Contribution to the Chemistry of the Belousov−Zhabotinsky Reaction. Products of the Ferriin−Bromomalonic Acid and the Ferriin−Malonic Acid Reactions

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In the present mechanistic schemes of the ferroin-catalyzed oscillatory Belousov−Zhabotinsky (BZ) reaction the oxidation of the organic substrates (bromomalonic or malonic acid) by ferriin (the oxidized form of the catalyst) plays an important role. As the organic products of these reactions were not yet identified experimentally, they were studied here by an HPLC technique. It was found that the main organic oxidation product of bromomalonic acid is bromo-ethene-tricarboxylic acid (BrEETRA), the same compound that is formed when bromomalonic acid is oxidized by Ce^{4+} (another catalyst of the BZ reaction). Formation of BrEETRA is explained here by a new mechanism that is more realistic than the one suggested earlier. To find any oxidation product of malonic acid in the ferriin−malonic acid reaction was not successful, however. Neither ethane-tetracarboxylic acid (ETA) nor malonyl malonate (MAMA), the usual products of the Ce^{4+}−malonic acid reaction, nor any other organic acid, not even CO_2, was found as a product of the reaction. We propose that malonic acid is not oxidized in the ferriin−malonic acid reaction, and it plays only the role of a complex forming catalyst in a process where Fe^{3+} oxidizes mostly its phenantroline ligand.

Introduction

Motivation. Various forms of the Belousov−Zhabotinsky (BZ) reaction are the most studied chemical oscillators.[1−3] The main process in a BZ reaction is the oxidation of an organic substrate by acidic bromate promoted by a catalyst. In the classical, most popular version of the BZ reaction the organic substrate is malonic acid and the catalyst is cerium or ferroin.

The majority of the mechanistic studies on the BZ reaction has focused on the cerium-catalyzed systems.[4−9] In these studies, among others, it was important to identify the products of the Ce^{4+}−organic substrate reactions. To this end products of the Ce^{4+}−malonic acid (MA) and of the Ce^{4+}−bromomalonic acid (BrMA) reactions were studied with HPLC.[10−12] It was found that in the Ce^{4+}−malonic acid reaction the organic products are ethane-tetracarboxylic acid (ETA) and malonyl malonate (MAMA) which are formed by the recombination of different malonyl radicals.[10,11] A more complex product of the radical reactions, bromo-ethene-tricarboxylic acid (BrEETRA) was found when bromomalonic acid was oxidized by Ce^{4+} ions.[12]

The aim of this work is to study analogous reactions between ferriin and the same two organic substrates, namely malonic and bromomalonic acids. One motivation of this research is that there are characteristic differences between the dynamic behavior of the cerium and ferroin-catalyzed systems as was observed by Smoes[13] more than 20 years ago. Thus it is 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. Another motivation is that most of the chemical wave experiments[14] were made with ferroin- or bathoferroin-catalyzed BZ systems, and a few years ago even Turing structures were observed with this catalyst in microemulsion systems.[15] An effective rate constant of ferriin reduction in the BZ reaction was determined by Nagy-Ungvárai and co-workers.[16]

Previous Work by Jwo, Treindl, and Co-workers. The kinetics of the ferriin−bromomalonic acid reaction was first studied by Jwo and co-workers[17] in 1993 who followed the reduction of ferriin under aerobic conditions by spectrophotometry. They applied an excess of BrMA and measured the pseudo-first-order rate constant of the reaction. According to their Figure 9 in ref 17, that rate constant was proportional to the bromomalonic acid concentration, and thus they were able to calculate a second-order rate constant for the reaction which was 11.7 $M^{-1}\ s^{-1}$ at 20 °C in 1 M sulfuric acid.

Jwo and co-workers[17] also studied the kinetics of the ferriin−malonic acid reaction under aerobic conditions with the same spectroscopic technique as in the case of BrMA substrate. They measured the pseudo-first-order rate constant k_{obs}(MA) of the reduction of ferriin applying a great excess of the reductant malonic acid. It was found that depicting $1/k_{obs}$(MA) vs 1/[MA] gave a straight line suggesting a fast preequilibrium prior to the actual reaction. According to their Figure 4 in ref 17, $1/k_{obs}$(MA) = 410 s at 20 °C in 1 M H_2SO_4. They remark in paragraph D of their work[17] that the rates of these reactions under deaerated conditions are "considerably slower", but they did not quantify this statement. On the basis of their data, we can estimate that the ratio of the rates measured under aerobic and anaerobic conditions, respectively, is around or less than 10.

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In 2003 Treindl and co-workers[18] reinvestigated the ferriin−malonic acid reaction by a different technique, recording the potential of a platinum electrode during the reaction. Most of their measurements were made under aerobic conditions and in 0.2 M H_2SO_4. They confirmed the observation of Jwo et al. that the reaction is faster under aerobic conditions. Moreover, they found that the electrode potential vs time diagram has a sigmoid shape: the rate of the potential drop accelerates nearing to the end of the reaction which indicates an autocatalytic process.

Here we analyze the products of the ferriin−bromomalonic acid and the ferriin−malonic acid reactions with an HPLC technique. As we will see, while the interpretation of the experimental results for the ferriin−bromomalonic acid reaction is rather straightforward, it is more problematic when the substrate is malonic acid. This is why we start the discussion with the bromomalonic acid experiments and discuss the ferriin−malonic acid reaction afterward.

Experimental Section

Chemicals. *Commercial Products.* Malonic acid (Fluka, puriss), tartronic acid (Heraeus, puriss.), $Ce(SO_4)_2{\cdot}4H_2O$ (Merck, p.a.), oxalic acid (Merck, p.a.), mesoxalic acid (Sigma, p.a.), dibromoacetic acid (Fluka, purum), glyoxylic acid (Fluka, puriss), fumaric acid (Fluka, puriss), PbO_2 (Fluka, p.a.), and 0.025 M ferroin solution (Fluka, p.a.) were used as received. All solutions were prepared with doubly distilled water.

Preparation of Bromomalonic Acid Solutions. The potassium salt of bromomalonic acid was produced following the procedure of Försterling et al.[19] Bromomalonic acid solutions were prepared freshly by dissolving this potassium salt in 1 M sulfuric acid.

Preparation of Ferriin Solutions. Ferriin solution (0.01 M) (in 1 M H_2SO_4) was freshly prepared from ferroin solution with two different methods: (i) 2 mL 0.025−0.026 M ferroin solution was mixed with 0.5 mL 0.1 M $Ce(SO_4)_2$ solution (in 1 M H_2SO_4) and with 2.5 mL 1.8 M H_2SO_4 (here care was taken that a small excess of ferroin be applied to minimize Ce^{4+} in the ferriin solution) or (ii) 7.5 mL 1.66 M H_2SO_4 solution and 0.035 g PbO_2 powder were added into 5 mL ferroin solution and then stirred for 1 h in an ice bath. Then the solution was centrifuged to remove the unreacted PbO_2 and the $PbSO_4$ produced in the reaction. The freshly prepared 0.01 M ferriin solution (in 1 M H_2SO_4) was used immediately. In most cases ferriin was prepared with the more simple method i, as parallel experiments carried out in a nitrogen atmosphere with the two different ferriin solutions gave practically the same results.

The Ferriin−Malonic Acid/Bromomalonic Acid Reaction in N_2 or O_2 Atmosphere. A 30 mL three-necked vessel was used as a reactor. One neck was used for the gas inlet, a second for the reactant inlet, and the third for the gas outlet. Backward diffusion of air was prevented by bubbling the gas through water after leaving the reactor.

The reaction of malonic acid/bromomalonic acid with ferriin was examined in 1 M sulfuric acid medium at room temperature (22 ± 2 °C). We used two solutions containing the organic acid and ferriin, respectively. Both reagents were dissolved in 1 M sulfuric acid. The reactions were carried out as a batch experiment. Ferriin (2 mL, 0.01 M) in 1 M H_2SO_4 was added to 2 mL organic acid (1 M MA or 0.5 M BrMA) dissolved also in 1 M H_2SO_4 while bubbling N_2 gas continuously through the reaction mixture. Both solutions were freshly deaerated with N_2 before the experiments. To compare our results with those obtained by Jwo et al.,[17] some experiments with the ferriin−malonic acid reaction were carried out also in an O_2 atmosphere instead of N_2. Samples were taken after different reaction times (usually 10 s, 2, 4, 8, 16, 30, 60, 120, and 240 min) and were analyzed with HPLC.

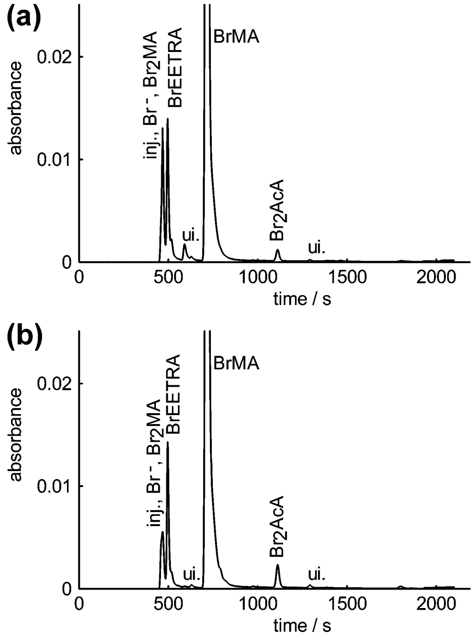


Figure 1. HPLC recording of the products of the ferriin−BrMA reaction. Initial concentrations: $[\text{ferriin}]_0 = 5 \times 10^{-3}$ M, $[\text{BrMA}]_0 = 0.25$ M, $[H_2SO_4]_0 = 1$ M. The sample was taken at (a) 10 s, (b) 240 min after the start of the reaction. Concentrations of two identified products of the reaction: (a) $[\text{BrEETRA}] = 1.3 \times 10^{-3}$ M, $[Br_2AcA] = 4.8 \times 10^{-4}$ M, (b) $[\text{BrEETRA}] = 1.3 \times 10^{-3}$ M, $[Br_2AcA] = 9.2 \times 10^{-4}$ M. There are also two small unidentified peaks in both Figures, marked with “ui.”.

Analytical Methods. *HPLC.* HPLC experiments were performed with 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[20] was at 45 °C and the 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. Because the sulfuric acid concentration in the reaction medium (1 M) was 100 times more concentrated than in the eluent (0.01 M), the samples were diluted 100 times prior to the HPLC analysis. The organic acid concentrations given in the captions of figures refer to their original values (that is before the 100 times dilution for HPLC). The same HPLC conditions have been applied successfully in a series of previous investigations to separate various organic acid intermediates of the BZ reaction. No decomposition of those acids was observed under these conditions. For further details see refs 10−12, 21.

Results and Discussion

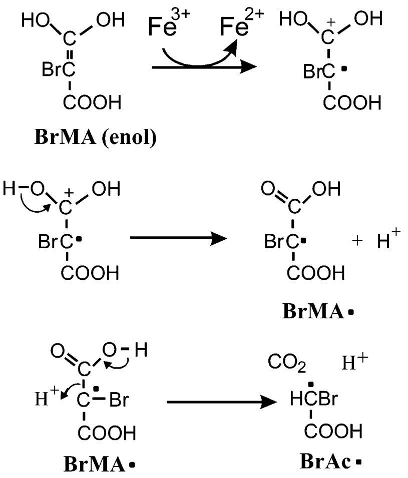
The Ferriin−Bromomalonic Acid Reaction. *HPLC Analysis of the Products in the Case of Short and Long Reaction Times.* HPLC recordings of the reaction products of the ferriin−bromomalonic acid reaction after 10 s and 240 min reaction times are shown in Figure 1. (Further measurements were made at 2, 4, 8, 16, 30, and 120 min, but those results are not shown here.)

Let us start the peak identification with the peaks of the major components as they appear in Figure 1b. The first peak is the injection peak whose height is increased by a factor of 5 compared to the chromatogram of the BrMA solution (not shown here). There are two possible components which can be responsible for the observed increase of the injection peak (retention time $t_r = 473$ s): bromide ions or dibromomalonic acid (Br_2MA) or a combination of them. (These possibilities will be discussed later.) The second peak can be assigned to BrEETRA ($t_r = 503$ s). Next we can see an unidentified small peak (at $t_r = 600$ s) with a small shoulder, then the large peak of the unreacted BrMA ($t_r = 723$ s) followed by a small peak of dibromoacetic acid (Br_2AcA, $t_r = 1123$ s). The latter is a product of the ferriin−BrMA reaction because the original BrMA solution contained only trace levels of Br_2AcA and Br_2-MA. We can see another tiny peak ($t_r = 1316$ s), but this is not a product of the reaction because it appears in the BrMA standard.

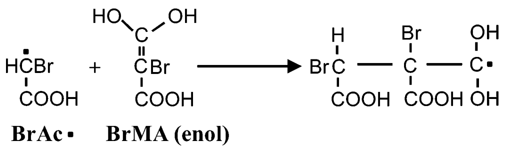
On the basis of the second-order rate constant measured by Jwo and co-workers (11.7 $M^{-1}s^{-1}$), and regarding the relatively high BrMA concentration (0.25 M) used in our experiments, we estimate that the reaction is nearly complete within 1−2 s after mixing. This suggests that the product distribution must not depend on the reaction time whenever that time is longer than 1 or 2 s. Really, the composition of the various samples was the same between 8 and 240 min reaction times. On the other hand, there were deviations from the final equilibrium composition in the case of shorter reaction times, e.g., 10 s (compare Figure 1a and 1b).

For reaction times below 4 min (especially for the 10 s reaction time as Figure 1 a shows), the following three characteristic differences can be observed compared to the longer reaction times: (i) the injection peak is about two times higher, (ii) a small peak with a shoulder can be seen between the BrEETRA and BrMA peaks. For longer reaction times the small peak disappears; only the shoulder remains as a separate peak, and (iii) the Br_2AcAc peak is two times smaller. Above 8 min reaction time, such differences cannot be observed, and the same chromatogram can be measured independently of the reaction time. Because the time scale of the ferriin−BrMA reaction is much shorter than 10 s, the observed deviations cannot be explained by the primary reaction. Thus it is a logical conclusion that these changes on the time scale of few minutes are caused by subsequent reactions of the primary reaction products.

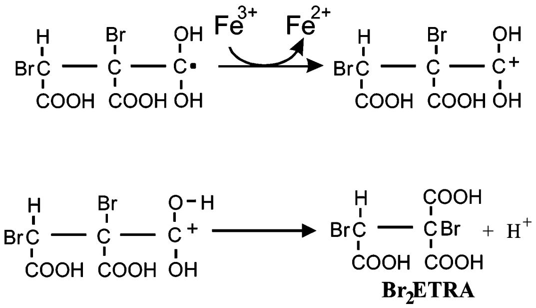
Mechanism for the BrEETRA Formation. We propose a mechanism for the production of BrEETRA in the ferriin−BrMA reaction that also applies to the Ce^{4+}−BrMA reaction. The first step is a one-electron oxidation of the enol form of BrMA by ferriin followed by the decarboxylation of the bromomalonyl radical in the acidic medium:



Here the simultaneous moving of two electron pairs results in decarboxylation and in releasing a hydrogen ion from the oxygen and bonding another one to the carbon atom. In the next step the bromoacetyl radical reacts with the double bond of the enol form of BrMA:

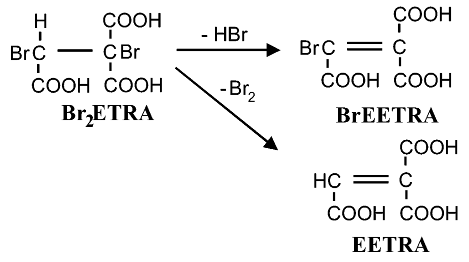


This new radical, which is actually a hydrated acyl radical, can be oxidized further by ferriin to dibromoethanetricarboxylic acid (Br_2ETRA):



A similar mechanism was proposed by Narasaka[22] for organic free radical producing oxidations by Mn^{3+} and Ce^{4+} in the presence of olefinic compounds. In one of his schemes, Mn^{3+} reacts with an organic acid, giving a free radical that decarboxylates. The decarboxylated free radical then reacts with a double bond-containing molecule to yield a hydrated acyl radical intermediate similar to ours. Finally, another Mn^{3+} ion oxidizes that hydrated acyl radical to the final product, again in an analogy to the scheme proposed here.

The last step is the loss of an HBr molecule from Br_2ETRA to form BrEETRA. Regarding the initial ferriin concentration (5×10^{-3} M), a 100% yield predicts 2.5×10^{-3} M BrEETRA after the reaction. The observed 1.3×10^{-3} M means a 52% yield for BrEETRA only. Obviously, some other products are also formed in the reaction. To explain this, we propose the following scheme for the decomposition of Br_2ETRA:



We remark that the above decomposition of Br_2ETRA is a fast process because Br_2ETRA was never observed as a separate peak; moreover, on the time scale of the experiments, the BrEETRA peak was stable. In the following paragraph we present arguments supporting the above scheme.

Br_2AcA Formation. It is known that Br_2MA decarboxylates at room temperature,[23] and it is logical to assume that this is the source of Br_2AcA. We observe that whenever the first peak (which includes Br_2MA) becomes smaller, the Br_2AcA peak increases (see Figure 1a and 1b). If we accept this hypothesis, then we must also find a reasonable explanation for the Br_2-MA production in this system. One possibility is that ferriin

oxidizes bromide (which is formed in the decomposition of Br_2ETRA to BrEETRA), and the bromine produced brominates BrMA to Br_2MA. However, according to the measurements of Jwo et al.,[17] ferriin is reduced by BrMA much faster than by bromide. Under such circumstances, no measurable amount of bromine can appear because ferriin is reduced to ferroin rapidly by the excess BrMA. Another mechanism of bromine formation is that Br_2ETRA decomposes releasing not only HBr but also bromine:

$$\mathrm{Br_2ETRA \rightarrow Br_2 + EETRA}$$

that brominates BrMA:

$$\mathrm{Br_2 + BrMA \rightarrow Br_2MA + Br^- + H^+}$$

This theory predicts simultaneous formation of EETRA with Br_2MA. Unfortunately direct support for this by identifying an EETRA peak (t_r = 700 s) is prevented by the strong BrMA peak appearing at 723 s.

Comparing the initial ferriin concentration to the concentration of Br_2MA formed, the relative yield for Br_2MA is about 36%. This means that BrEETRA and Br_2MA are the major products in the ferriin−BrMA reaction because they together give 88% of all products. As the small unidentified peak at 600 s indicates, however, other products appear but in relatively minor concentrations.

Finally, while we remark that the injection peak coincides with that of the bromide, and this prevents calculation of the concentration of bromide produced in the ferriin−bromomalonic acid reaction, a rough estimate based on Figure 1b suggests a bromide concentration of $(3\pm1) \times 10^{-3}$ M, which is in agreement with the theoretical 2.5×10^{-3} M.

The Ferriin−Malonic Acid Reaction. *HPLC Analysis of the Products at Short and Long Reaction Times.* HPLC recordings of the reaction products of the ferriin−malonic acid reaction after 10 s and 240 min reaction times are shown in Figure 2. A series of measurements were also made at other reaction times, but all the chromatograms are nearly identical within the experimental error.)

The sensitivity in Figure 2 is 5 times higher than in Figure 1. This is because we were not able to identify any significant reaction products of the ferriin−malonic acid reaction. In the case of the Ce^{4+}−malonic acid reaction, two products were found:[10,11] ethanetetracarboxylic acid (ETA, t_r = 600 s) and malonyl malonate (MAMA, t_r = 570 s). However, in the chromatograms of Figure 2, no traces of ETA or MAMA can be seen. Only two peaks can be identified: oxalic and mesoxalic acid (OA, t_r = 600 s and MOA, t_r = 638 s). These components appear only when ferriin is prepared with Ce^{4+} and when traces of oxygen are present. No OA or MOA is observed with the ferriin prepared by PbO_2. Chromatograms showing the presence of OA and MOA are displayed because these are the only reaction products where concentration determination is possible. As can be seen, these are very small, stoichiometrically insignificant concentrations, and the few unidentified peaks are of the same order or even smaller.

Mechanism for MOA and OA Formation. If ferriin is prepared with Ce^{4+}, a very small equilibrium concentration of Ce^{4+} is always present. Hegedüs et al.[24] studied the Ce^{4+}−malonic acid reaction in the presence of O_2 and found that malonyl radicals produced in the Ce^{4+}−malonic acid reaction can react with oxygen generating peroxymalonyl radicals. In a following step, when the Ce^{4+} concentration is low, the peroxymalonyl radical can react with malonic acid to produce a new malonyl radical and peroxymalonic acid. Hydrogen ions may catalyze a rearrangement of peroxymalonic acid to mesoxalic acid. In this way, mesoxalic acid is produced in a chain reaction, and even a very low Ce^{4+} concentration produces a measurable amount of MOA, which can be oxidized to OA by Ce^{4+}. In support of the above mechanism, separate measurements (not shown here) show that the MOA peak is increased considerably by bubbling oxygen through the reaction mixture.

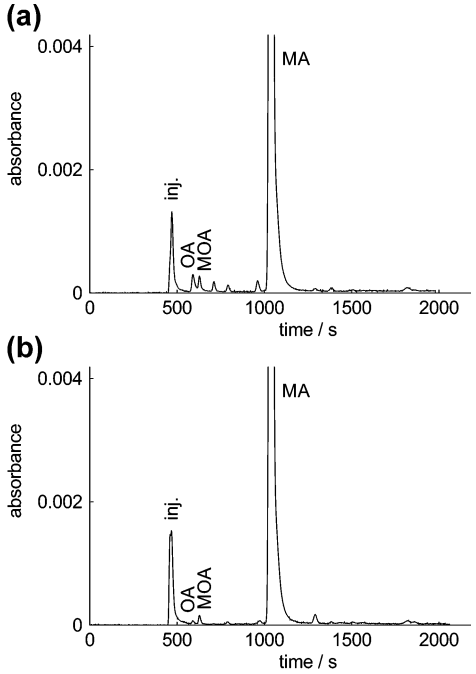


Figure 2. HPLC recording of the products of the ferriin−MA reaction. Initial concentrations: $[\text{ferriin}]_0 = 5 \times 10^{-3}$ M, $[\text{MA}]_0 = 0.5$ M, $[\text{H}_2\text{SO}_4]_0 = 1$ M. The sample was taken at (a) 10 s, (b) 240 min after the start of the reaction. Concentrations of some minor components in part a: $[\text{OA}] = 3.0 \times 10^{-4}$ M, $[\text{MOA}] = 5.5 \times 10^{-4}$ M. The same components in part b: $[\text{OA}] = 8.6 \times 10^{-5}$ M, $[\text{MOA}] = 3.4 \times 10^{-4}$ M.

On the Role of Malonic Acid in the Reduction of Ferriin. When Jwo et al.[17] followed the ferriin−malonic acid reaction by spectrophotometry, they found that the time constant of the pseudo-first-order reaction of ferriin with an excess of malonic acid is 410 s at 20 °C in 1 M H_2SO_4. Regarding this time scale, it is sure that during a 10 s reaction time (Figure 2a) no significant change in the initial composition can appear, while after 240 min (Figure 2b) most of the reaction should be over. Thus we expect products of the reaction to appear as new peaks in Figure 2b. Nevertheless, if we compare Figures 2a and 2b we cannot see any significant change. Actually, except for a small unidentified peak at t_r = 1298 s, all other peaks are somewhat smaller after 240 min reaction time, i.e., no products appear. The next logical question is whether any consumption of malonic acid can be observed. Because malonic acid is in high excess, any change in its peak height is relatively small and difficult to detect. In a separate experiment, when ferriin and malonic acid are present at the same low concentration, $[\text{ferriin}]_0 = [\text{MA}]_0 = 5 \times 10^{-3}$ M, after 20 min reaction time, a small but measurable (18%) decrease of the MA peak is observed. Thus HPLC measurements indicate that there is a reaction between ferriin and malonic acid but do not provide any information about the product(s). Oxidation products of malonic acid should be organic acids or CO_2. Because no organic acid products were found by HPLC, CO_2 evolution was checked by a sensitive technique described in refs 23 and 25. The result was negative; no CO_2 was generated.

All these observations can be rationalized, however, if we assume a slow complex forming reaction between ferriin or ferroin and malonic acid. Ferriin, ferroin, and their complexes are fixed on the cation-exchange resin of the HPLC. Thus it is only the uncomplexed malonic acid that appears in the chromatogram.

Malonic acid is not oxidized in this reaction in 1 M H_2SO_4. On the other hand, a chemical reaction reducing Fe(III) to Fe(II) takes place as both spectrophotometric[17] and potentiometric[18] experiments prove. It was found[26] that in an alkaline medium, ferriin can oxidize its ligand to 1,10-phenantroline-*N*-oxide and some oxygen is also produced in the process. It was proposed[27] that in a first step ferriin oxidizes OH^- ions to •OH radicals:

$$\mathrm{Fe(N\text{-}N)_3}^{3+} + \mathrm{OH}^- \leftrightarrow \mathrm{Fe(N\text{-}N)_3}^{2+} + \bullet\mathrm{OH}$$

This reaction, however, cannot be significant in our experiments, because in 1 M H_2SO_4 the hydroxide ion concentration is too small. Thus instead of that scheme, it is reasonable to assume the following rate-determining step:

$$\mathrm{Fe(N\text{-}N)_3}^{3+} + \mathrm{H_2O} \leftrightarrow \mathrm{Fe(N\text{-}N)_3}^{2+} + \mathrm{H}^+ + \bullet\mathrm{OH}$$

and this scheme can also explain why H^+ slows down the rate of the reaction, as it was observed by Treindl and co-workers.[18] They found that the rate of the ferriin reduction is proportional to the reciprocal of the sulfuric acid concentration. It is possible that the rate of this reaction might be also affected by the malonic acid concentration via complex formation.

Another peculiar feature, the observed effect of the oxygen on the rate of the reaction,[18] is probably due to the fact that the reduction product Fe(II) complex can decompose and subsequently be oxidized by the oxygen of the air to uncomplexed Fe(III). Nord and Pizzino[28] proved that oxygen is necessary for the decomposition of ferroin in sodium hydroxide solutions. While studying the ferriin−hydroxyde ion reaction, Nord and Wernberg[27] observed the reoxidation of Fe(II) products using an oxygen electrode. If we assume that uncomplexed Fe(III), the final product of this reaction sequence can accelerate the reduction of ferriin by hydroxide ions that could provide an explanation even for the observed autocatalytic character of the reaction.[18]

Finally it is worthwhile to mention that ferriin cannot oxidize oxalic acid. To prove this was an easier task because CO_2 is the only oxidation product in this case. Thus we tried to detect carbon dioxide evolution in a ferriin−oxalic acid reaction mixture in 1 M sulfuric acid medium applying a rather sensitive CO_2 measuring technique[23,25] but with no success. This negative result is important because Jwo and co-workers found that oxalic acid affects the reduction of ferriin in an analogous way to malonic acid.

Conclusions

(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

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

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

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 too low to be detected by ESR.[29]

(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

$$\mathrm{M}^{(\mathrm{N}+1)+} + \mathrm{RH} \rightarrow \mathrm{M}^{\mathrm{N}+} + \mathrm{H}^+ + \mathrm{R}\bullet$$

reaction does not recombine with another radical as was proposed earlier (which reaction has a small probability at low radical concentrations), but it reacts with a double-bond-containing compound (here this is the enol form of BrMA):

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

and the new radical formed this way reacts again with the oxidized form of the catalyst:

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

Without providing the details, we mention here that 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[6] 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. That conclusion is corroborated by the following further negative results:

(i) Neumann[30] was able to find malonyl radicals only in the Ce^{4+}−malonic acid reaction but not in a ferriin−malonic acid mixture. Obviously, the two reactions have a different character.[31]

(ii) According to the HPLC analysis of whole BZ systems[9] ETA and MAMA were found only in the Ce^{4+}-catalyzed BZ system but not in the ferroin-catalyzed one.

Finally we comment why BrMA can be oxidized by ferriin while MA can be oxidized only by Ce^{4+}. A part of the answer is that Ce^{4+} is a stronger oxidant than ferriin, the standard redox potentials being 1.44 and 1.06 V, respectively.[32] The oxidants react with the π electron pair in the enol form of these organic acids. The bromine atom has a partial negative charge in BrMA due to an inductive effect, and this negative center is attracted by the positive charge of the Fe^{3+} in the ferriin. This way the π electron pair gets closer to Fe^{3+} and reduces it to Fe^{2+}. In the case of MA the surrounding of the π electron pair is partially positive due to the inductive effect of the oxygen atoms in MA; consequently the reaction between the π electron pair and the positively charged oxidant ion is more difficult.

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