Formation of BrO_2 in the Belousov-Zhabotinsky-System-Investigation of the Ce^{3+}/BrO_3^--Reaction *

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The reaction between Ce^{3+} and bromate was studied in sulfuric acid solution using a dual wavelength spectrometer. From the spectral dependence of the absorbance in the region from 450 to 600 nm it is concluded that BrO_2 is an intermediate of the reaction. The kinetics of formation and decay of BrO_2 is compared to theoretical models.

In a preceding paper [1] it was shown that BrO_2-oscillations can be detected in the Belousov-Zhabotinsky-system by following the absorbance in the spectral region from 400 to 600 nm. According to the theory given by Field, Kőrös and Noyes [2] for the BZ-system, BrO_2 is responsible for the autocatalysis of the Ce^{3+}/BrO_3^--reaction. For this reason we have tried to detect BrO_2 as an intermediate in this reaction.

Experimental Procedure

Using the same dual wavelength spectrometer as described in [1] we have monitored the Ce^{3+}/BrO_3^--reaction simultaneously at 400 and 550 nm. 200 ml of a solution of $NaBrO_3$ (0.1 m) in 2 n-H_2SO_4 in a stirred cell of 10 cm path length were thermostated at 20 °C and bubbled with N_2 (99.99%) for about 1 hour, and 200 µl of a 0.05 m $Ce_2(SO_4)_3$-solution in 2 n-H_2SO_4 were added by a syringe yielding a Ce^{3+}-concentration of $1 \cdot 10^{-4}$ m. The absorbance A at 400 and 550 nm is given as a function of time in Figure 1 a. The 400 nm-curve is identical with the wellknown time-dependence of the Ce^{4+}-absorbance [3]. Since the 550 nm-curve undergoes a maximum value it is clear that this curve is due to the absorbance of an intermediate occuring during the Ce^{3+}/BrO_3^--reaction.

By increasing the BrO_3^--concentration from 0.1 to 1.0 m the curves in Fig. 1 b are obtained. The maximum value of $A_{550\,\text{nm}}/A_{400\,\text{nm}}$ is about twice the value in Figure 1 a. This ratio can be further increased by a factor of about 3 by using 10^{-5} m Ce^{3+}-solutions in 1 m BrO_3^-. Under these conditions it was possible to obtain the absorption spectrum of the intermediate monitored at 550 nm using the following procedure: the kinetics of the Ce^{3+}/BrO_3^--reaction was measured simultaneously at 400 nm and at a second wavelength λ, changing λ stepwise from 445 nm to 601 nm. Taking each time the absorbance at wavelength λ (A_λ) exactly 15.5 s after the injection of Ce^{3+} and subtracting the Ce^{4+}-contribution $((A_{Ce^{4+}})_\lambda)$ the absorbance A_{Int} of the intermediate

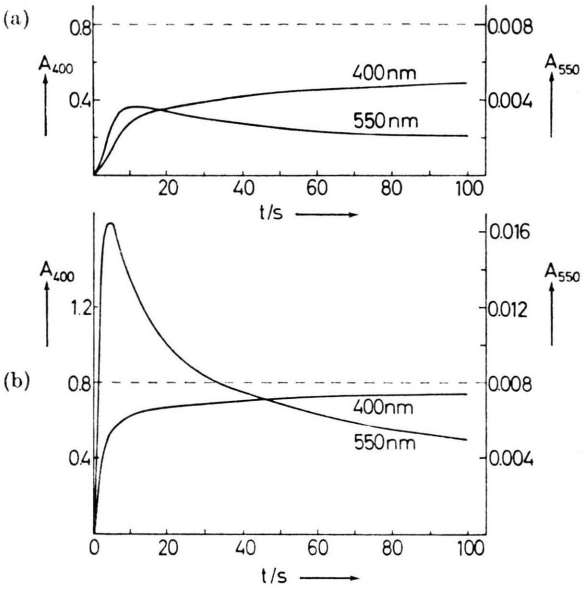

Fig. 1. Kinetics of the Ce^{3+}/BrO_3^--reaction followed by measuring simultaneously the 400 nm and 550 nm absorbance (A_{400}, A_{550}) of the solution. The initial concentration of Ce^{3+} is $1 \cdot 10^{-4}$ m; the concentration of BrO_3^- is 0.1 m (a) and 1.0 m (b). The optical path length is 10 cm, and the temperature is 20 °C. The dashed lines refer to the absorbance expected for quantitative formation of Ce^{4+}.

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Table 1. Evaluation of the absorption spectrum of the intermediate of the Ce^{3+}/BrO_3^--reaction. A_λ = Absorbance at wavelength λ, $(A_{Ce^{4+}})_\lambda$ = contribution of the Ce^{4+}-absorbance at wavelength λ (measured 15.5 s after injection of Ce^{3+} into the BrO_3^--solution). The concentrations used are $[BrO_3^-] = 1.0$ m, $[H_2SO_4] = 1.0$ m, $[Ce^{3+}]_{t=0} = 1 \cdot 10^{-5}$ m.

Run	λ/nm	A_λ	$(A_{Ce^{4+}})_\lambda$	$A_{Int} = A_\lambda - (A_{Ce^{4+}})_\lambda$
1	445	0.0125	0.0063	0.0062
2	468	0.0108	0.0021	0.0087
3	480	0.0105	0.0015	0.0090
4	501	0.0087	0.0007	0.0080
5	525	0.0060	0.0002	0.0058
6	550	0.0034	0.0000	0.0034
7	576	0.0016	0.0000	0.0016
8	601	0.0004	0.0000	0.0004

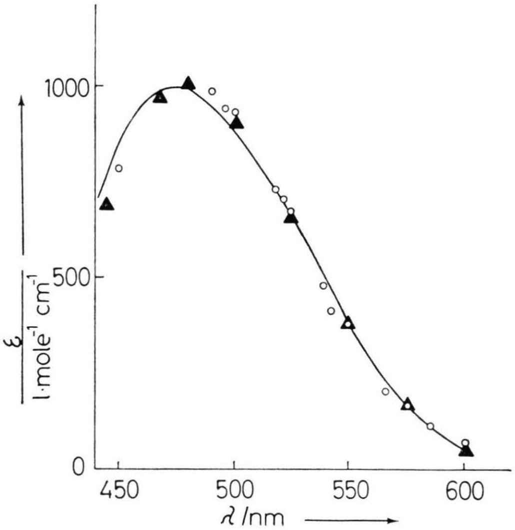

Fig. 2. Absorption curve of BrO_2 (full line) [4, 5]; spectral dependence of the oscillation amplitudes in the BZ-system after subtracting the Ce^{4+}-contribution (circles) [1]; spectral dependence of the intermediate absorbance in the Ce^{3+}/BrO_3^--reaction (triangles, values from Table 1). The ε-values are those reported by Buxton and Dainton [4]; the circles and triangles are arbitrarily scaled in such a way that the 550 nm-values agree with the BrO_2-absorption curve.

was obtained as a function of wavelength (Table 1). A_{Int} is plotted versus λ in Fig. 2 (triangles) in such a way that the 550 nm value agrees with the curve given by Buxton and Dainton [4] and by Amichai et al. [5]. From Fig. 2 it is evident that the absorption spectrum of the intermediate occuring in the Ce^{3+}/BrO_3^--reaction is identical with the spectrum of BrO_2 detected in the BZ-system (circles in Figure 2).

Discussion

From these experiments we conclude that the 550 nm-curves in Fig. 1 are mainly due to the absorption of BrO_2. From these curves the BrO_2-concentration was calculated by subtracting the contribution of Ce^{4+} in the same manner as demonstrated in Table 1 and using the BrO_2-absorption coefficients given by Buxton and Dainton [4]. As an example, the time dependence of the Ce^{4+}- and BrO_2-concentrations is given in Fig. 3 a using a system which is typical for the Belousov-Zhabotinsky-reaction (0.1 m BrO_3^- in 2 n-H_2SO_4, initial Ce^{3+}-concentration of $2 \cdot 10^{-4}$ m).

This result is compared in Fig. 3 b with calculated curves based on the mechanism and the rate constants given by Field, Körös and Noyes [2]. There is a qualitative agreement of the experimental and calculated curves. In a quantitative respect, the calculated rates of formation of Ce^{4+} and of BrO_2 are about ten times higher than the experimental values, and this holds for the calculated BrO_2-concentrations too. The maximum rate of Ce^{4+}-formation is observed before the maximum concentration of BrO_2 is reached (Figure 3 a). This result seems to be

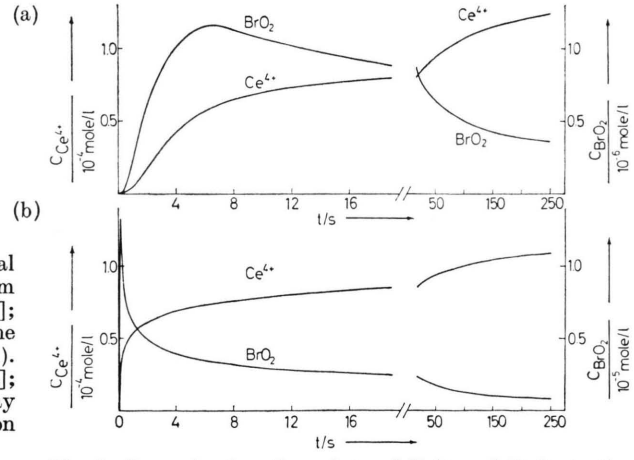

Fig. 3. Concentration-time-plots of Ce^{4+} and BrO_2 in the Ce^{3+}/BrO_3^--reaction. a) Experimental curves. The concentrations used are $[BrO_3^-] = 0.1$ m, $[H_2SO_4] = 1.0$ m and $[Ce^{3+}]_{t=0} = 2 \cdot 10^{-4}$ m. The solution was bubbled with N_2 about 1 h before injecting Ce^{3+}; the temperature was 20 °C. b) Calculated curves based on the mechanism and the rate constants given by Field, Körös and Noyes [2]. The initial conditions for BrO_3^-, H^+ and Ce^{3+} agree with the experimental values; the initial value for $[Br^-]$ was assumed to be 10^{-7} m (this value follows from titration of the BrO_3^--solution with $AgNO_3$); $[HOBr]_0$, $[HBrO_2]_0$ and $[Br_2]_0$ were set to zero. The set of differential equations was solved by Gear's integration method [6].

reasonable since the rate of Ce^{4+}-formation is assumed to be proportional to the product of the Ce^{3+}- and BrO_2-concentrations [2], and there is a competition between decreasing Ce^{3+}- and increasing BrO_2-concentration. In the case of the calculated curves (Fig. 3 b), however, the decay of BrO_2 is so fast that the BrO_2-maximum is reached at a very low Ce^{4+}-concentration already, and thus the maximum rate of Ce^{4+}-formation is predicted to coincide with the BrO_2-maximum.

The reason for these discrepancies may be the uncertainties in the rate constants given by Field, Körös and Noyes [2]. The constants involving the Ce^{3+}- and Ce^{4+}-reactions are roughly estimated only, and the experimental values of the BrO_2-rate constants are obtained in alkaline or neutral solution [4, 5]. Calculations based on modefied rate constants given by Edelson, Noyes and Field [7] lead to similar discrepancies.

Our results indicate that the qualitative features of the Ce^{3+}/BrO_3^--reaction are well described by the theory of Field, Körös and Noyes. On the other hand, further experiments are needed to check the mechanism and to evaluate the rate constants of the elementary steps of the reaction.

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