of a complete BZ system catalyzed by ferroin was also performed under anaerobic conditions [5], and the concentration of the following components was measured in the course of the reaction:

a) major components: acidic bromate (BrO_3^-), malonic acid (MA), bromomalonic acid (BrMA),

b) radical recombination products: Bromoethene tricarboxylic acid (BrEETRA),

c) oxidized intermediates: oxalic (OA), mesoxalic (MOA) and tartronic (TA) acids,

d) brominated products: dibromo- (Br$_2$AcA) and tribromo (Br$_3$AcA) acetic acids.

As Figure 9 shows, the potential oscillations start without any induction period with small amplitude that grows rapidly to a certain level. Then the oscillations continue but the amplitude is changing irregularly. After two hours oscillations disappear with a finite amplitude. Compared to the cerium system both the time period of the oscillations and the length of the oscillatory regime is shorter. Also the growth of the time period during the oscillatory regime is less pronounced.
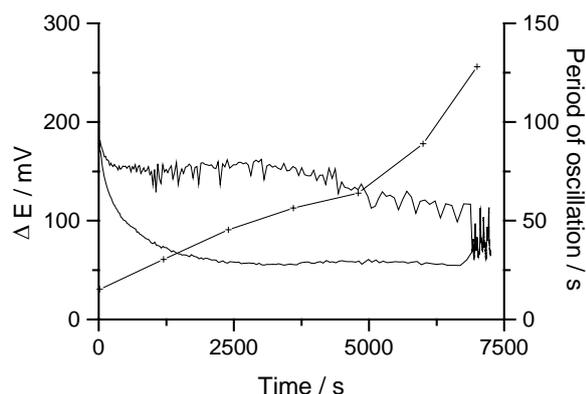

Figure 9
Evolution of bromide electrode potential minima and maxima and the time period of the oscillations in a ferroin-catalysed BZ reaction in batch. [MA]$_0$ = 0.15 M, [NaBrO$_3$]$_0$ = 0.15 M, [ferroin] = 5×10^{-3} M, [H$_2$SO$_4$] = 0.5 M.

Evolution of chemical concentrations as measured by HPLC

In Figure 10 a) concentration of the main components (MA, BrMA and BrO_3^-) is displayed in the course of the ferroin catalysed oscillatory reaction. While the pattern in some respects is similar to that of the cerium catalysed system shown in Fig. 8, there are important differences as well.   An even more important difference is that recombination products of malonyl radicals, that is MAMA and ETA, are absent. This indicates that a direct attack of the oxidized form of the catalyst on malonic acid, which produces malonyl radicals in the case of Ce^{4+}, is missing in the case of ferriin. Independent experiments [5] show, however, that while the oxidation of malonic acid in the ferriin - malonic acid reaction is slow or negligible bromomalonic acid is oxidized in a fast ferriin - bromomalonic acid reaction where the main product is BrEETRA.
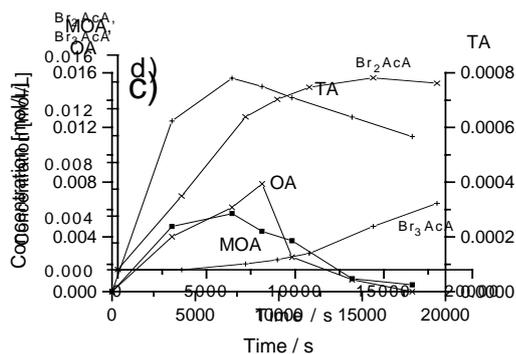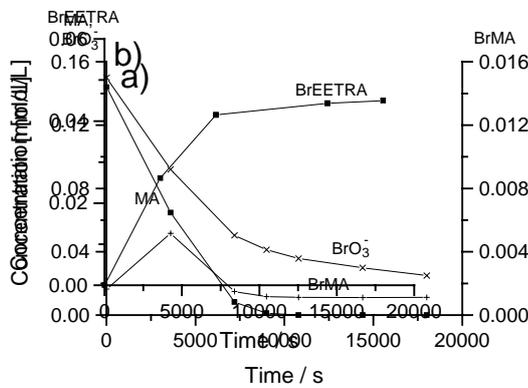
Figure 10
Concentration evolution of bromate and various organic components in the course of the ferroin-catalysed batch reaction.
a) Main components: acidic bromate, malonic acid (left scale) and bromomalonic acid (right scale).
b) The only radical recombination product found in this system, bromoethenetricarboxylic acid.
c) Oxidized intermediates: oxalic, mesoxalic (left scale) and tartronic acids (right scale).
d) Brominated products: Br_2AcA and Br_3AcA.

In Figure 10 c) the concentration of the measured oxidized intermediates (OA, MOA and TA) is depicted as a function of time in the ferroin catalysed system. The most important difference compared to the cerium catalysed system is the appearance of a relatively high concentration of mesoxalic acid. Both OA and MOA maintains this high concentration in the course of the oscillations then reaches the maximum concentration at the end of the oscillatory regime and decreases only afterward. This difference between the cerium and ferroin systems is probably due to the fact that while Ce^{4+} reacts rapidly with OA and MOA ferriin is not able to oxidize these substrates. Thus in the ferroin catalysed systems OA and MOA are oxidized by acidic bromate directly. The average tartronic acid concentration is also higher here by a factor of two or three and its maximum occurs not at the beginning but close to the end of the oscillatory regime.

Figure 10 d) shows the brominated products of the ferroin system. The Br_2AcA concentration is about the same as in the Ce^{4+} system but the concentration of Br_3AcA is higher by factor of four.

The results of the HPLC analysis show that while all the stable components of the BZ oscillators can be measured with this technique there are still unknown processes in the mechanism of these complex chemical systems. This is because various radicals play an important role in the mechanism and only their relatively stable recombination products can be measured by HPLC.

All of these results indicate that there are many differences in the mechanism of the cerium and the ferroin catalysed systems. As it is also evident that there are more unknown details in the ferroin system in the present work our model calculations will concentrate on the "classical" cerium catalysed system which was also the subject of most previous modelling efforts.

8.) Based on the HPLC measurements and on the suggested mechanism the MBM model of the cerium ion catalyzed BZ reaction was constructed [5]. Applying this model the concentration evolution of the following components were calculated and compared with the experiments:

a) major components: BrO_3^-, MA and BrMA,

b)radical recombination products: ETA+MAMA and BrEETRA,

c)oxidized intermediates: OA, MOA and TA,

d)brominated products: Br_2AcA and Br_3AcAs.

Model calculations for the cerium catalysed BZ reaction [5]

We discuss this model using a three step procedure. First, we focus on the inorganic subset. Second, we include all reactions necessary to model a BZ system starting with pure bromomalonic acid as a substrate; in this case oscillations start immediately with a finite amplitude after the addition of the catalyst, without showing an induction period. Third, we add all reactions occurring in a BZ system starting with pure malonic acid or with a mixture of malonic acid and bromomalonic acid; in this case an induction period appears indicating that oscillations can only start if additional organic intermediates appear. Finally, we will compare model calculations with experimental data for selected initial conditions.

We test the model in two typical cases:

i)   for a BZ system starting with pure bromomalonic acid (Figure 11) and

ii)   for a BZ system starting with pure malonic acid (Figure 12).

Regarding the Figures 11 and 12 for bromomalonic acid substrate the agreement is excellent while for malonic acid substrate there is one disagreement: the time period of oscillations in the model calculations is somewhat longer than in the experiments. The amplitudes of the Ce^{4+} oscillations agree well in both cases.
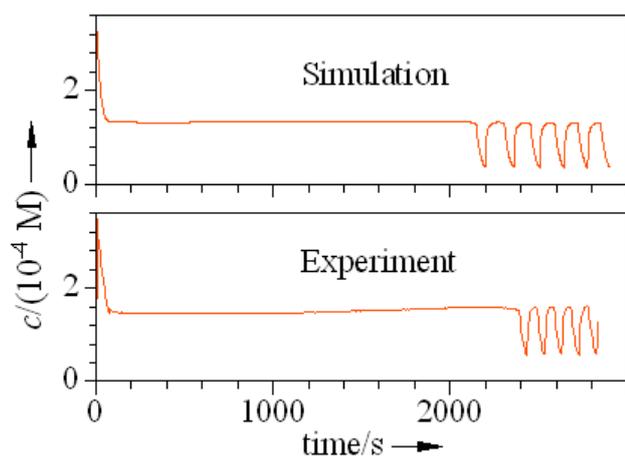
Figure 11

Experimental and calculated Ce^{4+} oscillations in a BZ system with pure bromomalonic acid as initial substrate. Initial concentrations: $[BrMA]_0 = 0.05$ M, $[BrO_3^-]_0 = 0.15$ M, $[Ce^{4+}]_0 = 3.56 \times 10^{-4}$ M, 1 M sulfuric acid, temperature 20 °C.

Figure 12

Experimental and calculated Ce^{4+} oscillations in a BZ system with pure malonic acid as initial substrate. Initial concentrations: $[MA]_0 = 0.05$ M, $[BrO_3^-]_0 = 0.15$ M, $[Ce^{4+}]_0 = 3.56 \times 10^{-4}$ M, 1 M sulfuric acid, temperature 20 °C.

Comparison of experimental and calculated concentration – time diagrams

After testing the model simulations were performed with the initial concentrations used for the HPLC experiments. As a detailed comparison for all components would require too many diagrams as figures these diagrams are not shown here but put on the web: http://www.fke.bme.hu/Research/BZ_Simulation/index.html. Here we discuss the agreements or disagreements between the theoretical and experimental curves only qualitatively.

Model calculations

Due to the differences between the cerium and ferroin systems the MBM model suggested here is focussed on the cerium catalysed BZ oscillators exclusively.

i) At low catalyst concentrations there is a good agreement between the model and experiments regarding the Ce^{4+} oscillations.

ii) Calculated concentration-time diagrams were compared with the experimental ones for various components measured with HPLC in a BZ system with higher Ce^{4+} concentration. While a qualitative agreement was found for many components the model seriously overestimates tartronic acid and underestimates BrEETRA.

iii) Six new hypothetical reactions are suggested for future improvements of the model. Nevertheless, it is hoped that the MBM model already in its present form can provide a realistic description of many cerium catalysed BZ systems.

Possibilities of application

One motivation of this research was that there are characteristic differences between the dynamic behavior of the cerium and ferroin catalyzed systems as was observed more than 20 years ago. Thus it was worthwhile to examine whether the products of the reaction between the oxidized form of the catalyst and the substrate are the same with Ce^{4+} and ferriin catalyst. We should get a better insight into the chemical wave experiments were made with ferroin – or bathoferroin – catalyzed BZ systems A few years ago even Turing structures were observed with this catalyst in microemulsion systems.

The model based on experimental data should help the better understanding of cerium catalysed full BZ systems. Beside this the suggested six new hypothetical reactions should prove the viability of the model.

The MBM model after the already mentioned revision should give a correct mechanism for the organic subset of the BZ reaction. Later it would be a possible change for the Oregonator model.

Among the analogy of the cerium and ferroin catalysed BZ systems similar model should build for the ferrroin catalysed systems, which should help the understanding of spatial and temporal phenomena like Turing structures.

Finally we remark that HPLC technique developed here can be applied advatageously to study other oxidation reactions whenever the oxidation is carried out in a sulfuric acid medium. Then the reaction can be stopped simply by dilution and the sample obtained this way can be injected directly to the HPLC apparatus where the eluent is also diluted sulfuric acid.

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