HPLC Studies on the Organic Subset of the Oscillatory BZ Reaction. 3. Products of the Ce^{4+}−Bromomalonic Acid Reaction

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Using HPLC technique, two different pathways were found for the oxidation of bromomalonic acid by Ce^{4+}. One route is dominant when the Ce^{4+} concentration is low compared to that of bromomalonic acid (BrMA). The end products of this reaction route are bromoethenetricarboxylic acid (BrEETRA), CO_2, and Br^-. For this route two slightly different mechanisms (both are based on radical−radical recombination reactions) are proposed, which can explain the formation of BrEETRA. The other pathway is dominant when Ce^{4+} is in excess. This route leads to a complete oxidation of BrMA to CO_2. No intermediates of this route were found, however.

Introduction

The first two papers of this series[1,2] dealt with the products of the Ce^{4+}−malonic acid (MA) reaction. The first molecular intermediates of that reaction were recombination products of organic free radicals.[1,2] Two product peaks were found with HPLC technique. One of them was identified as ethanetetracarboxylic acid (ETA), a recombination product of two alkyl malonyl radicals. The other product is malonyl malonate (MAMA), a recombination product of an alkyl and a carboxylato malonyl radical.

The aim of the present study is to identify the products of the Ce^{4+}−bromomalonic acid (BrMA) reaction. This reaction is a part of both negative feedback loops[3,4] of the oscillatory BZ reaction, as it is a simultaneous source for organic free radicals and for bromide ions as well. Despite this crucial role, the reaction itself is poorly understood. The first suggestion was already made by Zhabotinsky:[5,6]

$$Ce^{4+} + BrMA \rightarrow Ce^{3+} + Br^- + \text{other products} \quad \text{(R1)}$$

Later on in the FKN mechanism[7,8] and in the Oregonator model[8−10] of the BZ reaction this scheme became a part of the so-called process C, which is usually written in the following form:

$$2Ce^{4+} + MA + BrMA \rightarrow fBr^- + \text{other products} \quad \text{(R2)}$$

Originally[7,9] it was assumed that "other products" include formic acid, but this hypothesis was later abandoned.[8,10] The most recent suggestion for the products was made again by Zhabotinsky and co-workers.[11] They proposed that in the analogous ferriin−BrMA reaction the first radical intermediate is alkyl bromomalonyl radical, and its self-recombination gives dibromoethanetetracarboxylic acid:

$$2^{\bullet}CBr(COOH)_2 \rightarrow C_2Br_2(COOH)_4 \quad \text{(R3)}$$

Furthermore it was assumed that in a next step this molecular intermediate decomposes rapidly to give rise to bromide ions and unknown products:

$$C_2Br_2(COOH)_4 \rightarrow 2H^+ + 2Br^- + \text{products} \quad \text{(R4)}$$

It is all these uncertainties and the importance of the Ce(IV)−BrMA reaction in the mechanism that initiated our present HPLC study on this problem.

Experimental Section

Materials. *Commercial Products.* Malonic acid, maleic acid, fumaric acid, diethyl ether (Fluka, puriss.), tetraethyl 1,1,2,2-ethanetetracarboxylate, dibromoacetic acid (Fluka purum), triethyl 1,1,2-ethanetricarboxylate, tetraethyl ethenetetracarboxylate (Aldrich, 99%), $Ce(SO_4)_2$ (Riedel-deHaen, p.A.), and H_2SO_4 (Merck, p.A.) were used as received.

Preparations. Bromomalonic acid was prepared following the procedure of Försterling et al.[12] To produce the potassium salt of ETA and the potassium salt of 1,1,2-ethanetricarboxylic acid (ETRA), the method of Sirimungkala et al.[2] was applied. The potassium salt of ethenetetracarboxylic acid (EETA) was prepared in a similar way. A 6.32-g (20 mmol) portion of tetraethyl ethenetetracarboxylate was dissolved in 60 mL of methanol; then 60 mL of 5 M KOH in methanol was added dropwise with continuous stirring, which was continued for 6 h at room temperature. The white precipitate was filtered and dried (yield: 7.8 g). This product was recrystallized by dissolving it in 40 mL of water and then reprecipitating the clean potassium salt with 40 mL of methanol, which was added dropwise under continuous stirring. The dry weight of the product was 3.2 g. Triethyl ethenetricarboxylate was prepared from tetraethyl ethenetetracarboxylate according to the method of Patterson et al.[13] The boiling point, ^1H NMR, ^{13}C NMR, and mass spectra were in agreement with the published data. The potassium salt of ethenetricarboxylic acid (EETRA) was

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obtained by the hydrolysis of the ester. A 2.4-g sample of liquid ester was dissolved in 20 mL of methanol. A 25-mL portion of 5 M KOH in methanol was added dropwise with continuous boiling and stirring. A yellowish precipitate was formed immediately. After refluxing for 7 h the mixture was stirred and kept warm for another 14 h. The precipitate was filtered, washed with methanol, and dried in vacuum. The resulting potassium salt (0.58 g) was analyzed with HPLC. The peak of EETRA was detected at 700 s. The only contaminant, a small peak at 500 s, was due to some ethenetetracarboxylic acid, a starting material of the synthesis. Another procedure for a quick preparation of an EETRA solution for HPLC used the potassium salt of EETA as a starting material. A 100-mg sample of it was dissolved in 4 mL of 10 M H_2SO_4 and was kept at 100 °C for 40 min. After this treatment all EETA was decarboxylated to EETRA, but as this product decarboxylated further, fumaric and maleic acids also appeared. To remove these contaminants 6 mL of water was added to the solution and extracted with 10 mL of ether three times. A 250-μL portion of the aqueous phase was diluted to 100 mL and analyzed by HPLC. This sample was an EETRA solution practically free of contaminants.

Reactions. *Reaction of Ce^{4+} with BrMA.* The whole procedure was carried out at room temperature and in a N_2 atmosphere. First 5 mL of 0.2 M BrMA in 1 M H_2SO_4 and 35 mL of 0.1 M $Ce(SO_4)_2$ in 1 M H_2SO_4 was bubbled with N_2; then the Ce^{4+} solution was added dropwise (this lasted about 2 h) to the BrMA solution with continuous stirring. After the last drop the stirring continued for an additional 4 h until the yellow color of Ce^{4+} disappeared, showing that the reaction was over. An HPLC of the product solution (diluted by a factor of 100) is shown in Figure 1. In this product solution besides Br^- and the unknown end product P1 there was some BrMA and organic contaminants. To make further chemical experiments exclusively with P1, other organic compounds were removed. To this end 10 mL of the product solution was extracted three times with 10 mL of ether. Further chemical reactions were performed with this *"solution of P1"* (see Figure 2a).

Reaction of P1 with Zn in Dilute Sulfuric Acid. A 100-μL solution of P1 was diluted to 10 mL with water, and 50 mg of Zn powder was added at room temperature. After 10 min of continuous stirring the solution was filtered and was analyzed by HPLC without further dilution.

Reaction of P1 with Fe^{2+}. To a 100-μL solution of P1 5 mL of H_2O and 1 mL of 0.1 M $Fe(NH_4)_2(SO_4)_2$ solution was added. The mixture was bubbled continuously with N_2 while 1 mL of 1 M NaOH was introduced. The bubbling of N_2 was continued for 5 min. The sample was next mixed with 0.5 mL of 1 M H_2SO_4 and diluted to 10 mL. Finally the solution was filtered and analyzed by HPLC without further dilution. This was the only sample with a higher than normal (0.08 M instead of the usual 0.01 M) sulfate concentration. This is the explanation for the sulfate peak in Figure 4.

Analytical Techniques. In the present experiments the same HPLC apparatus (Shimadzu with SPD-10A dual wavelength UV detector working at 220 nm and equipped with a Merck Polyspher OA KC column) and instrumental parameters were applied as by Sirimungkala et al.[2] For HPLC analysis solutions containing H_2SO_4 were diluted such that its final concentration was 0.01 M in the sample, which was equal to eluent concentrations; in the special case of samples containing 1 M H_2SO_4 usually 100-μL aliquots were diluted to 10 mL. An HP-8452A photodiode array spectrophotometer was used to take the spectra.

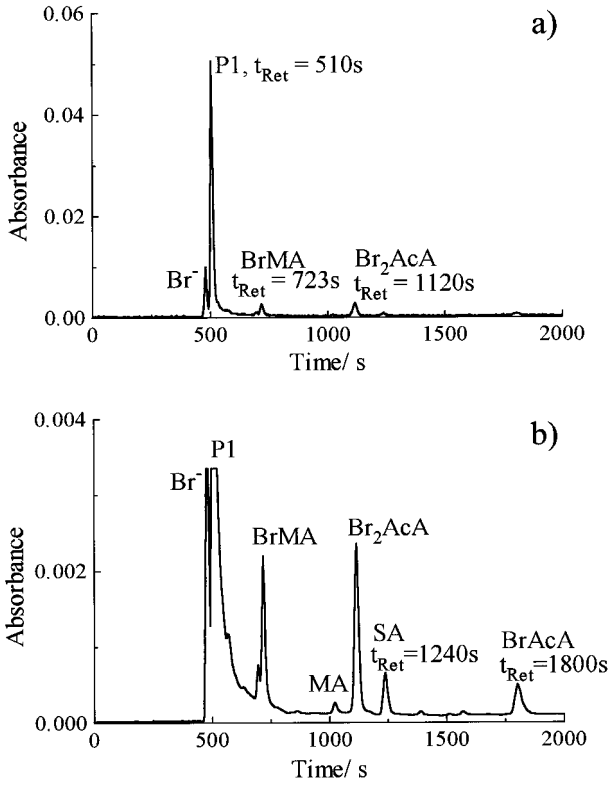

Figure 1. Reaction products of the Ce^{4+}−BrMA reaction. Virtual initial concentrations (assuming an instantaneous mixing of the reagents without reaction): $[BrMA]_0 = 25$ mM, $[Ce^{4+}]_0 = 88$ mM, $[H_2SO_4] = 1$ M. See the Materials paragraph for further details of the preparation. HPLC of the products (a) with low and (b) with high sensitivity. In the reaction mixture besides the products P1 and Br^- and the starting material BrMA there are some other components in very low concentrations. Malonic, bromoacetic, and dibromoacetic acids (MA, BrAcA, and Br_2AcA) are not products, as they are already contaminants of BrMA. We have no explanation for the trace amounts of succinic acid (SA) indicated by the high-sensitivity chromatogram.

Results and Discussion

HPLC chromatograms of the products of the Ce^{4+}−BrMA reaction are given in Figure 1 measured with a low (Figure 1a) and also with a high (Figure 1b) sensitivity.

Besides bromide, only one major product peak can be observed at 510 s close to the bromide peak. This is an organic acid not known from our previous studies and will be denoted as P1. All the following experiments were aimed to identify P1. At first we assumed that this peak is due to a first molecular intermediate, which could react further with Ce^{4+}. However, the height of this peak does not change while standing overnight with an excess of Ce^{4+} in 1 M H_2SO_4. Thus the unknown compound P1 should be an inert end product of the reaction. This is in sharp contrast with the Ce^{4+}−MA reaction where both of the first molecular products, ETA and MAMA, were even more reactive with Ce^{4+} than malonic acid itself. This gives the hint that unlike MA, BrMA, ETA, or MAMA the product P1 does not contain an "active hydrogen". Moreover, as any hydrogen bound to a carbon atom in a molecule with many carboxylic groups would be a more or less active hydrogen, we can conclude that there are no C−H groups in P1. This conclusion is further strengthened by the fact that in the NMR spectrum of the methyl ester of P1 (dissolved in $CDCl_3$ after a methylation with diazomethane[14]) no other H NMR shifts were found except of those due to the methyl hydrogens.

In the following our strategy was to perform chemical reactions on P1. If a product of such a reaction could be identified

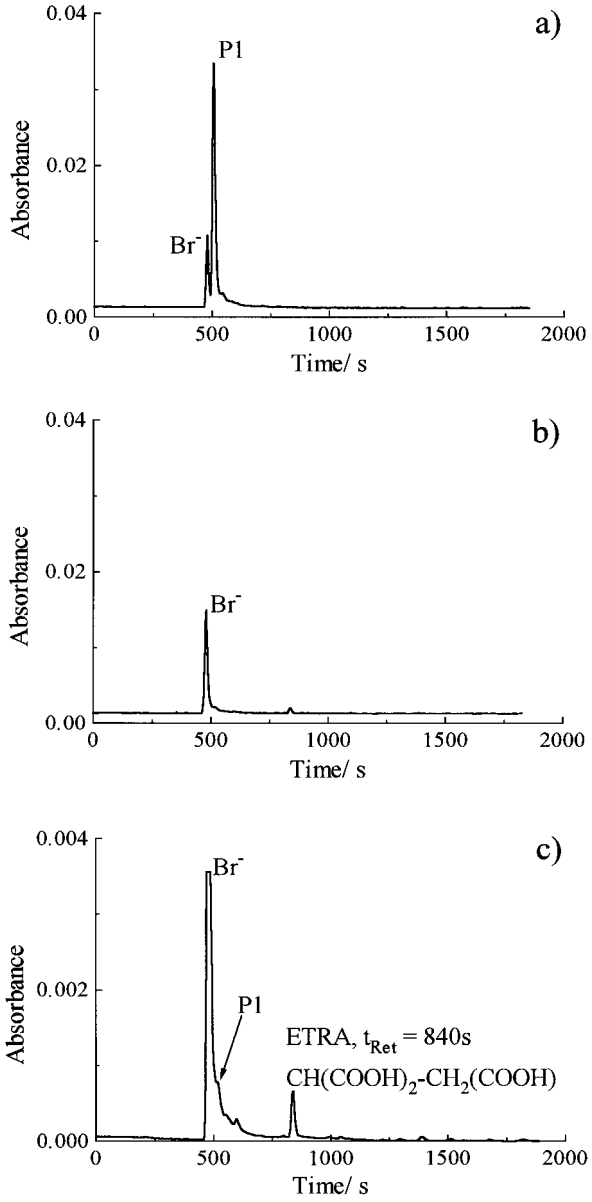

Figure 2. HPLC chromatograms of P1 before and after a reduction with Zn. (a) Purified solution of P1 (the purification is described the Materials paragraph) before the reaction. (No other peaks can be seen with higher sensitivities either.) (b) Reaction products of P1 with Zn + H_2SO_4 recorded with the same sensitivity as in part a. Observe the increase in the Br^- peak. (c) The same products but with higher sensitivity to show the peak due to ETRA. Details of the reaction are given in the Materials section.

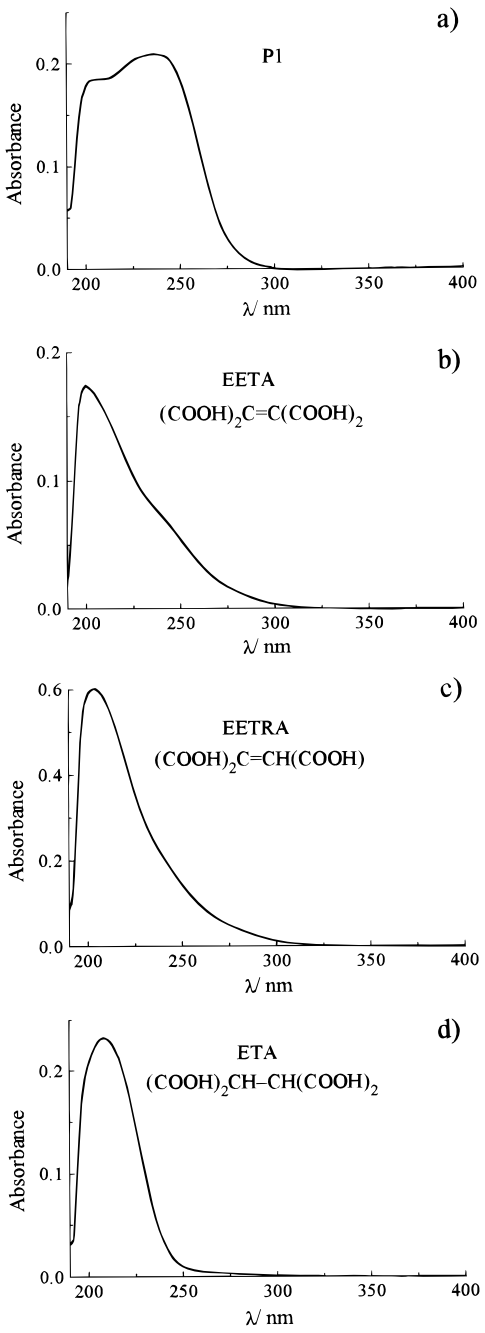

Figure 3. UV spectra of (a) P1, ($c = (3 \pm 1) \times 10^{-5}$ M[16]), (b) EETA ($c = 10^{-5}$ M), (c) EETRA ($c = (4 \pm 1) \times 10^{-4}$ M[17]), (d) ETA ($c = 1.1 \times 10^{-3}$ M). Observe the increasing absorbance around $\lambda = 250$ nm from d to a. All spectra were taken in 1 M sulfuric acid with the same solvent in the reference path. Path length: 1 cm.

by HPLC, this might help to identify P1 itself. To this end, a solution of P1 relatively free of organic contaminants (see Figure 2a) was prepared as described in the Experimental Section.

In the beginning we tried hydrolysis and decarboxylation reactions following our earlier experience but without success. Next, as P1 was inert toward oxidation, we tried its reduction with nascent H_2 (Zn + H_2SO_4). This worked: P1 disappeared nearly completely after the reduction and a product peak appeared, which was identified as ethanetricarboxylic acid (ETRA) on the basis of its retention time (Figure 2b,c). In addition, the peak due to bromide ions also became higher after the reaction. The same result could also be obtained if the reduction was carried out with hydrogen gas in the presence of Pt catalyst. All these suggest that P1 is a bromine-containing carboxylic acid with the same carbon skeleton as ethanetricarboxylic acid.

Thus the carbon skeleton of P1, its carboxylic groups, and the fact that it contains bromine all were established. At this stage—as P1 should not have any C−H bonds—only two possibilities remained. P1 is either 1,1,2-tribromoethanetricarboxylic acid or bromoethenetricarboxylic acid. The first case seemed less probable, as the formation of such a compound with three bromine atoms would be difficult to explain by any mechanism. In the second case P1 would include a carbon−carbon double bound, which should have a characteristic absorbance in the UV region. To check this possibility, we compared the UV spectrum of P1 with that of some analogous compounds with a C═C bond: ethenetetracarboxylic acid (EETA), ethenetricarboxylic acid (EETRA), and one without a C═C bond: ethanetetracarboxylic acid (ETA) (see Figure 3).

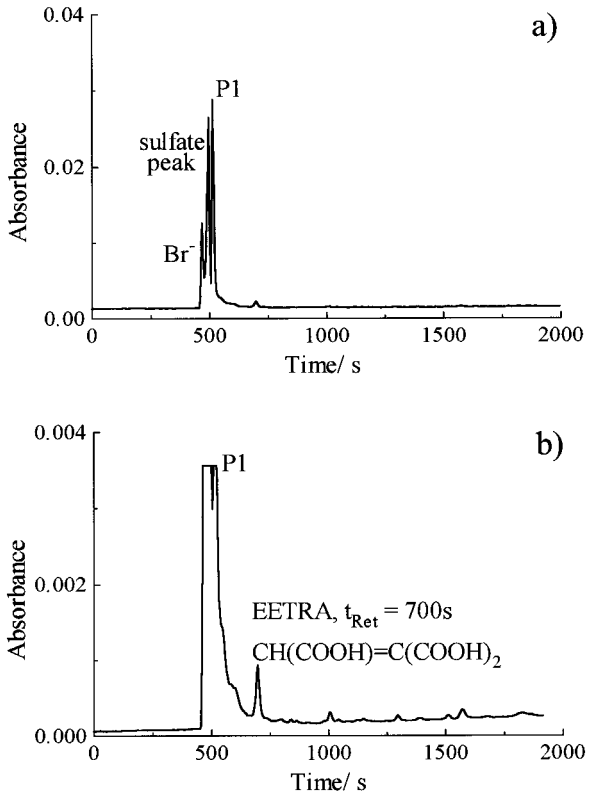

Figure 4. Reaction products of P1 with Fe^{2+} (see the Materials section for details of the reaction.) (a) HPLC chromatogram with the same sensitivity as in Figure 2a (where P1 is shown before the reaction). Observe the increase of the Br^- and the decrease of the P1 peak after the reaction. The new peak is due to the high sulfate content of the sample (see Materials). (b) The same chromatogram with higher sensitivity to show the EETRA peak.

The electronic structure of polycarboxylic acids of ethene should be similar to that of hexatriene if the electronegativity differences between O and C atoms are neglected. In hexatriene the HOMO−LUMO $\pi\pi^*$ transition occurs at 250 nm.[15] The UV spectra of EETA and EETRA show the appearance of a shoulder band around 250 nm, and a strong absorption band is observed for P1 at this wavelength. In contrast, no significant 250 nm absorption is found for the saturated compound ETA.

Thus all indirect evidence suggested that P1 is bromoethenetricarboxylic acid (BrEETRA).We decided to obtain a final proof with a reaction, which would remove bromine from P1 without saturating its double bond. If our hypothesis is correct, then the product should be EETRA, the retention time of which was known to us. (Two different syntheses of EETRA are given in the Experimental Section.) We found that Fe^{2+} in an alkaline medium can remove bromine from BrMA, producing MA and bromide ions. We tried the same reagent with P1, and a fraction of P1 was indeed transformed to EETRA (see Figure 4).

Mechanistic Proposals. As we have seen, an important conclusion is that the organic end product of the Ce^{4+}−BrMA reaction is BrEETRA. Answering this question of the organic end product, however, raises two further logical questions:

(i) Which sequence of reactions can lead to BrEETRA?

(ii) Is this pathway a unique one or are different routes leading to a complete oxidation of BrMA to CO_2 also possible? (For example, in the case of the Ce^{4+}−methyl malonic acid reaction different oxidation pathways were found recently by Kvenberg et al.[18] In that case, however, both pathways led to the same end product, namely, acetic acid.) The following mechanistic proposals will try to address the above two questions.

Pathway Leading to the End Product BrEETRA. The emergence of BrEETRA can be explained with two slightly different mechanisms. Both start with the production of alkyl bromomalonyl radicals in analogy with the Ce^{4+}−MA reaction:

$$Ce^{4+} + HCBr(COOH)_2 \rightarrow {}^{\bullet}CBr(COOH)_2 + Ce^{3+} + H^+ \quad (R5)$$

According to the first version, in the next step two radicals recombine to form dibromo-1,1,2,2-ethanetetracarboxylic acid (Br_2ETA in analogy with ETA):

$$2\,{}^{\bullet}CBr(COOH)_2 \rightarrow (COOH)_2BrC{-}CBr(COOH)_2 \quad (R6)$$

Until this point the steps of this mechanism are the same as was suggested by Zhabotinsky and co-workers[5] and analogous to the formation of ETA in the Ce^{4+}−MA reaction.[1] It is rather probable, however, that Br_2ETA unlike ETA is not a stable compound but decarboxylates. Thus in the next step 1,2-dibromoethanetricarboxylic acid (Br_2ETRA) appears:

$$(COOH)_2BrC{-}CBr(COOH)_2 \rightarrow CO_2 + (COOH)_2BrC{-}CHBrCOOH \quad (R7)$$

Moreover, the intermediate BrETRA is not stable either and loses HBr to give rise to the unsaturated end product:

$$(COOH)_2BrC{-}CHBrCOOH \rightarrow (COOH)_2C{=}CBrCOOH + H^+ + Br^- \quad (R8)$$

Another possible sequence of reactions giving the same end product is when, before the recombination, one of the bromomalonyl radicals decarboxylates first. The resulting alkylbromoacetyl radical would then recombine with a bromomalonyl radical to form the intermedate Br_2ETRA. Br_2ETRA next loses HBr as in the other mechanism.

Both mechanisms have some problems. The critical point of the first mechanism is that a rather fast decarboxylation of Br_2ETA should be assumed, which is much faster than that of the other polycarboxylic acids we studied previously. For example, the fastest decarboxylation we have observed among the BZ intermediate organic acids is shown by Br_2MA, with a half-life of about 1 h at room temperature in a 1 M H_2SO_4. On the other hand the several strongly electronegative substituents in Br_2ETA may explain its unusually fast decarboxylation. The problem with the second mechanism is that no self-recombination products of the assumed alkylbromoacetyl radical (like dibromosuccinic acid) have been found by HPLC. This problem can be solved, however, if we assume that that the bromoacetyl radicals are more reactive and can react not only with bromomalonyl radicals but with Ce^{4+} as well. In this case their concentration can be very low and self-recombination is less probable. As can be seen presently, we have no basis to prefer one or the other mechanism. The stoichiometry of the whole process is the same in both cases:

$$2Ce^{4+} + 2BrMA \rightarrow 2Ce^{3+} + 3H^+ + CO_2 + BrEETRA + Br^- \quad (R9)$$

This stoichiometry is in good agreement with earlier findings of Jwo and Noyes[19] and Försterling et al.[12] The latter found that in N_2 atmosphere roughly 2 Ce^{4+} produced 1 Br^- ion when

BrMA was in great excess. This is also the overall stoichiometry of process C in the FKN mechanism (when $f = 1$) and step (O5) in the Oregonator.[8]

Pathway Leading to the End Product CO_2. In the previous paragraph we pointed out that the stoichiometry of the process leading to BrEETRA is in agreement with earlier theories. On the other hand Försterling et al. found that the agreement is good only when the molar concentration of Ce^{4+} was a mere 1−2% of the BrMA concentration.[12] At higher Ce^{4+} concentrations, however, the stoichiometry was different, and more cerium ions were needed to generate one bromide ion. For example, if [Ce^{4+}] was increased to 10% of the [BrMA], then 2.7 Ce^{4+} was necessary to yield 1 Br^-. Returning to our experiments, when we realized that P1 is inert toward further oxidation by Ce^{4+}, we applied a rather large excess of this reagent to obtain higher levels of the end product. We observed that 1 BrMA can consume about 4 Ce^{4+} and that in this case only about 40% of the initial BrMA ends up as BrEETRA; the remaining 60% is oxidized to CO_2 completely. (The estimation is based on the reaction of P1 with Zn. Assuming a quantitative transformation of P1 to ETRA, the concentration of BrEETRA should be equal to that of ETRA formed in the reaction. ETRA concentrations can be calculated using an HPLC peak height−ETRA concentration calibration diagram, which is linear in this range.) In other words, there is another pathway for the Ce^{4+} oxidation of BrMA besides the one leading to BrEETRA. It is difficult to identify that pathway, however, because no intermediate was found by HPLC. One possibility would be the formation of carboxylato type bromomalonyl radicals and a recombination product analogous to MAMA, namely, bromomalonyl bromomalonate (BrMABrMA):

$$(COOH)_2BrC-O-CO-CHBrCOOH$$

This compound would hydrolyze to give bromotartronic acid (BrTA) and BrMA, in analogy to the hydrolysis of MAMA.[2] Sirimungkala found,[20] however, that bromotartronic acid hydrolyzes quickly to give mesoxalic acid (MOA):

$$BrTA + H_2O \rightarrow MOA + Br^- + H^+ \qquad (R10)$$

It is also known[19] that Ce^{4+} rapidly oxidizes mesoxalic acid to CO_2. This would complete the pathway leading to CO_2. While this seemed a reasonable solution for the unknown pathway, unfortunately no traces of mesoxalic acid was found as an intermediate by HPLC. Regarding the relative rates of the Ce^{4+}−BrMA and Ce^{4+}−MOA reactions and the sensitivity of our HPLC apparatus, some MOA should have been found if this pathway is significant. Thus a reaction route via MOA cannot be an important one. (It is interesting to remark that this is not the case with the ferriin oxidation of BrMA: in that reaction some MOA appears besides BrEETRA.[21]) The other possibility would be a direct reaction of Ce^{4+}, for example, with alkyl bromoacetyl radicals. The production of glyoxylic acid (GOA) in this pathway should be avoided, however, because neither GOA nor formic acid (an oxidation product of GOA[22]) was found by HPLC. Thus we can conclude that the reaction route leading to the complete oxidation of BrMA goes via rather reactive intermediates and HPLC studies could only exclude certain candidates but, until now, provided no evidence for these intermediates. The role of this route in the whole BZ system is not clear either. Further HPLC studies are planned to collect more data on this problem.

Conclusion

In the most studied chemical oscillator, the BZ reaction with malonic acid substrate, the Ce^{4+}−bromomalonic acid reaction plays a central role[5−10] in the explanation of the oscillations. Nevertheless, neither the exact stoichiometry of this reaction nor any mechanistic details were known until now. The present study identified two routes for this oxidation process characterized by the following stoichiometries:

$$2Ce^{4+} + 2BrMA \rightarrow 2Ce^{3+} + 3H^+ + CO_2 + BrEETRA + Br^- \qquad (R9)$$

$$6Ce^{4+} + BrMA + 2H_2O \rightarrow 6Ce^{3+} + 7H^+ + 3CO_2 + Br^- \qquad (R11)$$

where bromoethenetricarboxylic acid (BrEETRA) is a new product reported for the first time here. For route R9 two slightly different mechanisms were proposed, while mechanistic details of route R11 are still unclear.

Reaction R9 dominates when Ce^{4+} is at a low concentration; this is the case under the conditions of the oscillating BZ reaction. Reaction R11 dominates when Ce^{4+} is in large excess. Our results strongly support a mechanism suggested earlier for the ruthenium-catalyzed BZ reaction[23] based on two feedback loops involving bromomalonyl radicals and bromide. The observation that BrEETRA is an inert reaction product which cannot be further oxidized or brominated under BZ conditions will be very helpful in the development of new theories explaining the induction period in the cerium-catalyzed BZ reaction.

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(16) The concentration of P1 was estimated from the ETRA concentration measured after the reduction of P1 by Zn. The UV spectrum was taken using a sample purified by HPLC. This was necessary to remove Ce^{3+}, which absorbs in the UV.

(17) As the potassium salt of EETRA was rather hygroscopic, its concentration is only an estimation.

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