Formation of BrO_2 in the Belousov-Zhabotinsky-System — Investigation of the $HBrO_2/BrO_3^-$-Reaction

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The reaction between $HBrO_2$ and bromate was studied in sulfuric acid solution. From the spectral dependence of the absorbance in the region from 400 to 600 nm it is concluded that BrO_2 is an intermediate of the reaction. From the maximum concentration of BrO_2 the equilibrium constant of the BrO_2/Br_2O_4-equilibrium is evaluated; furthermore, a value for the ratio of the rate constants for the $HBrO_2/BrO_3^-$-reaction and the disproportionation reaction of $HBrO_2$ is given.

The autocatalytic formation of Ce^{4+} is one of the essential reactions in the Belousov-Zhabotinsky-system [1, 2]. Within the reaction scheme proposed by Field, Kőrös, and Noyes [3] (FKN-theory) this reaction is assumed to proceed in two elementary steps:

$$Ce^{3+} + BrO_2 + H^+ \xrightarrow{k_1} Ce^{4+} + HBrO_2\,, \qquad (R1)$$

$$HBrO_2 + BrO_3^- + H^+ \xrightarrow{k_2} 2\,BrO_2 + H_2O\,. \qquad (R2)$$

In preceding experiments [4, 5, 6] we have been able to detect BrO_2 formed in this reaction. The kinetics experimentally observed was found to be in qualitative agreement with the FKN-reaction scheme. In a quantitative respect, however, the experimental results disagreed with theory; as an example, the BrO_2-concentrations experimentally obtained were 1/10 of the calculated values only. In order to overcome this discrepany, reaction (R2) was investigated in more detail.

Experimental Procedure

Since $HBrO_2$ is not stable in acid solution, we have studied reaction (R2) by injecting $NaBrO_2$ (solved in 0.1 m NaOH) into a 1 m solution of $NaBrO_3$ in 1 m sulfuric acid assuming that the reaction

$$BrO_2^- + H^+ \rightarrow HBrO_2 \qquad (R3)$$

is much faster than all other reactions under consideration.

Care was taken to use reagents of high purity. 1 m H_2SO_4 was prepared by dilution of conc. H_2SO_4 (p.a. Merck) in bidistilled water. $NaBrO_3$ (p.a. Fluka) was twice recrystallized from hot water. The absorption spectrum of solutions of $NaBrO_3$ in 1 m H_2SO_4 changed significantly in the course of purification (Fig. 1); this fact is mainly due to the elimination of Br^-- and BrO^--impurities. We were not able to reduce the residual 480 nm-absorption band by further recrystallization. $NaBrO_2$ was prepared by a modified procedure [7] basing on the synthesis described by Breiss [8]. The product was three times recrystallized from 0.1 m NaOH; the absorption spectrum given in Fig. 2 was found to be in excellent agreement with the spectra reported in [8, 9]. The residual Br^--impurity of this product was estimated using the following procedure: alkaline solutions of $NaBrO_2$ (initial concentration $2.81 \cdot 10^{-4}$ m) were injected into 1 m sulfuric acid and the absorption spectra of the reaction products were taken (Figure 3). In the case of curve 1, $NaBrO_2$ was used without further purification; in the case of curve 2, the alkaline solution of $NaBrO_2$ had been purified from Br^- by adding silver nitrate and removing the AgBr-precipitate by ultracentrifugation. The difference spectrum of curves 1 and 2 was found to agree with the spectrum of Br_2 (curve 3). From the absorbance $A = 0.018$ at $\lambda = 400$ nm the Br_2-concentration $1.1 \cdot 10^{-5}$ m was calculated

$(\varepsilon_{Br_2} = 172\ l \cdot mole^{-1} \cdot cm^{-1})$.

Assuming the reaction path

$$3\,Br^- + HBrO_2 + 3\,H^+ \rightarrow 2\,Br_2 + 2\,H_2O$$

the concentration of the Br^--impurity was estimat-

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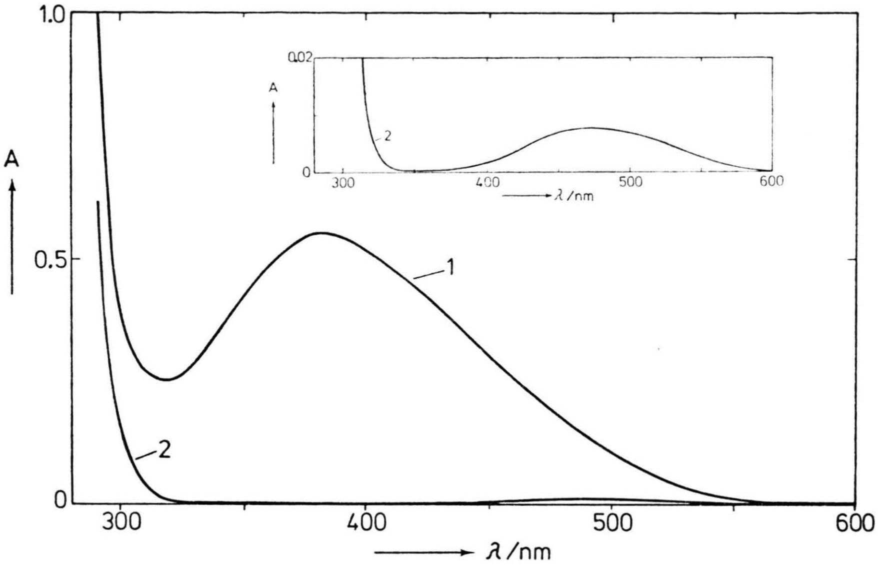

Fig. 1. Absorption spectrum of a 1 m solution of $NaBrO_3$ in 1 m sulfuric acid; optical path length 10 cm.
Curve 1: $NaBrO_3$, pa. product (Fluka); the strong absorbance in the region from 320 to 400 nm is due to HOBr- and Br_2-impurities.
Curve 2: $NaBrO_3$, product twice recrystallized from hot water.

ed to be $1.7 \cdot 10^{-5}$ m, that is about $5^0/_0$. It was not possible for us to reduce this impurity by further recrystallization.

In order to study reaction (R2), a 1 m solution of $NaBrO_3$ in 1 m H_2SO_4 was thermostated at 20 °C in a stirred reaction cell (volume 120 ml, optical path length 10 cm). After bubbling nitrogen through the solution for about 30 minutes (in order to eliminate oxygen), 200 µl of a $7.2 \cdot 10^{-4}$ m $NaBrO_2$ solution (in 0.1 m NaOH) were injected (leading to an initial concentration $c_I = 1.2 \cdot 10^{-6}$ m); the change ΔA of the absorbance at 488 nm was monitored using the same dual wavelength spectrometer arrangement as previously described [4] (Fig. 4, left scale). A fast rise of the absorbance (rise time less than the mixing time of about one second) and a slow decay are observed, indicating the formation of an intermediate.

According to reaction (R2) this intermediate is expected to be identical with BrO_2. In order to prove this identity the intermediate spectrum was taken using the following procedure: the kinetics of

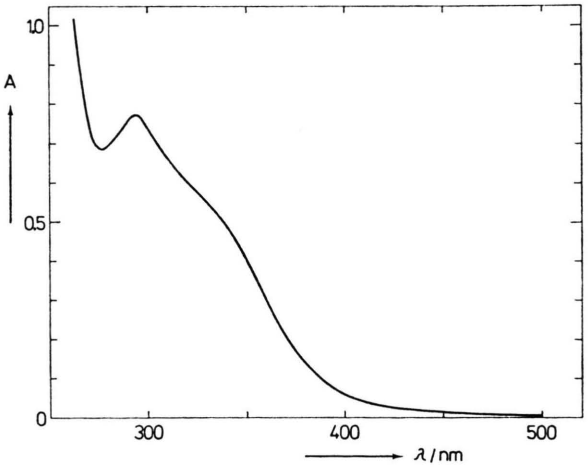

Fig. 2. Absorption spectrum of the stock solution of $NaBrO_2$ ($3.9 \cdot 10^{-2}$ m) in 0.1 m aqueous sodium hydroxide; optical path length 2 mm.

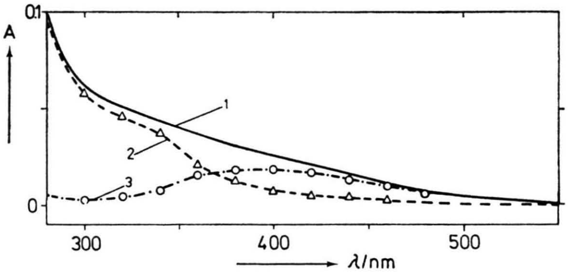

Fig. 3. Estimation of the Br^--impurities of $NaBrO_2$. An alkaline solution of $NaBrO_2$ was injected into 1 m sulfuric acid (initial concentration $2.81 \cdot 10^{-4}$ m) and the absorption spectra of the reaction products were taken; optical path length 10 cm.
Curve 1 (full line): $NaBrO_2$, product as used in Figure 2.
Curve 2 (dashed line): $NaBrO_2$, purified by adding silver nitrate to the alkaline solution and removing the AgBr-precipitate by ultracentrifugation.
Curve 2 (triangles: HOBr absorption spectrum [10].
Curve 3 (dash-dotted line): difference of curves 1 and 2.
Curve 3 (circles): Br_2-absorption spectrum [10, 11].

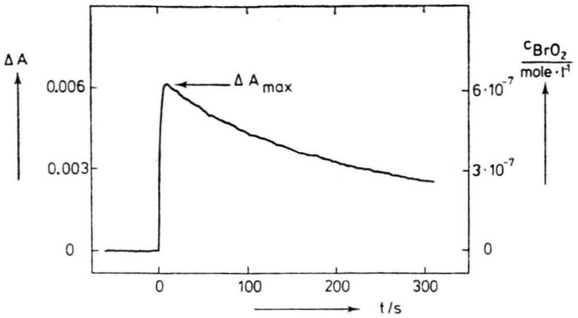

Fig. 4. Change of absorbance ΔA (left scale) after injecting $NaBrO_2$ (initial concentration $c_I = 1.2 \cdot 10^{-6}$ m) into a 1 m solution of $NaBrO_3$ in 1 m sulfuric acid. Optical path length 10 cm, temperature 20.0 °C, monitoring wavelength 488 nm (spectral band width 10 nm, double interference filter arrangement), reference wavelength 670 nm (dual wavelength method). Right scale: concentration of the reaction product BrO_2, calculated on the basis of $\varepsilon_{488} = 975\ l \cdot mole^{-1} \cdot cm^{-1}$ [12].

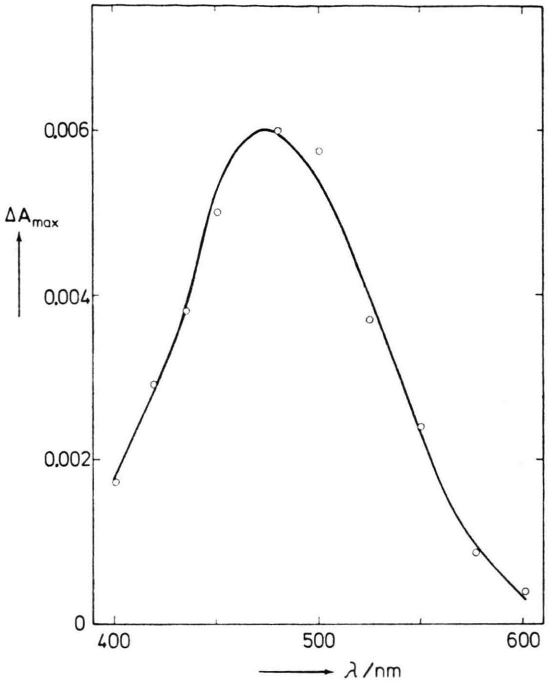

Fig. 5. Maximum value ΔA_{max} of the absorbance change of the intermediate of the $HBrO_2/BrO_3^-$-reaction (Fig. 4) as a function of wavelength (circles; spectral band width 20 nm, optical path length 10 cm) compared to the absorption spectrum of BrO_2 [12]; the spectrum is scaled in such a way that it agrees with experiment at 480 nm.

the $HBrO_2/BrO_3^-$-reaction was measured at different wavelengths λ, changing λ stepwise from 400 to 600 nm; each time, the maximum value ΔA_{max} of the absorbance change was taken and plotted as a function of wavelength (Fig. 5, circles). In fact, these values are in good agreement with the absorption spectrum of BrO_2 reported by Buxton and Dainton [12] (Fig. 5, full line). This proof for the occurrence of BrO_2 as an intermediate seems to be more direct than in our former experiments [4, 5, 6], since no corrections for the absorbance of other species were needed.

Using the ε-values of Buxton and Dainton [12] ($\varepsilon_{488} = 975\ l \cdot mole^{-1} \cdot cm^{-1}$) the BrO_2-concentrations were calculated (Fig. 4, right scale). Assuming reaction (R 2) to be the only reaction in our system, the maximum BrO_2-concentration is expected to be twice the initial concentration c_I of $NaBrO_2$. From Fig. 4 it is evident, however, that the maximum value of the BrO_2-concentration is $c_{BrO_2,max} = 0.63 \cdot 10^{-6}$ m only instead of $2.4 \cdot 10^{-6}$ m as expected from the stoichiometry of reaction (R 2).

Apparently, the kinetics of the reaction under consideration must be much more complicated than given by (R 2). Firstly, reaction (R 2) must be modified by including the dimer Br_2O_4 [3, 12]

$$HBrO_2 + BrO_3^- + H^+ \xrightarrow{k_2} Br_2O_4 + H_2O\,, \qquad (R\,2a)$$

$$Br_2O_4 \overset{K}{\rightleftharpoons} 2\,BrO_2\,. \qquad (R\,2b)$$

Secondly, the competitive reaction

$$2\,HBrO_2 \xrightarrow{k_4} HOBr + BrO_3^- + H^+ \qquad (R\,4)$$

must be taken into account [3, 13]. From these equations the yield of BrO_2 is expected to be lower than estimated from (R 2); this yield should increase with decreasing initial concentration c_I of $NaBrO_2$.

In order to check this modified reaction scheme we have repeated our experiment described above (Fig. 4) by changing the initial concentration c_I in the range from $2.8 \cdot 10^{-4}$ m to $3.1 \cdot 10^{-8}$ m; a strong dependence of the yield $c_{BrO_2,max}/c_I$ is to be observed as a function of c_I (Table 1, Figure 6). By similar experiments the equilibrium constant K in (R 2b)

$$K = c^2_{BrO_2}/c_{Br_2O_4} \qquad (1)$$

was evaluated: equal amounts of $NaBrO_2$ were injected twice into the bromate solution, the second injection taking place a few seconds later than the first one; after each injection, the maximum concentration of BrO_2 (c_1 and c_2, respectively) was measured (Fig. 7, Table 2). Under these experimental conditions, the initial concentration c_I is the same in each case leading to the same rates of reactions (R2a) and (R4), respectively. The only difference is to be seen in respect to the initial concentration of BrO_2: zero concentration before the first injection, concentration c_1 before the second injection. If (R2a) and (R2b) are valid the total concentration of Br^{4+}-species

$$c_{\text{tot}} = c_{\text{BrO}_2} + 2\,c_{\text{Br}_2\text{O}_4} \tag{2}$$

is expected to be doubled when the first injection of $NaBrO_2$ is followed by a second one:

$$c_{\text{tot},\,2} = 2\,c_{\text{tot},\,1}\,. \tag{3}$$

From (1), (2) and (3) K is calculated:

$$K = (2\,c_1{}^2 - c_2{}^2)/(\tfrac{1}{2}c_2 - c_1)\,. \tag{4}$$

Using the values given in Table 2 a mean value of $K = 1.5 \cdot 10^{-6}$ mole · l^{-1} is obtained. Inserting this value in (1) and (2) the total concentration $c_{\text{tot, max}}$ immediately after the first injection is to be calculated:

$$c_{\text{tot, max}} = c_{\text{BrO}_2\text{, max}} + 2\,c^2_{\text{BrO}_2\text{, max}}/K\,. \tag{5}$$

Table 1. Maximum concentration $c_{\text{BrO}_2\text{, max}}$ and ratio $c_{\text{BrO}_2\text{, max}}/c_{\text{I}}$ as a function of the initial concentration c_{I} of $NaBrO_2$ for the procedure described in Figure 4. c_{BrO_2} was calculated from the change of absorbance ΔA at 488 nm (spectral bandwidth 10 nm as in Fig. 4) on the basis of $\varepsilon_{488} = 975$ l · mole^{-1} cm^{-1}.

c_{I} / mole · l^{-1}	$c_{\text{BrO}_2\text{, max}}$ / mole · l^{-1}	$c_{\text{BrO}_2\text{, max}}$ / c_{I}
$2.83 \cdot 10^{-4}$	$4.60 \cdot 10^{-6}$	0.0163
$1.50 \cdot 10^{-4}$	$2.80 \cdot 10^{-6}$	0.0186
$9.06 \cdot 10^{-5}$	$2.67 \cdot 10^{-6}$	0.0295
$6.00 \cdot 10^{-5}$	$2.44 \cdot 10^{-6}$	0.0407
$1.50 \cdot 10^{-5}$	$1.83 \cdot 10^{-6}$	0.122
$9.06 \cdot 10^{-6}$	$1.76 \cdot 10^{-6}$	0.194
$6.00 \cdot 10^{-6}$	$1.42 \cdot 10^{-6}$	0.237
$4.50 \cdot 10^{-6}$	$1.35 \cdot 10^{-6}$	0.300
$2.86 \cdot 10^{-6}$	$1.14 \cdot 10^{-6}$	0.398
$1.50 \cdot 10^{-6}$	$6.76 \cdot 10^{-7}$	0.450
$1.40 \cdot 10^{-6}$	$7.47 \cdot 10^{-7}$	0.533
$1.20 \cdot 10^{-6}$	$6.27 \cdot 10^{-7}$	0.523
$9.06 \cdot 10^{-7}$	$5.99 \cdot 10^{-7}$	0.661
$6.00 \cdot 10^{-7}$	$4.07 \cdot 10^{-7}$	0.678
$2.83 \cdot 10^{-7}$	$2.42 \cdot 10^{-7}$	0.855
$1.36 \cdot 10^{-7}$	$1.38 \cdot 10^{-7}$	1.015
$9.06 \cdot 10^{-8}$	$1.05 \cdot 10^{-7}$	1.16
$6.12 \cdot 10^{-8}$	$7.88 \cdot 10^{-8}$	1.29
$4.50 \cdot 10^{-8}$	$6.04 \cdot 10^{-8}$	1.34
$3.42 \cdot 10^{-8}$	$4.19 \cdot 10^{-8}$	1.23
$3.06 \cdot 10^{-8}$	$4.22 \cdot 10^{-8}$	1.38

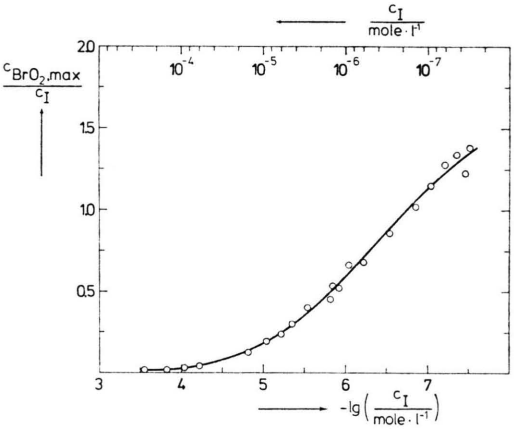

Fig. 6. Ratio $c_{\text{BrO}_2\text{, max}}/c_{\text{I}}$ ($c_{\text{BrO}_2\text{, max}}$ = maximum concentration of BrO_2, c_{I} = initial concentration of $NaBrO_2$) as a function of c_{I}. Circles: experimental values, taken from Table 1. Full Line: least square fit of the experimental values.

Table 2. Maximum concentrations c_1 and c_2 of BrO_2 after the first and second injection of $NaBrO_2$ into a 1 m solution of $NaBrO_3$ in 1 m sulfuric acid (see Fig. 7) as a function of the initial concentration c_{I} of $NaBrO_2$ (monitoring wavelength 488 nm and spectral bandwidth 10 nm). The equilibrium constant K (column 4) is calculated from (4); a mean value $(1.5 \pm 0.2) \cdot 10^{-6}$ mole · l^{-1} is obtained.

c_{I} / mole · l^{-1}	c_1 / mole · l^{-1}	c_2 / mole · l^{-1}	K / mole · l^{-1}
$9.06 \cdot 10^{-8}$	$1.05 \cdot 10^{-7}$	$1.91 \cdot 10^{-7}$	$1.5 \cdot 10^{-6}$
$2.88 \cdot 10^{-7}$	$2.45 \cdot 10^{-7}$	$4.19 \cdot 10^{-7}$	$1.6 \cdot 10^{-6}$
$4.80 \cdot 10^{-7}$	$3.68 \cdot 10^{-7}$	$6.17 \cdot 10^{-7}$	$1.8 \cdot 10^{-6}$
$9.06 \cdot 10^{-7}$	$5.99 \cdot 10^{-7}$	$9.46 \cdot 10^{-7}$	$1.4 \cdot 10^{-6}$
$2.40 \cdot 10^{-6}$	$8.14 \cdot 10^{-7}$	$1.27 \cdot 10^{-6}$	$1.6 \cdot 10^{-6}$
$4.50 \cdot 10^{-6}$	$1.35 \cdot 10^{-6}$	$2.02 \cdot 10^{-6}$	$1.3 \cdot 10^{-6}$

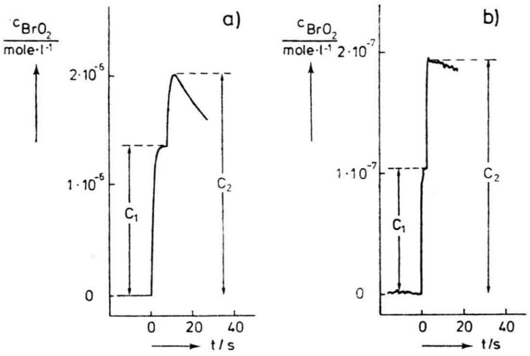

Fig. 7. Measurement of the maximum concentrations c_1 and c_2 of BrO_2 after the first and second injection of $NaBrO_2$ into a 1 m solution of $NaBrO_3$ in 1 m sulfuric acid. Initial concentration of $NaBrO_2$ at each injection $4.50 \cdot 10^{-6}$ m (a), $9.06 \cdot 10^{-8}$ m (b). Monitoring wavelength 488 nm, spectral band width 10 nm.

$c_{\mathrm{tot,\,max}}$ is listed in Table 3 (column 4). The ratio $c_{\mathrm{tot,\,max}}/c_{\mathrm{I}}$ (Table 3, column 5) is plotted in Fig. 8 as a function of c_{I}. If the competitive reaction (R4) were to be neglected, a constant value of $c_{\mathrm{tot,\,max}}/c_{\mathrm{I}}$ were to be expected; from Fig. 8 it is to be seen, however, that this ratio is decreasing with increasing concentration c_{I} indicating that (R4) must be taken into account:

$$\begin{aligned} \mathrm{d}c_{\mathrm{HBrO_2}}/\mathrm{d}t = &-k_2\, c_{\mathrm{BrO_3^-}}\, c_{\mathrm{H^+}}\, c_{\mathrm{HBrO_2}} \\ &-2\,k_4\, c^2_{\mathrm{HBrO_2}}, \qquad (6) \end{aligned}$$

$$\mathrm{d}c_{\mathrm{tot}}/\mathrm{d}t = 2\,k_2\, c_{\mathrm{BrO_3^-}}\, c_{\mathrm{H^+}}\, c_{\mathrm{HBrO_2}}\,. \qquad (7)$$

Table 3. Maximum concentration $c_{\mathrm{BrO_2,\,max}}$, total concentration $c_{\mathrm{tot,\,max}}$ from (5) and ratio $c_{\mathrm{tot,\,max}}/c_{\mathrm{I}}$ as a function of the initial concentration c_{I} of $NaBrO_2$. The values $c_{\mathrm{BrO_2,\,max}}$ are taken from the least square fit in Figure 6.

$\frac{c_{\mathrm{I}}}{\mathrm{mole}\cdot\mathrm{l}^{-1}}$	$\frac{c_{\mathrm{BrO_2,\,max}}}{\mathrm{mole}\cdot\mathrm{l}^{-1}}$	$\frac{c_{\mathrm{BrO_2,\,max}}}{c_{\mathrm{I}}}$	$\frac{c_{\mathrm{tot,\,max}}}{\mathrm{mole}\cdot\mathrm{l}^{-1}}$	$\frac{c_{\mathrm{tot,\,max}}}{c_{\mathrm{I}}}$
$1.50\cdot10^{-4}$	$2.80\cdot10^{-6}$	0.019	$1.32\cdot10^{-5}$	0.088
$1.00\cdot10^{-4}$	$2.5\ \cdot10^{-6}$	0.025	$1.08\cdot10^{-5}$	0.108
$6.00\cdot10^{-5}$	$2.44\cdot10^{-6}$	0.041	$1.04\cdot10^{-5}$	0.173
$3.16\cdot10^{-5}$	$2.36\cdot10^{-6}$	0.075	$9.80\cdot10^{-6}$	0.310
$1.58\cdot10^{-5}$	$2.05\cdot10^{-6}$	0.130	$7.65\cdot10^{-6}$	0.484
$1.00\cdot10^{-5}$	$1.74\cdot10^{-6}$	0.174	$5.78\cdot10^{-6}$	0.578
$5.00\cdot10^{-6}$	$1.35\cdot10^{-6}$	0.270	$3.78\cdot10^{-6}$	0.756
$3.16\cdot10^{-6}$	$1.10\cdot10^{-6}$	0.348	$2.71\cdot10^{-6}$	0.859
$1.00\cdot10^{-6}$	$5.83\cdot10^{-7}$	0.583	$1.04\cdot10^{-6}$	1.04
$3.16\cdot10^{-7}$	$2.71\cdot10^{-7}$	0.858	$3.69\cdot10^{-7}$	1.17
$1.58\cdot10^{-7}$	$1.62\cdot10^{-7}$	1.025	$1.97\cdot10^{-7}$	1.25
$1.00\cdot10^{-7}$	$1.13\cdot10^{-7}$	1.13	$1.30\cdot10^{-7}$	1.30
$6.31\cdot10^{-8}$	$0.78\cdot10^{-7}$	1.23	$0.86\cdot10^{-7}$	1.37
$3.16\cdot10^{-8}$	$0.43\cdot10^{-7}$	1.36	$0.46\cdot10^{-7}$	1.44

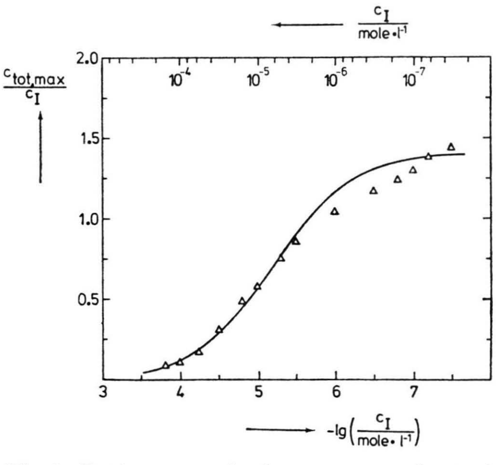

Fig. 8. Ratio $c_{\mathrm{tot,\,max}}/c_{\mathrm{I}}$ ($c_{\mathrm{tot,\,max}}$ = maximum total concentration of Br^{4+}-species according to (2)) as a function of the initial concentration c_{I} of $NaBrO_2$. Circles: experimental values from Table 3. Full line: calculated values based on Eq. (10a) ($F = 0.70$, $k_2'/k_4 = 5.0\cdot10^{-6}\,\mathrm{mole}\cdot\mathrm{l}^{-1}$).

These rate equations are easily solved using the initial conditions $(c_{\mathrm{HBrO_2}})_{t=0} = c_{\mathrm{I}}$ and $(c_{\mathrm{tot}})_{t=0} = 0$. Replacing the expression $(k_2\cdot c_{\mathrm{BrO_3^-}}\cdot c_{\mathrm{H^+}})$ by k_2' the following equation for c_{tot} is obtained [14]

$$c_{\mathrm{tot}} = \frac{k_2'}{k_4}\ln\left[1+\frac{2\,k_4}{k_2'}\,c_{\mathrm{I}}(1-\exp[-k_2't])\right]. \qquad (8)$$

The maximum concentration $c_{\mathrm{tot,\,max}}$ is obtained in the limit $t\to\infty$:

$$c_{\mathrm{tot,\,max}} = \frac{k_2'}{k_4}\ln\left[1+\frac{2\,k_4}{k_2'}\,c_{\mathrm{I}}\right]. \qquad (9)$$

Since we are interested in the ratio $c_{\mathrm{tot,max}}/c_{\mathrm{I}}$ we rewrite (9) in the form

$$\frac{c_{\mathrm{tot,\,max}}}{c_{\mathrm{I}}} = \frac{k_2'}{k_4}\,\frac{1}{c_{\mathrm{I}}}\ln\left[1+2\,\frac{k_4}{k_2'}\,c_{\mathrm{I}}\right]. \qquad (10)$$

From this expression it is clear that the ratio $c_{\mathrm{tot,\,max}}/c_{\mathrm{I}}$ will be 2 in the limit $c_{\mathrm{I}}\to0$. On the other hand, the experimental values plotted in Fig. 8 do not exceed a value of about 1.44; the reason for this discrepancy is not easily to be understood. In spite of this difficulty an attempt was made to fit the experimental values by the equation

$$\frac{c_{\mathrm{tot,\,max}}}{c_{\mathrm{I}}} = F\,\frac{k_2'}{k_4}\,\frac{1}{c_{\mathrm{I}}}\ln\left[1+2\,\frac{k_4}{k_2'}\,c_{\mathrm{I}}\right] \qquad (10\mathrm{a})$$

regarding F and k_2'/k_4 as adjustable parameters. A very good fit is obtained with values $F = 0.70$ and $k_2'/k_4 = 5.0\cdot10^{-6}\,\mathrm{mole}\cdot\mathrm{l}^{-1}$ (Fig. 8, full line).

Discussion

From our experiments conclusions are possible concerning the nature of the reaction products and the stoichiometry as well as the rate constants of the reactions (R2) and (R4).

Reaction (R4)

If a $2.81\cdot10^{-4}$ m solution of $NaBrO_2$ (after removal of the Br^--impurities by addition of $AgNO_3$) is injected into a solution of sulfuric acid, an absorption spectrum is obtained which is identical with the HOBr spectrum (Fig. 3, dashed line). From the absorbance $A = 0.058$ at 300 nm and the extinction coefficient 41 $\mathrm{l}\cdot\mathrm{mole}^{-1}\,\mathrm{cm}^{-1}$ the HOBr concentration is calculated to be $1.41\cdot10^{-4}$ mole/l. This is exactly half the value of the initial concentration of the $NaBrO_2$ injected, as expected from (R4). This is a direct proof that (R4) is quantitatively leading to HOBr, and that no Br_2 is formed. In principle, it should be possible to detect the reaction product BrO_3^- too; because of the overlap of the absorption spectra of HOBr and BrO_3^-, however, the experimental error will be too large to draw quantitative conclusions.

Reaction (R2)

From Fig. 5 it seems to be clear that BrO_2 is a reaction product of reaction (R2). Because of the competitive reaction (R4), HOBr must be formed simultaneously; since BrO_3^- is in large excess, small amounts of HOBr cannot be detected spectroscopically. On the other hand, if Br_2 were present as a reaction product, the shape of the absorption spectrum given in Fig. 5 (circles) should differ significantly from the BrO_2-spectrum (full line) in the region about 400 nm.

From our experiments the equilibrium constant K in (R2b) is found to be $K = 1.5 \cdot 10^{-6}$ mole · l^{-1}. This value differs by 4 orders of magnitude from the value $K = 1/19$ mole · $l^{-1} = 0.053$ mole · l^{-1} reported by Buxton and Dainton [12]. The latter result, however, is not consistent with the procedure described by the authors to evaluate their experiments. If their experimental oscilloscope traces are taken and the absorption values are inserted into their equation for K (Fig. 3, Eq. (10) in [12]), a value $K = 5.3 \cdot 10^{-5}$ mole · l^{-1} is obtained. The residual difference compared to our value may be due to the fact that in our experiments the solvent is sulfuric acid, whereas Buxton and Dainton were using neutral solutions.

In Fig. 8 the best fitting curve for our experimental ratio $c_{\mathrm{tot,max}}/c_{\mathrm{I}}$ is obtained if the value $5.0 \cdot 10^{-6}$ mole l^{-1} is assigned to the ratio k_2'/k_4. In the theory of Field, Kőrös and Noyes, the values $k_2 = 1 \cdot 10^4\, m^{-2}\, s^{-1}$ and $k_4 = 4 \cdot 10^7\, m^{-1}\, s^{-1}$ are assumed [3, 15]; these values are leading to the ratio $k_2'/k_4 = k_2 c_{\mathrm{BrO_3^-}} c_{\mathrm{H^+}}/k_4 = 2.5 \cdot 10^{-4}$ mole · l^{-1}. From our results it must be concluded that the reaction rate of (R2) compared to the reaction rate of (R4) is smaller by two orders of magnitude than assumed by FKN.

On the basis of our ratio k_2'/k_4 the kinetics of the Ce^{3+}/BrO_3^--reaction may be better understood: the autocatalytic formation of Ce^{4+} is slowed down if the competitive reaction (R4) is more important than assumed by FKN, and consequently the calculated BrO_2-concentrations must be significantly lower in accordance with our former experiments [5, 6].

As mentioned above, we failed in proving the exact 2:1-stoichiometry for the production of BrO_2 according to (R2). From Fig. 8 it follows that the ratio of $c_{\mathrm{tot,max}}$ (concentration of Br^{4+}-species formed including the dimer Br_2O_4) to c_{I} (initial concentration c_{I} of the $NaBrO_2$ injected) does not exceed a value of 1.44 in the limit $c_{\mathrm{I}} \to 0$ (in this limit the competitive reaction (R4) is to be neglected); this value is 30% lower than expected from (R2).

Certainly, some sources of error must be discussed. In the low concentration range of our experiments the stock solution of $NaBrO_2$ ($3.39 \cdot 10^{-2}$ m in 0.1 n NaOH) was diluted by a factor of 1000, and the resulting solution was injected into the bromate solution. It was checked spectroscopically that alkaline solutions of low concentration (down to 10^{-5} m) are stable; this check could not be performed, however, if the concentration was lower than 10^{-5} m. As pointed out already, the $NaBrO_2$ used was of 95% purity only. Consequently, the concentration of our stock solution was about 5% lower than assumed, and the ratios $c_{\mathrm{tot,max}}/c_{\mathrm{I}}$ should be corrected by a factor of 1.05. Furthermore, there is some uncertainty with regard to the extinction coefficients of BrO_2. If the values reported by Buxton and Dainton [12] were replaced by the values given by Barat et al. [16], the BrO_2-concentrations experimentally obtained should be larger by a factor of 1.05 than assumed in Table 1; if both corrections are taken into account, there is a 20% discrepancy left only. Moreover, the BrO_2 extinction coefficients have been measured in neutral solution, and they may be changed when sulfuric acid solutions are used.

In spite of these difficulties our experiments indicate that the reaction scheme (R2a), (R2b), (R4) is essentially valid when $HBrO_2$ is reacting with bromate in sulfuric acid solution. In a quantitative respect, the equilibrium constant K in (R2b) is lower by one order of magnitude than measured in neutral solution, and the ratio k_2/k_4 is found to be lower by two orders of magnitude than assumed within the FKN theory. On the basis of our results a quantitative understanding of the autocatalytic formation of Ce^{4+} in the Belousov-Zhabotinsky system may be possible.

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