

Chloride Induced Oscillations in the Classical Belousov-Zhabotinsky Reaction Explained by the “Radicalator”-Model

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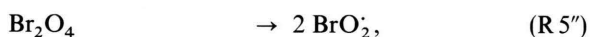
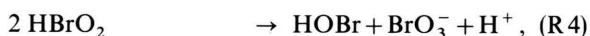
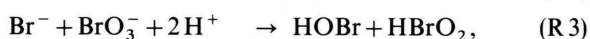
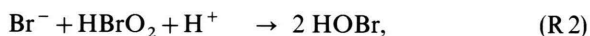
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We detected non-bromide controlled oscillations, which appear in a classical Belousov-Zhabotinsky (BZ) system at a high malonic acid/bromate ratio in the presence of added chloride. The oscillations start immediately after the addition of the catalyst. To explain the oscillations we assume control by a synergetic process involving both chloride ions and malonyl radicals. The experiments are well in accordance with calculations based on the “Radicalator” model. This model is also capable of explaining the rate of formation of CO_2 in the BZ system.

Key words: Belousov-Zhabotinsky reaction, Bromous acid, Chloride, Autocatalysis

Introduction

Chloride is assumed to be an inhibitor [1] of the autocatalytic oxidation of Ce^{3+} by bromate in sulfuric acid solution, the inorganic subset of the Belousov-Zhabotinsky (BZ) reaction [2, 3]. In the theory of Field, Körös and Noyes (FKN) [4] this reaction proceeds in the following steps [2] including the reactions necessary for bromide control:



From perturbation experiments with added chloride to BZ systems Váradí and Beck as well as Jacobs and Epstein [1] conclude that chloride ions react with the intermediate HBrO_2 in a similar way as bromide does:



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This way HBrO_2 can be continuously removed by added chloride and the autocatalysis cannot start. After some time, part of the chloride has been consumed during the reaction; as soon as the chloride concentration is below a critical value, the autocatalysis is no more inhibited.

In the investigations carried out so far with chloride added into the complete BZ system (with malonic acid as organic substrate) only an increase of the induction period can be observed [1].

We carried out experiments on BZ-systems with a high malonic acid/bromate ratio and with 1 M sulfuric acid as a solvent; surprisingly, we found oscillations immediately after the addition of the catalyst, if chloride was present in a certain concentration range.

Experiments

We investigated a BZ system with a high malonic acid to bromate ratio ($[\text{MA}]_0 = 0.6 \text{ M}$, $[\text{BrO}_3^-]_0 = 0.1 \text{ M}$, solvent 1 M sulfuric acid) started with Ce^{3+} (initial concentration = 0.001 M) in the absence and in the presence of added chloride. In the absence of chloride a steady state concentration of Ce^{4+} is established and oscillations start after an induction period of 350 s (Figure 1).

We have followed the reaction by measuring the absorbances A of Ce^{4+} (at 401 and 433 nm) and of BrO_2^{\cdot} (at 549 nm) and the potential change ΔU of an

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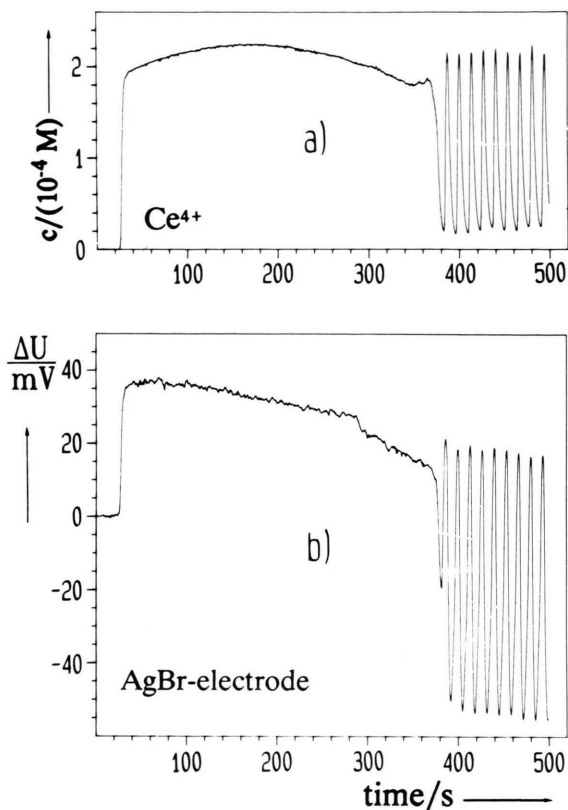


Fig. 1. Concentration of Ce^{4+} and potential change ΔU of an AgBr electrode in a BZ system with $[\text{MA}]_0 = 0.6 \text{ M}$, $[\text{BrO}_3^-]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, 1 M sulfuric acid solution at 25°C . The solution was bubbled with nitrogen. The optical path length was 10.7 cm; the concentration of Ce^{4+} was calculated from the measured absorbance at 433 nm with $\varepsilon = 200 \text{ M}^{-1} \text{ cm}^{-1}$. The potential U_1 before the addition of bromate was 139 mV, the potential U_2 after the addition of bromate was 153 mV. These values are different from the values given for the same system in [5], which was measured with a pressed AgBr electrode instead of a molten one used in the present investigation. It turns out that the molten electrode is less sensitive to the corrosion effects occurring in bromate solution. On the other hand, ΔU from the start of the reaction up to the maximum value is the same in both cases.

AgBr selective electrode. The experimental setup and the evaluation of the data were the same as previously described in the context of malonyl radical controlled oscillations in the BZ system carried out in 3 M sulfuric acid medium by Försterling et al. [5]. The only difference in the measurements was that an electrode with molten AgBr [6] was used instead of pressed AgBr pellets. It must be stressed that the experiments are strongly affected by trace impurities of chloride present in some commercially available malonic acid

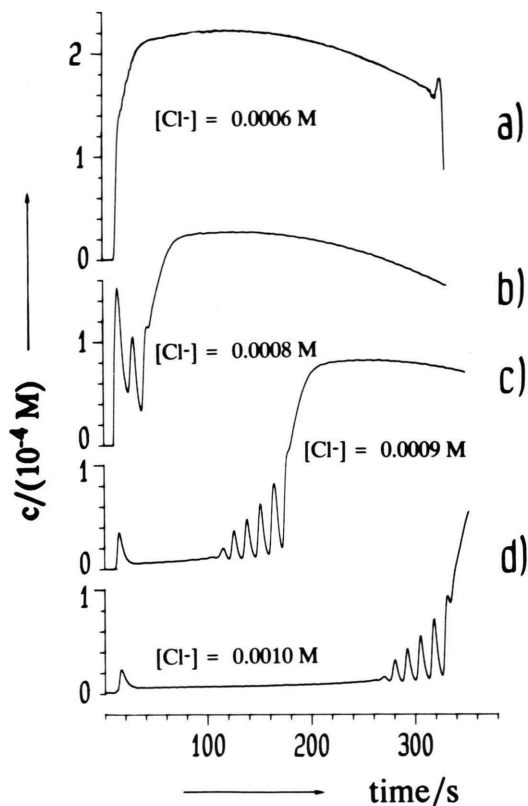


Fig. 2. Concentration c of Ce^{4+} in the same BZ system as in Fig. 1, but with added NaCl of initial concentrations 0.0006 M (a), 0.0008 M (b), 0.0009 M (c) and 0.0010 M (d). The solution was bubbled with nitrogen. The optical path length was 2 cm. The concentration of Ce^{4+} was calculated from the measured absorbance at 401 nm with $\varepsilon = 800 \text{ M}^{-1} \text{ cm}^{-1}$.

samples. For this reason it is necessary to purify the malonic acid carefully following a procedure proposed by Noszticzius et al. [7].

The reaction mixture was bubbled with nitrogen to exclude oxygen from the air dissolved in the solution. From the measured absorbances the concentrations of Ce^{4+} and of BrO_2^- were calculated [5]. In the actual procedure the following stock solutions were used: 5 M malonic acid, 0.1 M NaCl and 1 M NaBrO_3 , all dissolved in water; 5 M sulfuric acid; 0.05 M $\text{Ce}_2(\text{SO}_4)_3$, dissolved in 1 M sulfuric acid. A mixture of malonic acid, NaCl, sulfuric acid and water was bubbled with nitrogen for 10 min; separately, the NaBrO_3 solution and the cerium solution were also bubbled with nitrogen. After that, the NaBrO_3 solution was added to the malonic acid – NaCl – sulfuric acid solution leading to

a final concentration $[\text{H}_2\text{SO}_4] = 1 \text{ M}$. Nitrogen was bubbled again for 5 min and the reaction was started with the injection of cerium sulphate. It is important to note that bromate can react slowly with chloride on a longer time scale than used in the present experiments; for this reason the bromate was added shortly before the start of the reaction. The temperature was 25°C in all experiments.

The results of measurements of $[\text{Ce}^{4+}]$ at different chloride initial concentrations are displayed in Figure 2. Oscillations appear if the chloride initial concentration is above $0.6 \times 10^{-3} \text{ M}$; with increasing chloride concentration an induction period appears which increases significantly with increasing chloride initial concentration.

Although similar oscillations are known in the case of added iodide [8], no chloride induced oscillations have been described so far in literature. The system used in our present investigation is strongly related to a BZ system first studied by Rácz [9] in which the oscillations are controlled by malonyl radicals [5] instead of bromide as usually assumed in the FKN theory [4]. From this point of view it seems to be interesting to clarify the nature of the control intermediate in the chloride perturbed system.

Discussion

In an additional experiment, $[\text{Ce}^{4+}]$ and the change ΔU of the electrode potential were measured simultaneously in the case of system c) in Fig. 2 (chloride initial concentration 0.0009 M). The results are displayed in Figure 3. There are small oscillations of the electrode potential ΔU which are superimposed by a monotone increase of ΔU . Moreover, the potential is all time above the starting potential $U_2 = 153 \text{ mV}$ (measured after the addition of bromate into the acidic malonic acid a solution; before that addition the potential was $U_1 = 139 \text{ mV}$). Following the arguments given by Försterling et al. [5], bromide control of the oscillations can be completely excluded in this case. On the other hand, there is only a limited amount of chloride present in the system, and it is most improbable that chloride is formed periodically starting from (R 2 a).

If chloride were exclusively responsible for the oscillations, the same behavior as displayed in Fig. 2–3 would also be expected in the absence of malonic acid. For this reason the autocatalytic oxidation of Ce^{3+} by

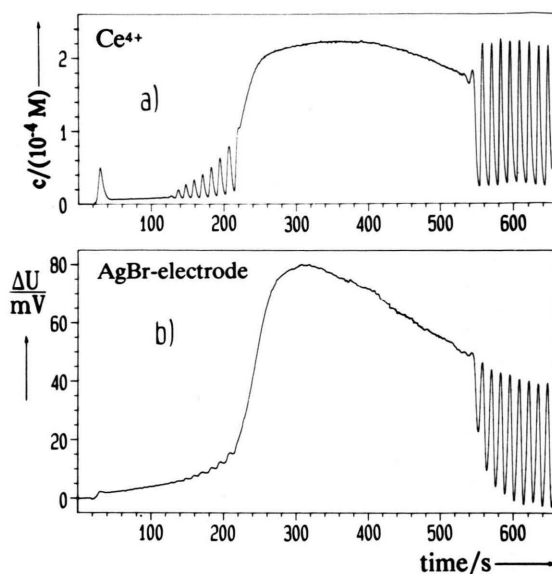


Fig. 3. Concentration c of Ce^{4+} and change ΔU of the electrode potential immediately after the addition of Ce^{3+} into the BZ system described in Figure 2c (initial concentration of added chloride $= 0.0009 \text{ M}$). The optical path length was 10.7 cm ; the concentration was calculated from the measured absorbance at 433 nm with $\epsilon(\text{Ce}^{4+}, 433) = 200 \text{ M}^{-1} \text{ cm}^{-1}$. It seems to be strange that the maximum potential change is $\Delta U = 80 \text{ mV}$ compared to $\Delta U = 40 \text{ mV}$ in the absence of added chloride (Figure 1). Obviously, HOCl formed during (R 2 a) reacts with excess Cl^- , and Cl_2 is formed this way. Since Cl_2 is able to oxidize Br^- , bromide ions are removed from the surface of the AgBr electrode. This process results in an additional corrosion potential leading to a positive shift of the electrode potential.

bromate ($[\text{BrO}_3^-]_0 = 0.1 \text{ M}$ and $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$) was investigated in the presence of added chloride. The results are displayed in Figure 4.

Surprisingly, the addition of chloride at a concentration of $0.9 \times 10^{-3} \text{ M}$ (as applied in the complete system in Fig. 3) does not inhibit the autocatalytic reaction at all. An inhibition appears, however, if $[\text{Cl}^-]_0$ exceeds $1.3 \times 10^{-3} \text{ M}$. That means that in the complete system showing chloride induced oscillations the concentration of added chloride is below the critical value needed for an inhibition of the autocatalysis. Most probably, the oscillations appear if a second inhibitor is produced during the initial part of the reaction. According to our results obtained previously [5] we assume that malonyl radicals play the role of that second control intermediate.

In order to support this assumption we repeated the experiment displayed in Figs. 2c and 3 bubbling oxygen instead of nitrogen through the reaction mixture.

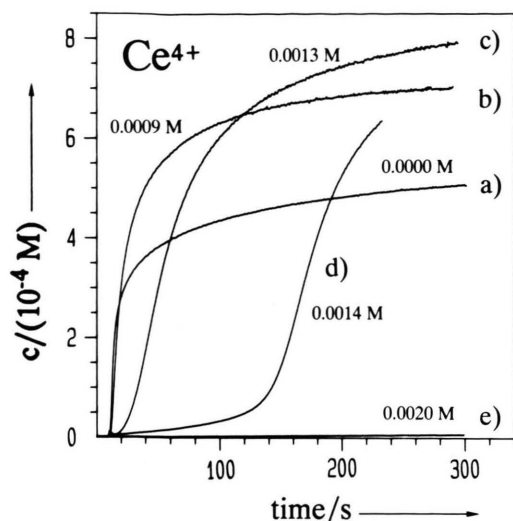


Fig. 4. Formation of Ce^{4+} during the autocatalytic oxidation of Ce^{3+} by bromate in the absence and the presence of added chloride. Initial concentrations: $[\text{BrO}_3^-]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, 1 M sulfuric acid solution. The initial concentrations of added NaCl as indicated in the Figure are: zero (a), 0.0009 M (b), 0.0013 M (c), 0.0014 M (d) and 0.0020 M (e). The optical path length was 2 cm , the concentration of Ce^{4+} was calculated from the absorbance at 401 nm .

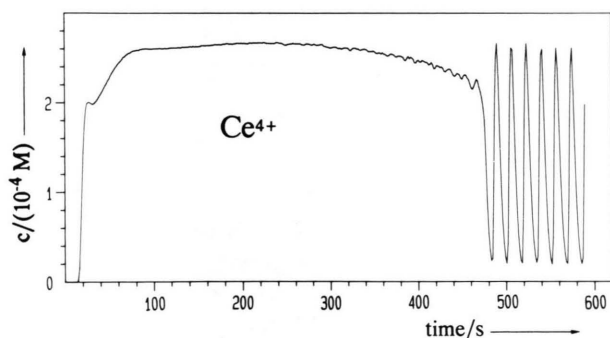
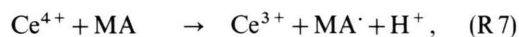


Fig. 5. Result of the same experiment as in Figs. 2c and 3, but the solution was bubbled with oxygen instead of nitrogen. The optical path length was 2 cm , the concentration of Ce^{4+} was calculated from the absorbance at 401 nm .

As can be seen from Fig. 5, no oscillations appear at the start of the reaction, but the normal oscillations starting at the end of the induction period are not affected by the oxygen. This result is well in accordance with the assumption that malonyl radicals rapidly remove BrO_2 radicals. In the presence of oxygen, peroxy radicals are formed and malonyl radical controlled oscillations cannot be expected. It should

be pointed out that the maximum Ce^{4+} concentration is larger in this case compared to Figs. 1 and 3 ($2.6 \times 10^{-4} \text{ M}$ instead of $2.2 \times 10^{-4} \text{ M}$); also the induction period is longer (460 s instead of about 350 s).

It is interesting to note that malonyl radical controlled oscillations have been found so far experimentally in 3 M sulfuric acid medium only, although those oscillations are also predicted by theory ("Radicalator" [5]) for 1 M sulfuric acid solution. The Radicalator model is based on the formation of malonyl radicals during the reaction (R7) of Ce^{4+} with malonic acid (MA) [10, 11]; these radicals disappear by (R8), their self-recombination [12], or by (R9), their reaction with BrO_2 [5, 13].



Bromomalonic acid (BrMA) is formed by



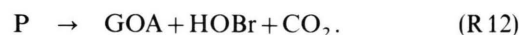
the reaction of HOBr with malonic acid [14].

Moreover, the reaction



is included in the model which is the source of HBrO_2 needed for the start of the autocatalytic reaction [5]. Rate constants for reactions (R 1) to (R 11) are summarized in Table 1.

In the calculations carried out so far with the Radicalator model [5] it was assumed that the primary reaction product P is inert within the autocatalytic reaction. Of course, P will not be a stable product and consecutive reactions have to be taken into account. Experimental evidence for such reactions is the high rate of formation of CO_2 starting immediately after the onset of the autocatalytic reaction in the BZ system [10]. That rate is higher by two orders of magnitude than the rate attributed to a decarboxylation process of malonyl radicals [11] in the absence of BrO_2 . As suggested by Field [16] P may be a complex, which decomposes into glyoxalic acid (GOA), HOBr and CO_2 :



There is one problem with this reaction, since Ruoff et al. [17] claim that GOA cannot be an intermediate in the BZ reaction. They propose a reaction path including mesoxalic acid (MOA) instead of GOA, which

Table 1. Rate constants k_i to k_{11} used in the calculations. The values refer to a temperature of 20 °C. Small corrections have been applied for k_5 , and k_6 compared to the values reported in [2]. The experiments leading to these rate constants were performed in 1 M sulfuric acid solution, and $[H^+] = 1$ M was assumed during the evaluation of the experimental data. Since $[H^+] = 1.29$ M is correct for 1 M sulfuric acid these rate constants are lower by a factor of 1.29 (33 and 6.2×10^4 instead of 42 and 8×10^4). k_{-6} was reduced from $8.9 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ [2] to $8.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$ regarding the results of recent direct experiments (H. D. Försterling, to be published).

Forward	Ref.	Reverse	Ref.
$k_1 = 8 \times 10^9 \text{ M}^{-2} \text{ s}^{-1}$	[2], [5], [15]	$k_{-1} = 80 \text{ s}^{-1}$	[5], [15]
$k_2 = 2.5 \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$	[5], [15]	$k_{-2} = 2 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$	[2], [15]
$k_{2a} = 1.5 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$	a)	$k_{-2} = 0$	
$k_3 = 1.6 \text{ M}^{-3} \text{ s}^{-1}$	[5], [15]	$k_{-3} = 3.2 \text{ M}^{-1} \text{ s}^{-1}$	[2]
$k_4 = 3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	[2], [5], [15]	$k_{-4} = 1 \times 10^{-8} \text{ M}^{-2} \text{ s}^{-1}$	[2]
$k_{5'} = 33 \text{ M}^{-2} \text{ s}^{-1}$	[2], a)	$k_{-5'} = 2.2 \times 10^3 \text{ s}^{-1}$	[2]
$k_{5''} = 7.4 \times 10^4 \text{ s}^{-1}$	[2]	$k_{-5''} = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[2]
$k_6 = 6.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$	[2], a)	$k_{-6} = 8.4 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$	[2], a)
$k_7 = 0.23 \text{ M}^{-1} \text{ s}^{-1}$	[11], [13]	$k_{-7} = 2.2 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$	[11], [13]
$k_8 = 3.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[12]	$k_{-8} = 0$	
$k_9 = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$	[5], [13]	$k_{-9} = 0$	
$k_{10} = 8.2 \text{ M}^{-1} \text{ s}^{-1}$	[14]	$k_{-10} = 0$	
$k_{11} = 7 \times 10^{-7} \text{ M}^{-3} \text{ s}^{-1}$	[5]	$k_{-11} = 0$	
$k_{12} = 1 \text{ s}^{-1}$	a)	$k_{-12} = 0$	
$k_{13} = 1 \text{ s}^{-1}$	a)	$k_{-13} = 0$	

a) This work

species can also be formed from P in a reaction similar to (R 12) and also with HOBr as an inert product. In this case CO_2 is formed in an additional step by decarboxylation of MOA. In order to avoid a set of model reactions with too many unknown rate constants, however, we want to maintain (R 12) in the moment.

In order to estimate an upper limit for the rate of formation of CO_2 we treat (R 12) as a fast reaction and the formation of malonyl radicals (R 7) as rate determining step; we obtain

$$d[\text{CO}_2]/dt = k_7 [\text{MA}]_0 [\text{Ce}^{4+}]. \quad (1)$$

Experimental [10] and calculated values of $d[\text{CO}_2]/dt$ for different initial conditions are summarized in Table 2 (calculation a). The experimental values are valid at the end of the induction period. It turns out that the values calculated from (1) are lower by a factor of 4 compared to the experiments. It must be stressed, however, that in the experiments $d[\text{CO}_2]/dt$ is strongly increasing from the start of the reaction until the end of the induction period; the experimental $d[\text{CO}_2]/dt$ during the initial phase of the reaction does not at all exceed the values calculated from (1). That means that reaction (R 12) is completely sufficient to account for the high rate of formation of CO_2 in the BZ system. Similar results are obtained in computer simulations based on (R 7), (R 8), (R 9) and (R 12), if k_{12} is in the order of 1 s^{-1} . In the following calculations this value will be used.

Table 2. Rate $d[\text{CO}_2]/dt$ calculated and measured for different initial concentrations of malonic acid, bromate and cerium. The experimental values $d[\text{CO}_2]/dt$ are valid at the end of the induction period. Calculations: a) Upper limit estimation using eq. (1) and the mean value $[\text{Ce}^{4+}]_m$ listed in column 4; b) Result of the Radicalator model with the reactions (R 1) to (R 13), rate constants see Table 1. The initial concentrations of BrO_3^- , MA and Ce^{4+} are the same as listed in columns 1 to 3; $[\text{HBrO}_2]_0 = 7 \times 10^{-7} \text{ M}$, $[\text{BrO}_2]_0 = 2 \times 10^{-7} \text{ M}$, $[\text{H}^+]_0 = 1.29 \text{ M}$.

$\frac{[\text{BrO}_3^-]}{\text{M}}$	$\frac{[\text{MA}]_0}{\text{M}}$	$\frac{[\text{Ce}^{4+}]}{10^{-4} \text{ M}}$	$\frac{[\text{Ce}^{4+}]_m}{10^{-5} \text{ M}}$	$\frac{d[\text{CO}_2]/dt}{10^{-6} \text{ M s}^{-1}}$		
				Experiment [10]	Calculation	
					a)	b)
0.1	0.1	1	2.8	2.5	0.6	0.5
0.1	0.1	2	6.2	5.3	1.4	0.9
0.1	0.1	5	14.0	11.0	3.2	2.2
0.1	0.1	10	25.0	19.0	5.7	4.0
0.03	0.1	3.45	6.2	2.9	1.4	0.5
0.3	0.1	1.32	6.2	5.0	1.4	0.8

On the other hand it is most probable that part of P reacts via (R 13), which is a one electron transfer reaction with HBrO_2 as a reaction product:



If HBrO_2 is formed this way, BrO_2 cannot be removed completely by malonyl radicals since BrO_2 is formed again via (R 5'), (R 5''). The fraction of HBrO_2 formed in (R 13) depends on the ratio k_{13}/k_{12} . Unfor-

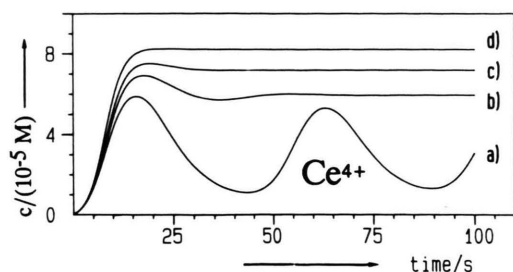


Fig. 6. Evaluation of the rate constant k_{13} . Results of model calculations on the concentration of Ce^{4+} in a complete system (initial concentrations $[\text{MA}]_0 = 0.6 \text{ M}$, $[\text{BrO}_3^-]_0 = 0.015 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{H}^+]_0 = 1.29 \text{ M}$) including reactions (R 12) and (R 13). Rate constants k_1 to k_{11} see Table 1, rate constant $k_{12} = 1 \text{ s}^{-1}$. The calculations were performed with different values for the rate constant k_{13} : zero (a), 0.2 s^{-1} (b), 0.4 s^{-1} (c), 1.0 s^{-1} (d).

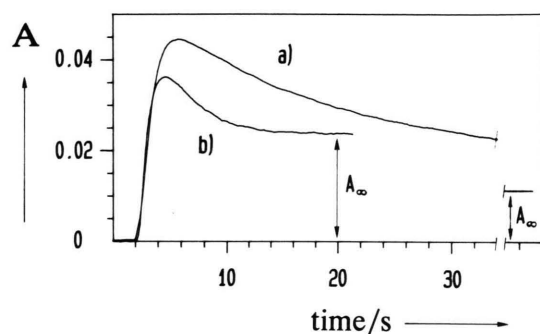


Fig. 7. Estimation of the rate constant k_{2a} . Absorbance A at 240 nm measured after the injection of $500 \mu\text{l}$ of a 0.0023 M NaBrO_2 solution into 140 ml 1 M sulfuric acid solution. a) No chloride added (only the decay of HBrO_2 due to its disproportionation can be seen). The final absorbance A_∞ is due to the absorbance of the reaction products HOBr and HBrO_3 . b) $2.1 \times 10^{-4} \text{ M}$ NaCl added. The higher final absorbance A_∞ is due to the additional absorbance of Cl_2 which is formed from the reaction product HOCl and excess chloride. The optical path length was 10.7 cm , dual wavelength technique was used (reference wavelength 320 nm).

unately, no direct experimental information on k_{13} is available. For this reason we treat k_{13} as an adjustable parameter. We performed model calculations for a BZ system with initial concentrations $[\text{MA}]_0 = 0.6 \text{ M}$, $[\text{BrO}_3^-]_0 = 0.015 \text{ M}$ and $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$. At such a high MA/bromate ratio no oscillations occur in an experiment carried out in 1 M sulfuric acid solution, contrary to the same system in 3 M sulfuric acid medium [5]. Different values of k_{13} are applied in the model calculations in order to see the change from the oscillating to the non-oscillating regime. The results are displayed in Figure 6. It turns out that with $k_{13} = 0$,

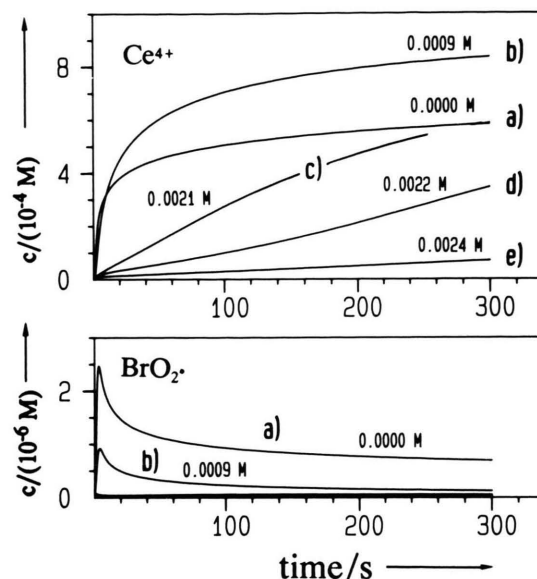


Fig. 8. Model calculations for the autocatalytic formation of Ce^{4+} and of BrO_2 in the absence and the presence of added chloride. Initial concentrations: $[\text{BrO}_3^-]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{H}^+]_0 = 1.29 \text{ M}$. The initial concentrations of added chloride as indicated in the Figure are: zero (a), 0.0009 M (b), 0.0021 M (c), 0.0022 M (d) and 0.0024 M (e). The BrO_2 concentrations in cases c) to e) are too small to be seen in the Figure.

0.2 and 0.4 s^{-1} oscillations appear. The oscillations disappear completely, however, with $k_{13} = 1 \text{ s}^{-1}$.

Reaction (R 2a) is responsible for the inhibitory effect of added chloride. Since no experimental data are available in literature, the kinetics of this reaction was followed spectroscopically. The absorbance A of HBrO_2 (initial concentration $8 \times 10^{-6} \text{ M}$) at 240 nm was measured in the absence and in the presence of added chloride (Figure 7). In the absence of chloride we observe the kinetics of the disproportionation of HBrO_2 (R 4); the final absorbance is due to the reaction products HOBr and HBrO_3 . In the presence of $2.1 \times 10^{-4} \text{ M}$ chloride the maximum value of the absorbance is smaller by 20% (due to (R 2a) during the mixing process), and the final absorbance is larger by a factor of two, due to the high absorbance of Cl_2 which is formed from excess chloride with the reaction product HOCl . It turns out that the decay of A is exponential in that case, and a first order rate constant $k'_{2a} = 0.32 \text{ s}^{-1}$ is obtained which leads to $k_{2a} = 0.32 / (2.1 \times 10^{-4} \text{ M}) = 1.5 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$.

Including this rate constant in the Radicalator model, we calculated the kinetics of Ce^{4+} and of BrO_2

during the autocatalytic reaction in the absence and the presence of added chloride (Figure 8). With no chloride added we obtain $[\text{Ce}^{4+}] = 5.8 \times 10^{-4} \text{ M}$ at $t = 300 \text{ s}$ compared to 5×10^{-4} in the experiment (Figure 4). With 0.0009 M chloride added we obtain $8.2 \times 10^{-4} \text{ M}$ compared to $7 \times 10^{-4} \text{ M}$ in the experiment. On the other hand, the calculated maximum BrO_2 concentration in the presence of chloride is only 30% compared to the chloride free sample. For comparison, the experimental BrO_2 concentration is displayed in Figure 9. Also in this case $[\text{BrO}_2]_{\text{max}}$ is in the same order as predicted by theory. There is only a small difference to theory, since in theory the decay of $[\text{BrO}_2]$ after the maximum is much faster than in the experiment. The reason for the low concentration of BrO_2 in the presence of chloride is clearly (R 2a); by this reaction HBrO_2 is removed from the autocatalytic system. It seems to be surprising that the concentration of Ce^{4+} at $t = 300 \text{ s}$ is higher by 30% in the presence of 0.0009 M Cl^- compared to the absence of chloride. We have to keep in mind, however, that the autocatalytic formation of Ce^{4+} is slowed down by (R-6), the reaction of Ce^{4+} with HBrO_2 . If HBrO_2 is removed from the system by reaction with Cl^- , the rate of (R-6) is decreased and more Ce^{4+} can be formed.

As can be seen from Fig. 8 the autocatalysis is inhibited at chloride concentrations above $2.1 \times 10^{-3} \text{ M}$ in the model, whereas $1.3 \times 10^{-3} \text{ M}$ are sufficient to inhibit in the experiment (Figure 4). This small discrepancy is most probably due to the fact that the rate of the autocatalysis at $[\text{H}^+] = 1.29 \text{ M}$ is overestimated in theory, as was outlined in [5] already.

Now we are able to apply the Radicalator model including the reactions (R 1) to (R 13) on the complete system with the set of rate constants summarized in Table 1. The results for the concentration of Ce^{4+} are displayed in Figure 10. There is an excellent agreement between theory and the experiments displayed in Figs. 2 and 3. At $[\text{Cl}^-]_0 = 0.0009 \text{ M}$ the rise of the Ce^{4+} curve is slowed down just as in the experiment at $[\text{Cl}^-]_0 = 0.0006 \text{ M}$. By only a very small increase of $[\text{Cl}^-]_0$ the system is shifted from the non-oscillatory to the oscillatory regime. The number of oscillations increases up to 7, if $[\text{Cl}^-]_0$ is increased to 0.0013 M , comparable to the 0.0009 M chloride case in the experiment. It must be stressed that the number of the oscillations in the calculations is nearly identical with the number observed in the experiments. Moreover, an extremely small increase of $[\text{Cl}^-]_0$ from 0.0014 M

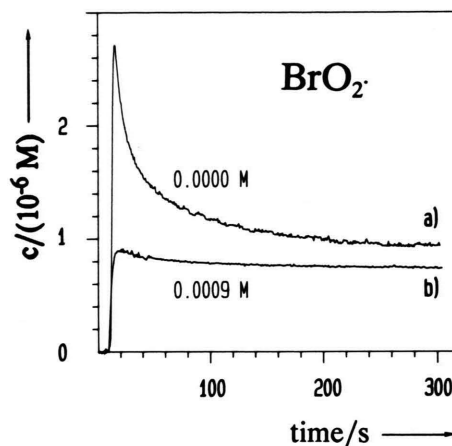


Fig. 9. Formation of BrO_2 during the autocatalytic oxidation of Ce^{3+} by bromate in the absence and the presence of added chloride. Initial concentrations of bromate and Ce^{3+} as in Figure 4. The concentrations of added chloride as indicated in the Figure are: zero (a) and 0.0009 M (b). The optical path length was 10.7 cm , the concentration of BrO_2 was calculated from the absorbance at 549 nm with $\epsilon = 387 \text{ M}^{-1} \text{ cm}^{-1}$.

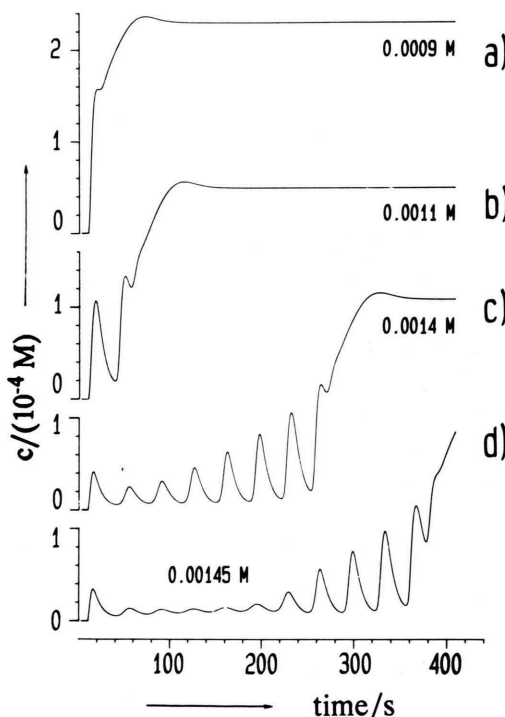


Fig. 10. Concentration c of Ce^{4+} calculated with the Radicalator model (including reactions (R 12) and (R 13)) for a complete system in the presence of added chloride (initial concentrations $[\text{MA}]_0 = 0.6 \text{ M}$, $[\text{BrO}_3^-]_0 = 0.1 \text{ M}$, $[\text{Ce}^{3+}]_0 = 0.001 \text{ M}$, $[\text{H}^+]_0 = 1.29 \text{ M}$). Rate constants k_1 to k_{13} see Table 1. Initial concentrations of added chloride are 0.0009 M (a), 0.0011 M (b), 0.0014 M (c) and 0.00145 M (d).

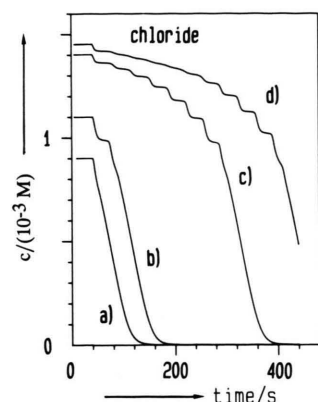


Fig. 11. Results of the same model calculation as in Fig. 10, but the concentration c of chloride is displayed.

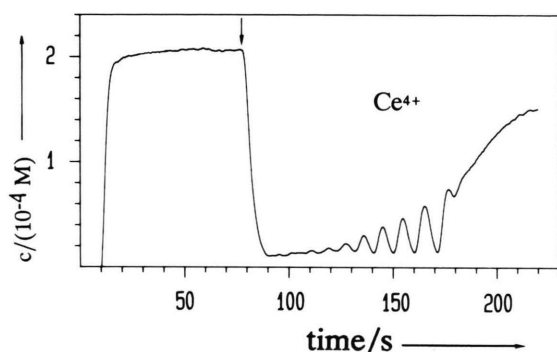


Fig. 12. Perturbation of a chloride free system (initial concentrations $[MA]_0 = 0.6$ M, $[BrO_3^-]_0 = 0.1$ M, $[Ce^{3+}]_0 = 0.001$ M, solvent 1 M sulfuric acid) by adding 0.0009 M chloride just 60 s after the addition of Ce^{3+} . The arrow indicates the injection of chloride. The optical path length was 2 cm, the concentration of Ce^{4+} was calculated from the absorbance at 401 nm.

to 0.00145 M leads to a significant delay of the onset of the oscillations, just as observed in the experiment. Even typical details of the experimental curves like the last small oscillation at the end of the complete series is well modelled by theory.

From the kinetics of $[Cl^-]$ we see that the oscillations disappear as soon as the chloride concentration falls below a critical level (Figure 11). The concentrations of Cl^- needed in the calculations are larger by a factor of 1.5 compared to the experiments displayed in Figure 2. Obviously, the reason for this small discrepancy is the same as already discussed in the case of the autocatalytic reaction. On the other hand, the calculated frequency of the oscillations is lower by a factor of two compared to that in the experiments.

A similar deviation was observed in a BZ system working in 3 M sulfuric acid solution (Rácz system [9]) [5]. Apparently, more experiments are needed to clarify the situation.

Moreover, we calculated the rate of formation of CO_2 using the Radicalator model for the BZ systems listed in Table 2 (calculation b). The results of these calculations are only slightly below the upper limit values estimated in calculation a. We have to admit, however, that our model does not account completely for the experimental rate of formation of CO_2 . In the experiment that rate is strongly increasing after the start of the autocatalytic reaction, whereas a constant rate is predicted by our theory. From this discrepancy we conclude that consecutive reactions, most probably among the organic intermediates, which are not included in the model, contribute to an additional formation of carbon dioxide in the system.

In order to support our thesis that both malonyl radical control and control by the added chloride is necessary for the onset of oscillations, we performed an additional experiment. In this experiment, the reaction is started with Ce^{3+} in a chloride free system. 60 s after the addition of Ce^{3+} (after this time period the steady state has been established) chloride in a concentration of 0.0009 M was added. As can be seen from Fig. 12, oscillations appear just after the addition of the chloride, as expected from our theory.

Conclusions

We conclude that the oscillations which appear in a chloride perturbed BZ system are controlled by a synergetic process involving both malonyl radicals and chloride ions as inhibitory species for the autocatalytic reaction. Our theoretical model, the Radicalator, is capable of explaining the most important features of this system. Especially, the model calculations are in accordance with the surprising experimental fact that the autocatalytic formation of Ce^{4+} is accelerated by added chloride at low initial concentrations. An inhibition of the autocatalysis occurs at chloride concentrations much higher than necessary for the onset of the chloride induced oscillations. Moreover, the Radicalator model predicts a high rate of formation of CO_2 after the onset of the autocatalytic reaction, which could not be explained so far by the FKN theory. We hope that the Radicalator model will also be helpful in solving problems in other BZ systems;

especially, silver ion perturbed systems should be re-examined on the basis of this model [15, 22–29].

As can be seen from Fig. 1, oscillations of bromide ions appear in our system after some induction period. A closer inspection of the oscillations reveals that the maxima of the electrode potential coincide with the maxima of the Ce^{4+} concentration [18]. That means that the autocatalytic reaction is inhibited just at the maxima of the HOBBr concentration. From this observation we conclude that the inhibition of the autocatalysis cannot be started exclusively by bromide ions as originally assumed in the FKN theory. After the completion of the inhibition, bromide ions accumulate in the solution (electrode potential below the starting value, see Figure 1). The autocatalysis does not start again before the bromide concentration is below a critical value. We suspect that the inhibition of the autocatalytic reaction is due to a synergetic process involving organic radicals and bromide ions as well. According to this assumption two different negative feedback loops have to be considered in any realistic model of the BZ reaction. This conclusion is also important for BZ systems investigated in a CSTR. In such systems phenomena like period doubling and chemical chaos can be observed experimentally [19]. It was not possible so far to see those phenomena in model calculations based on bromide control only (at least the region of chaotic behavior is by far much larger in the experiments than that calculated from the models). Györgyi and Field [20, 21] assume that chemical chaos arises from the coupling of oscillations in

different regions in the reactor; those different regions are established in a CSTR because the concentrations near the inlet cannot be identical with the concentrations in the bulk of the reactor even at a high stirring rate. Of course the same experimental observation can possibly be explained by the assumption of two different coupled negative feedback loops. It would be most interesting to investigate the dynamic behavior of an extended Radicalator model in which radical as well as bromide control are included. Further work with such a model is in progress.

There is still one open problem, however, namely that in the model calculations the reaction (R 13) with the rate constant $k_{13} = 1 \text{ s}^{-1}$ (which was deduced for 1 M sulfuric acid solution) will also inhibit oscillations in the Rácz system (which works in 3 M sulfuric acid solution [5]), contrary to experiment. We assume that the rate of (R 13) is strongly dependent on the acidity of the solution. To resolve this problem, additional direct ESR experiments in 3 M sulfuric acid solution are needed.

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