Contribution of Malonyl Radical Control in the Classical Belousov-Zhabotinsky Reaction

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In the original theory of the Belousov-Zhabotinsky reaction it is assumed that the oscillations are exclusively controlled by bromide ions. From uv/vls and ESR experiments on BZ systems started with Ce^{4+} we conclude that malonyl radicals play an important role as additional intermediates. The experiments are in agreement with calculations based on the Radicalator model.

Key words: Belousov-Zhabotinsky reaction, Cerium, Malonic acid, Bromate, Bromide, Feedback, Malonyl radicals.

Introduction

In the Belousov-Zhabotinsky (BZ) system [1] the oxidized form of the catalyst (like Ce^{4+}) is reduced by an organic substrate (like malonic acid (MA)). On the other hand, the reduced form of the catalyst (like Ce^{3+}) is oxidized by acidic bromate. The latter reaction proceeds by an autocatalytic process involving $BrO_2^{\cdot}$ radicals and $HBrO_2$ [2], [3]. The autocatalytic reaction can be switched off by species reacting with $BrO_2^{\cdot}$ directly (like malonyl radicals [4]) or with $HBrO_2$ (like Br^- [5], [6], [7]). In the original theory of the BZ reaction developed by Field, Körös and Noyes (FKN) [8] it is assumed that bromide is the only control variable.

Recently, Försterling and Noszticius [4] demonstrated that malonyl radicals (which are formed during the reaction of Ce^{4+} with malonic acid) react with $BrO_2^{\cdot}$ (which is formed during the autocatalytic reaction step) at a nearly diffusion controlled rate. From this point of view it seems reasonable to include malonyl radicals as possible control intermediates in the BZ reaction. Indeed, oscillations can be observed in some BZ systems with a high malonic acid/bromate ratio and 3 M sulfuric acid as a reaction medium, which are apparently controlled by malonyl radicals [9]. Moreover, by the addition of chloride into BZ systems in 1 M sulfuric acid, oscillations without any induction period can be induced; in this case a synergetic process involving both chloride ions and malonyl radicals is assumed to be responsible for the onset of oscillations [10]. A model based on radical control ("Radicalator") accounts for the observed phenomena [9], [10].

It is well known [11, 12] that one single oscillation occurs in some BZ systems (1 M sulfuric acid medium, starting the reaction by addition of Ce^{4+}) immediately after mixing the compounds. Oxygen can be considered as a scavenger of malonyl radicals, and in fact the single oscillation does not appear in solutions permanently saturated with pure oxygen. In some cases (low cerium concentration) the single oscillation is inhibited in air saturated solution [11 a] already; at high cerium concentration, air saturation is not sufficient for an inhibition [11 b], due to a complete consumption of the dissolved oxygen in the initial phase of the reaction. With increasing malonic acid concentration more malonyl radicals are formed, and there is some chance to detect more pronounced radical control in such systems. Following these considerations we have investigated BZ systems at different malonic acid concentrations with cerium as a catalyst.

Experiments

The reactions described in this paper were followed by photospectrometry at 401 and 450 nm (detection of Ce^{4+}) and at 549 nm (detection of $BrO_2^{\cdot}$ radicals); simultaneously, the potential of an AgBr electrode was measured. In another set of experiments the kinetics of malonyl radicals was measured by recording the

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ESR signal of a sample placed into the cavity of a Varian E 12 ESR spectrometer.

The experimental setup and the evaluation of the data are the same as described earlier [4, 9, 10]. For the potential measurements a homemade molten AgBr electrode [13] was used, which turned out to be not sensitive to Ce^{4+}, contrary to commercially available electrodes. The potential was measured with an AgCl reference electrode connected to the solution by a salt bridge with sintered glass diaphragms on both ends of the tubing filled with 1 M sulfuric acid. It is important to remark that the commercially available malonic acid should be purified following a procedure suggested by Noszticzius et al. [14], since trace impurities of chloride can affect the experimental results significantly. All measurements were performed at 25 °C.

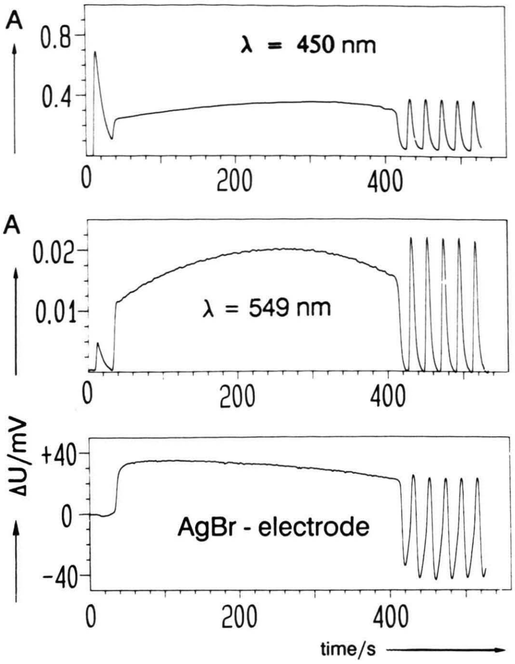

Fig. 1. Absorbances A at 450 and 549 nm and change ΔU of the electrode potential of an AgBr electrode in a BZ system with initial concentrations $[MA]_0 = 0.4$ M, $[HBrO_3]_0 = 0.1$ M and $[Ce^{4+}]_0 = 0.001$ M in 1 M sulfuric acid solution. The solution was bubbled with N_2 for 15 min before Ce^{4+} was added. Optical path length 10 cm, temperature 25 °C. The potential of the electrode was 170 mV in the H_2SO_4/malonic acid mixture and 185 mV after the addition of bromate. The signal at 450 nm is due to the absorbance of Ce^{4+}. The signal at 549 nm is a superposition of the absorbances of Ce^{4+} and of $BrO_2^{\cdot}$. In Fig. 2 the concentration of $BrO_2^{\cdot}$ is evaluated by subtracting the Ce^{4+} contribution.

Kinetic Measurements

140 ml of a mixture of malonic acid and bromate in 1 M sulfuric acid are bubbled with nitrogen gas (99.99% purity) outside the reaction cell for 15 minutes in order to remove dissolved oxygen. After that, the solution is transferred into the optical cell (path length 10 cm, volume 140 ml) equipped with a bromide selective electrode. During the measurement a stream of N_2 is applied above the solution in order to prevent any contact with air.

In a typical experiment, the initial concentrations of malonic acid and of bromate are 0.4 M and 0.1 M, respectively; 2.8 ml of a 0.05 M solution of $Ce(SO_4)_2$ in 1 M H_2SO_4 are added, leading to an initial concentration $[Ce^{4+}]_0 = 0.001$ M. The absorbances A at 450 and 549 nm and the potential change ΔU of the AgBr electrode are displayed in Figure 1. From A_{450} the concentration of Ce^{4+} is calculated by using the extinction coefficient $\varepsilon(Ce^{4+}) = 100\ M^{-1}\ cm^{-1}$ at 450 nm (contribution of $BrO_2^{\cdot}$ neglected). On the other hand, at 549 nm there is a small absorbance of Ce^{4+}, and the absorbance of $BrO_2^{\cdot}$ must be calculated by subtracting the Ce^{4+} contribution. We find [15, 16]:

$$A(BrO_2^{\cdot}, 549) = A_{549} - A_{450}\, \varepsilon(Ce^{4+}, 549)/\varepsilon(Ce^{4+}, 450) \qquad (1)$$

with $\varepsilon(Ce^{4+}, 549) = 0.7\ M^{-1}\ cm^{-1}$. This way the concentrations of Ce^{4+} and of $BrO_2^{\cdot}$ are calculated from the experimental curves (Figure 2). $[Ce^{4+}]$ decreases from the maximum value ($c_0 = 0.001$ M) to 0.0001 M within 26 s. After that a sudden increase of the signals appears: the concentration of Ce^{4+} jumps up until a stationary state is reached; simultaneously, a jump of $BrO_2^{\cdot}$ appears, indicating that the autocatalytic oxidation of Ce^{3+} by bromate is inhibited in the first 26 s after the addition of Ce^{4+}. Additionally, a jump of the electrode potential occurs towards a higher potential, apparently due to the formation of HOBr after the start of the autocatalytic oxidation of Ce^{3+} by bromate. Using the same argument as discussed in [9], it can be derived from the behaviour of the electrode that the inhibition of the autocatalytic reaction is not due to the formation of bromide. Moreover, it is unreasonable to believe that bromide can be formed during the very short time period between the addition of Ce^{4+} and the observed jump of the Ce^{4+} concentration. Bromomalonic acid (as a source of bromide) cannot be present, since no HOBr (which is the final

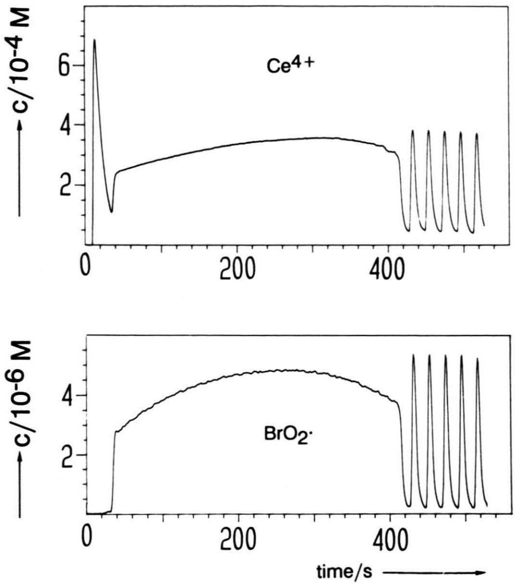

Fig. 2. Concentrations of Ce^{4+} and of $BrO_2^{\cdot}$ calculated from (1) on the basis of the absorbances *A* displayed in Fig. 1 (optical path length $d = 10$ cm, $\varepsilon(Ce^{4+}, 450 \text{ nm}) = 100$, $\varepsilon(Ce^{4+}, 549 \text{ nm}) = 0.7$, $\varepsilon(BrO_2^{\cdot}, 549 \text{ nm}) = 387 \ M^{-1} cm^{-1}$).

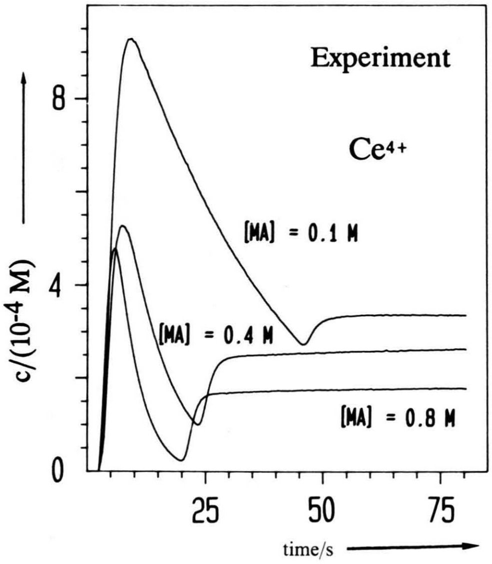

Fig. 3. Kinetics of Ce^{4+} in BZ systems with $[HBrO_3]_0 = 0.1$ M and $[Ce^{4+}]_0 = 0.001$ M and increasing concentrations of malonic acid ($[MA]_0 = 0.1$ M, 0.4 M, and 0.8 M) in 1 M sulfuric acid. The solution was bubbled with N_2. The absorbance was measured at 401 nm in a reaction cell with a volume of 15 ml and an optical pathlength of 2 cm ($\varepsilon(Ce^{4+}) = 800 \ M^{-1} cm^{-1}$).

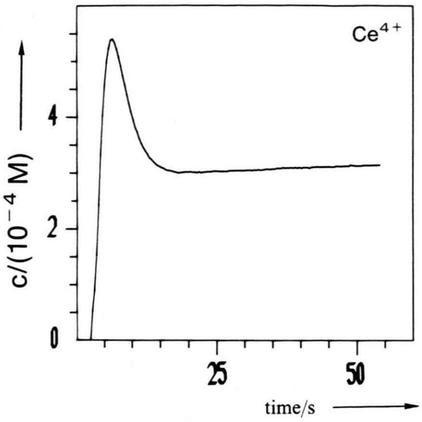

Fig. 4. Kinetics of Ce^{4+} in the same system as displayed in Figs. 1 and 2, but with a gas stream of O_2 applied instead of N_2. The absorbance was measured at 401 nm in a reaction cell with a volume of 15 ml and an optical pathlength of 2 cm ($\varepsilon(Ce^{4+}) = 800 \ M^{-1} cm^{-1}$).

product of the oxidation of Ce^{3+} by bromate) is formed during the inhibition of the autocatalytic reaction.

After an induction period of 400 s regular oscillations start, which are typical for a bromide controlled BZ system.

The single oscillation shown in Figs. 1 and 2 does not appear if the reaction is started by the addition of Ce^{3+} instead of Ce^{4+}. In this case malonyl radicals are not formed in the very beginning of the reaction and the autocatalytic reaction starts immediately on the addition of the catalyst (for example, see Fig. 1 in Ref. [10]).

The effect of malonyl radicals in the experiment displayed in Figs. 1 and 2 increases with increasing initial concentration of malonic acid from 0.1 M to 0.8 M (Figure 3).

Finally, the experiment with $[MA]_0 = 0.4$ M (Figs. 1 to 3) was repeated bubbling pure oxygen instead of nitrogen through the solution. The result is displayed in Figure 4. As expected for the removal of malonyl radicals by oxygen, no single oscillation appears in this case. A similar result was obtained in [11 a] for an air saturated system ($[MA] = 0.1$ M, $[NaBrO_3] = 0.1$ M, $[Ce^{4+}] = 1 \times 10^{-4}$ M in 1 M H_2SO_4).

Discussion

For an explanation of the observed single oscillations we performed model calculations including the reaction of malonyl radicals with $BrO_2^{\cdot}$. We suggest that the Radicalator model developed earlier [9, 10] is capable of explaining the observed phenomena. In this model we start with the reactions important for the inorganic reaction steps in the BZ reaction [2]:

$$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O, \tag{R 1}$$

$$Br^- + HBrO_2 + H^+ \rightarrow 2\,HOBr, \tag{R 2}$$

$$Br^- + BrO_3^- + 2\,H^+ \rightarrow HOBr + HBrO_2, \tag{R 3}$$

$$2\,HBrO_2 \rightarrow HOBr + BrO_3^- + H^+, \tag{R 4}$$

$$HBrO_2 + BrO_3^- + H^+ \rightarrow Br_2O_4 + H_2O, \tag{R 5'}$$

$$Br_2O_4 \rightarrow 2\,BrO_2^{\cdot}, \tag{R 5''}$$

$$Ce^{3+} + BrO_2^{\cdot} + H^+ \rightarrow Ce^{4+} + HBrO_2\,. \tag{R 6}$$

The reaction of malonic acid MA with Ce^{4+} [17], the selfdecay of the malonyl radicals $MA^{\cdot}$ [18] (leading to MA and tartronic acid TA) and the reaction of malonyl radicals with $BrO_2^{\cdot}$ [4] are added to the reaction scheme:

$$Ce^{4+} + MA \rightarrow Ce^{3+} + MA^{\cdot} + H^+, \tag{R 7}$$

$$2\,MA^{\cdot} + H_2O \rightarrow MA + TA, \tag{R 8}$$

$$MA^{\cdot} + BrO_2^{\cdot} \rightarrow P\,. \tag{R 9}$$

The reaction of MA with HOBr

$$HOBr + MA \rightarrow BrMA + H_2O \tag{R 10}$$

is responsible for the formation of bromomalonic acid (BrMA) [19].

For the start of the autocatalytic reaction of Ce^{3+} with bromate a small amount of $HBrO_2$ (or $BrO_2^{\cdot}$) is needed. It is well known that acidic bromate is unstable, and HOBr as well as Br_2 are formed. Most probably this decomposition is due to the reaction

$$2\,BrO_3^- + 2\,H^+ \rightarrow HBrO_2 + HBrO_4\,. \tag{R 11}$$

There is evidence for this reaction because $BrO_2^{\cdot}$ can be identified as an intermediate in strongly acidic bromate solutions [9]. By increasing the concentration of sulfuric acid from 1 M to 10 M a very high concentration of $BrO_2^{\cdot}$ (about 9×10^{-5} M) can be obtained (Figure 5).

It was shown earlier [10] that the primary reaction product P decomposes in two different reaction paths:

$$P \rightarrow GOA + HOBr + CO_2, \tag{R 12}$$

$$P + H_2O \rightarrow TA + HBrO_2\,. \tag{R 13}$$

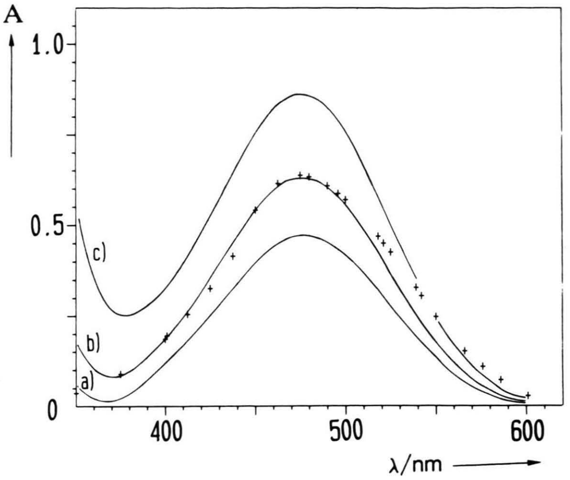

Fig. 5. Formation of $BrO_2^{\cdot}$ in a strongly acidic bromate solution followed by its absorption spectrum ($[BrO_3^-] = 0.2$ M in 10 M H_2SO_4). The solution is prepared by mixing 10 ml conc. H_2SO_4 (96%), 6 ml water and 4 ml 1 M aqueous $NaBrO_3$ solution at a temperature of −15 °C following a procedure of Noszticzius et al. [20]. The solution is placed into a well stirred optical cell (reference 10 M H_2SO_4, pathlength 10 cm) in the compartment of a photospectrometer thermostated at 20 °C. Curves a–c (full lines) correspond to different temperatures T during the warming up process: a) $T = 13$ °C, b) $T = 15$ °C, c) $T = 16$ °C.

For curve b) the $BrO_2^{\cdot}$ spectrum reported by Buxton and Dainton (crosses) [21] is given for comparison. It turns out that the measured spectrum b) is nearly identical with the Buxton and Dainton spectrum in the wavelength range from 370 to 500 nm. In the range from 500 to 600 nm there is some significant deviation, however, although earlier spectra obtained in bromate chemistry experiments in 1 M H_2SO_4 solution [16, 22, 23, 24] agree with the Buxton and Dainton experiment within the limit of error. One possible explanation for the observed deviation seems to be the fact that in the experiment presented here 10 M sulfuric acid is used as a solvent, and the spectrum is changed due to the formation of $(HBrO_2^{\cdot})^+$ as suggested by Zhabotinsky [25]. Below 370 nm the absorbance is higher than expected for $BrO_2^{\cdot}$ due to the simultaneous formation of HOBr in the reaction sequence (R 5''), (R 5') and (R 4).

From the maximum absorbance $A_{max} = 0.87$ in curve c) the concentration $[BrO_2^{\cdot}] = 8.7 \times 10^{-5}$ M can be calculated ($\varepsilon_{max} = 1000$ M^{-1} cm^{-1} [21], optical pathlength 10 cm).

From the rate of formation of CO_2 in a BZ system, a rate constant $k_{12} = 1\,s^{-1}$ was estimated. Moreover, from the experimental fact that a 0.015 M bromate, 0.6 M MA, 0.001 M Ce^{3+} system in 1 M sulfuric acid does not oscillate immediately after the addition of the catalyst, a rate constant $k_{13} = 1\,s^{-1}$ was derived [10].

In our model no direct reaction of malonyl radicals with bromate is included, although Brusa et al. [18] report a fast consumption of $MA^{\cdot}$ radicals if bromate is added to their reaction mixture. It must be pointed out, however, that Brusa et al. performed their exper-

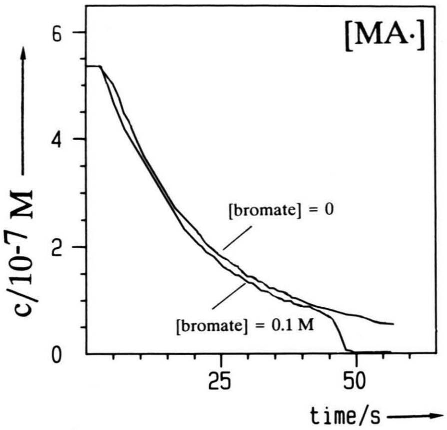

Fig. 6. Kinetics of malonyl radicals MA˙ during the reaction of Ce^{4+} (initial concentration 0.02 M) with malonic acid (0.4 M) in 1 M sulfuric acid in the absence and in the presence of bromate (0.1 M). The concentration of MA˙ was calculated from the ESR signal as described in [4].

iments in perchloric acid as a reaction medium instead of sulfuric acid as usual in the BZ system. For this reason we repeated their experiment with 1 M sulfuric acid as a solvent. Following the procedure described in [4] a solution of $Ce(SO_4)_2$ (0.04 M) and a solution of malonic acid (0.8 M) (each solved in 1 M H_2SO_4) were pumped into the mixing chamber of an ESR cell. At a constant flow of the reagents a constant ESR signal was obtained. The flow was stopped and the decay of the ESR signal was recorded (Fig. 6, upper curve). In a second experiment, $NaBrO_3$ (0.2 M) was added to the Ce^{4+}-solution. As can be seen from Fig. 6 (lower curve) the kinetics of MA˙ is unchanged in the presence of bromate up to a reaction time of 45 s. After that time the autocatalytic oxidation of Ce^{3+} by bromate starts; $BrO_2^{\cdot}$ is formed as an intermediate which species removes the MA˙ radicals completely, and the ESR signal drops down to zero.

This behaviour can directly be seen in Fig. 7, where the kinetics of MA˙ (Fig. 7b) is compared to the kinetics of Ce^{4+} (Fig. 7a) in the same experiment. After an induction period of about 40 s, oscillations of $[Ce^{4+}]$ and of [MA˙] start. The signal of the malonyl radicals reappears just after the first oscillation maximum of Ce^{4+}. In this experiment the solution cannot be stirred (since the reaction mixture is inside the flat ESR cell) and further oscillations of MA˙ cannot be observed due to the formation of spatial inhomogeneities in the cell.

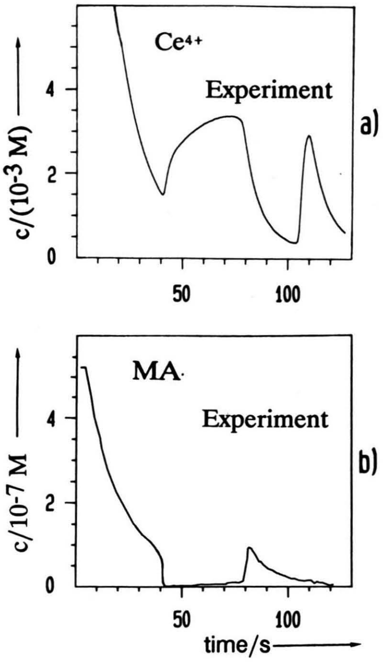

Fig. 7. Concentrations c of Ce^{4+} (a) and of malonyl radicals MA˙ (b) in a BZ system with initial concentrations $[MA]_0 = 0.4$ M, $[BrO_3^-]_0 = 0.1$ M and $[Ce^{4+}]_0 = 0.02$ M (solvent 1 M sulfuric acid). In the ESR experiment the reactants were mixed in a flow cell [4]; the signal was monitored after the flow was stopped.

In order to follow a larger number of oscillations of MA˙, we performed an additional experiment. The reactants were mixed in a well stirred reaction vessel and the solution was continuously pumped through the ESR cell at a high rate (130 ml/min). This way the oscillations going on in the reaction vessel could be monitored by the ESR signal with a delay of about 2 s (Figure 8).

Now we focus our attention on the single oscillation discussed above (Figure 3). Model calculations for a system with $[MA]_0 = 0.1$ M, $[NaBrO_3]_0 = 0.1$ M $[Ce^{4+}]_0 = 0.001$ M (1 M sulfuric acid medium) reveal that the Ce^{4+}-kinetics is well modelled with $k_{13} = 1.0\ s^{-1}$, which value is consistent with former model calculations [10]. It can be seen in Fig. 9 that k_{13} values lower than $1.0\ s^{-1}$ cannot account for the observed kinetics displayed in Figure 3. Moreover, the kinetics of $BrO_2^{\cdot}$ exhibits an overshoot if $k_{13} < 1.0\ s^{-1}$ is used in the calculation. No $BrO_2^{\cdot}$ overshoot appears in the experiments (Figure 2). This way we have an additional argument supporting the choice of k_{13} in our model. Model calculations in the same range of

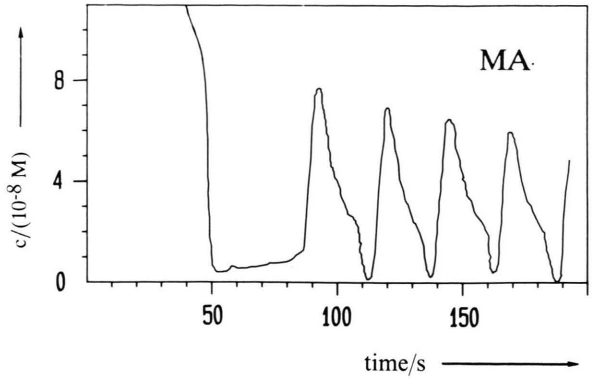

Fig. 8. Concentration c of the malonyl radicals $MA^{\cdot}$ in the same system as in Fig. 7, but the ESR measurement was done in continuous flow system, and the sensitivity of the measurement was increased by a factor of 5. The initial phase of the reaction is out of the range of the instrument.

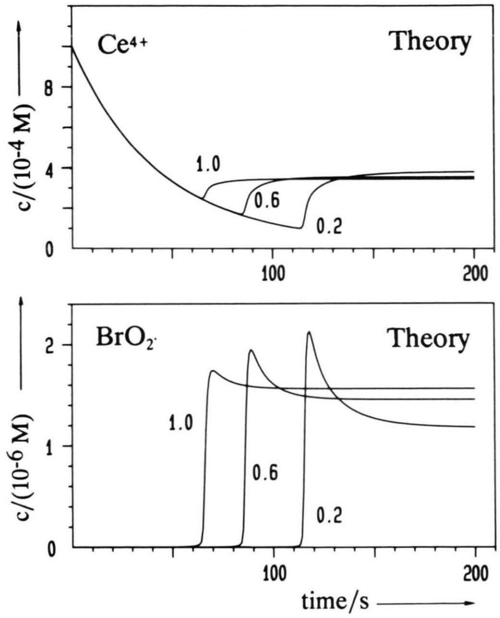

Fig. 9. Evaluation of the rate konstant k_{13} by model calculations on a BZ system with initial concentrations $[MA]_0 = 0.1$ M, $[BrO_3^-]_0 = 0.1$ M, $[Ce^{4+}]_0 = 0.001$ M in 1 M sulfuric acid ($[H^+] = 1.29$ M). For rate constants k_1 to k_{12} see Table 1. The rate constant k_{13} is changed from 0.2 to 1.0 s^{-1}.

concentrations as in Fig. 3 demonstrate that our model explains the single oscillation quantitatively (Figure 10).

In Fig. 11 the calculated kinetics of Ce^{4+} and of $MA^{\cdot}$ is displayed for the same system as considered in Figure 7. Also in the case of the malonyl radicals a good agreement between theory and experiment is

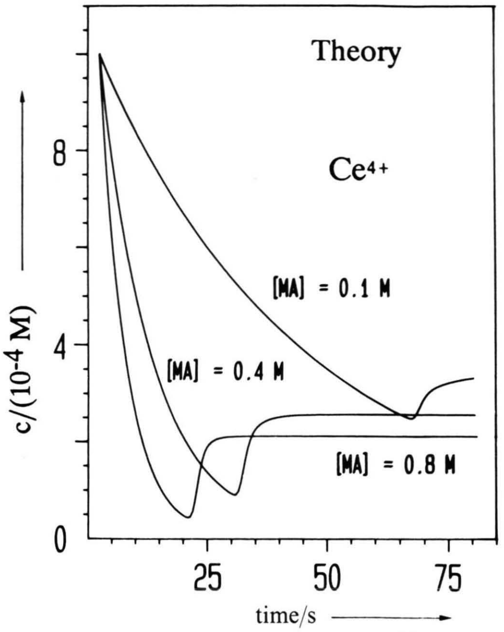

Fig. 10. Calculated concentration of Ce^{4+} for the systems described in Fig. 3 (with k_1 to k_{13} from Table 1).

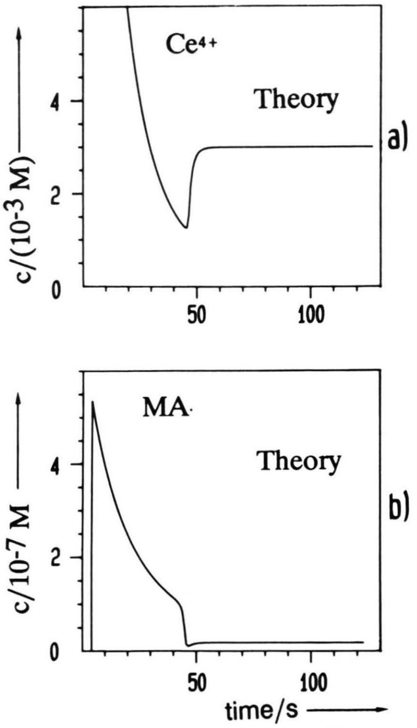

Fig. 11. Calculated kinetics of $[Ce^{4+}]$ (a) and of $[MA^{\cdot}]$ (b) for the BZ system described in Fig. 7 (with k_1 to k_{13} from Table 1).

Table 1. Rate constants k_1 to k_{13} 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 [26] 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 8.9×10^3 M^{-1} s^{-1} [2] to 8.4×10^3 M^{-1} s^{-1} regarding the results of recent experiments (H. D. Försterling, to be published).

Forward	Ref.	Reverse	Ref.
$k_1 = 8 \times 10^9$ M^{-2} s^{-1}	[2, 7, 9]	$k_{-1} = 80$ s^{-1}	[7, 9]
$k_2 = 2.5 \times 10^6$ M^{-2} s^{-1}	[7, 9]	$k_{-2} = 2 \times 10^{-5}$ M^{-1} s^{-1}	[2, 7]
$k_3 = 1.6$ M^{-3} s^{-1}	[7, 9]	$k_{-3} = 3.2$ M^{-1} s^{-1}	[2]
$k_4 = 3 \times 10^3$ M^{-1} s^{-1}	[2, 7, 9]	$k_{-4} = 1 \times 10^{-8}$ M^{-2} s^{-1}	[2]
$k_{5'} = 33$ M^{-2} s^{-1}	[2, 10]	$k_{-5'} = 2.2 \times 10^3$ s^{-1}	[2]
$k_{5''} = 7.4 \times 10^4$ s^{-1}	[2]	$k_{-5''} = 1.4 \times 10^9$ M^{-1} s^{-1}	[2]
$k_6 = 6.2 \times 10^4$ M^{-2} s^{-1}	[2, 10]	$k_{-6} = 8.4 \times 10^3$ M^{-1} s^{-1}	[2, 10]
$k_7 = 0.23$ M^{-1} s^{-1}	[4, 17]	$k_{-7} = 2.2 \times 10^4$ M^{-2} s^{-1}	[4, 17]
$k_8 = 3.2 \times 10^9$ M^{-1} s^{-1}	[18]	$k_{-8} = 0$	
$k_9 = 5 \times 10^9$ M^{-1} s^{-1}	[4, 9]	$k_{-9} = 0$	
$k_{10} = 8.2$ M^{-1} s^{-1}	[19]	$k_{-10} = 0$	
$k_{11} = 7 \times 10^{-7}$ M^{-3} s^{-1}	[9]	$k_{-11} = 0$	
$k_{12} = 1$ s^{-1}	[10]	$k_{-12} = 0$	
$k_{13} = 1$ s^{-1}	[10] [a]	$k_{-13} = 0$	

[a] This work.

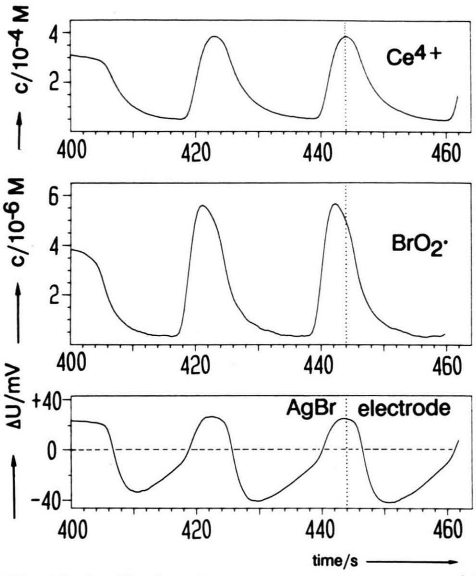

Fig. 12. Oscillations in the concentrations of Ce^{4+} and $BrO_2^{\cdot}$ and in the potential change ΔU of the AgBr electrode. The system is the same as in Figs. 1 and 2. The first 3 oscillations in that system (starting at $t = 400$ s) are displayed. The dashed line in the ΔU-curve indicates the starting potential ($U = 185$ mV). The dotted line at $t = 444$ s corresponds to the inhibition point of the autocatalytic reaction at the maximum of the Ce^{4+} curve.

obtained. It must be mentioned, however, that our theory cannot explain the onset of the oscillations after the end of the induction period. The reason for this failure is that consecutive reactions occurring during the induction period (like the accumulation of bromomalonic acid) are not yet taken into account in the model.

Conclusions

We have demonstrated that the Radicalator model explains the single oscillation appearing in BZ systems started with Ce^{4+}. We conclude that malonyl radicals are important in the theory of the BZ reaction as a second control intermediate besides bromide. Of course, the model in its present form does not explain the onset of oscillations because all consecutive reactions appearing in the induction period (like accumulation of bromomalonic acid) are not yet included in the model. In our opinion, the control by malonyl radicals must be accompanied by control by bromide in most BZ systems, although bromide seems not to be necessary at a high acidity and a high MA/bromate ratio [9]. As an example we consider the system already described in Figs. 1 and 2. The oscillations of Ce^{4+}, $BrO_2^{\cdot}$ and of the potential of the AgBr electrode appearing immediately after the end of the induction period are displayed in more detail in Figure 12. It must be noted that the potential of the AgBr electrode is below the starting value (dashed line in Figure 12) during the inhibitory phase of the autocatalytic reaction (e.g. time period from 426 s to 440 s). That means the electrode potential responds to an excess of bromide ions during that time. The autocatalytic reaction starts again as soon as the bromide concentration is below a critical value. This interpretation is completely in accordance with the accepted concept of bromide control [8]. On the other hand, the potential of the AgBr electrode is above the starting value when the autocatalytic reaction is switched on (e.g. time period from 440 s to 444 s). That means that the electrode responds to an excess of HOBr. In this case the bromide concentration is kept at a very low level by means of reaction (R 1). In spite of this extremely low bromide concentration the autocatalytic reaction is switched off at $t = 444$ s as can be seen from the maximum of $[Ce^{4+}]$ and the shoulder appearing in $[BrO_2^{\cdot}]$.

It is hard to believe that the switching off process is controlled by bromide. It is much more probable that a direct reaction of organic radicals with $BrO_2^{\cdot}$ radicals is responsible for the inhibition of the autocatalytic reaction. It is important to remark that the autocatalytic reaction starts when the bromide concentration is below the critical value, but the same reaction gets inhibited at a bromide concentration which is not above the critical level. After the end of the induction period, bromomalonic acid accumulates in the solution, and we suggest that the inhibition of the autocatalysis is due to a reaction of bromomalonyl radicals. Investigations exploring the role of bromomalonyl radicals are in progress.

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