Formation of BrO$_3^-$ 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$_3^-$ is an intermediate of the reaction. From the maximum concentration of BrO$_3^-$ the equilibrium constant of the BrO$_2$/BrO$_3^-$-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, Körös, and Noyes [3] (FKN-theory) this reaction is assumed to proceed in two elementary steps:

$$\text{Ce}^{3+} + \text{BrO}_2 + \text{H}^+ \rightarrow \text{Ce}^{4+} + \text{HBrO}_2 \quad \text{(R1)}$$

$$\text{HBrO}_2 + \text{BrO}_3^- + \text{H}^+ \rightarrow 2 \text{BrO}_2 + \text{H}_2\text{O} \quad \text{(R2)}$$

In preceding experiments [4, 5, 6] we have been able to detect BrO$_2^-$ formed in this reaction. The reaction products were

$$\text{BrO}_2^- + \text{H}^+ \rightarrow \text{HBrO}_2 \quad \text{(R3)}$$

much faster than all other reactions under consideration.

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ed to be $1.7 \times 10^{-5}$ m, that is about 5%. 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$_2$SO$_4$ 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 $7.2 \times 10^{-4}$ m NaBrO$_2$ solution (in 0.1 m NaOH) were injected (leading to an initial concentration $c_1 = 1.2 \times 10^{-6}$ m); the change $\Delta A$ 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. 1. Absorption spectrum of a 1 m solution of NaBrO$_3$ in 1 m sulfuric acid; optical path length 10 cm. 
Curve 1: NaBrO$_3$, 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.

Fig. 2. Absorption spectrum of the stock solution of NaBrO$_2$ (3.9 $\times$ 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 $\times$ 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].
the HBrO2/BrO3−-reaction was measured at different wavelengths λ, changing λ stepwise from 400 to 600 nm; each time, the maximum value ΔAmax 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 BrO2 reported by Buxton and Dainton [12] (Fig. 5, full line). This proof for the occurrence of BrO2 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] (ε_{488} = 975 l · mole⁻¹ · cm⁻¹) the BrO2-concentrations were calculated (Fig. 4, right scale). Assuming reaction (R2) to be the only reaction in our system, the maximum BrO2-concentration is expected to be twice the initial concentration c1 of NaBrO2. From Fig. 4 it is evident, however, that the maximum value of the BrO2-concentration is c_{BrO2,max} = 0.63 · 10⁻⁶ m only instead of 2.4 · 10⁻⁶ m as expected from the stoichiometry of reaction (R2).

Apparently, the kinetics of the reaction under consideration must be much more complicated than given by (R2). Firstly, reaction (R2) must be modified by including the dimer Br2O4 [3, 12]

\[ \text{HBrO}_2 + \text{BrO}_3^{-} + \text{H}^{+} \xrightarrow{k_1} \text{Br}_2\text{O}_4 + \text{H}_2\text{O}, \]  

(R2a)

\[ \text{Br}_2\text{O}_4 \rightleftharpoons 2\text{BrO}_2. \]  

(R2b)

Secondly, the competitive reaction

\[ 2\text{HBrO}_2 \xrightarrow{k_4} \text{HOBr} + \text{BrO}_3^{-} + \text{H}^{+} \]  

(R4)

must be taken into account [3, 13]. From these equations the yield of BrO2 is expected to be lower than estimated from (R2); this yield should increase with decreasing initial concentration c1 of NaBrO2.

In order to check this modified reaction scheme we have repeated our experiment described above (Fig. 4) by changing the initial concentration c1 in the range from 2.8 · 10⁻⁴ m to 3.1 · 10⁻⁸ m; a strong dependence of the yield c_{BrO2,max}/c1 is to be observed as a function of c1 (Table 1, Figure 6). By similar experiments the equilibrium constant \( K \) in (R2b)

\[ K = \frac{c_{\text{BrO}_2}^2}{c_{\text{BrO}_4}} \]  

(1)

was evaluated: equal amounts of NaBrO2 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 BrO2 (c1 and c2, respectively) was measured (Fig. 7, Table 2). Under these experimental conditions, the initial concentration c1 is the same in each case leading to the same rates of reac-
tions (R2a) and (R4), respectively. The only difference is to be seen in respect to the initial concentration of BrO2: zero concentration before the first injection, concentration $c_1$ before the second injection. If (R2a) and (R2b) are valid the total

Table 2. Maximum concentrations $c_1$ and $c_2$ of BrO2 after the first and second injection of NaBrO2 into a 1 m solution of NaBrO3 in 1 m sulfuric acid (see Fig. 7) as a function of the initial concentration $c_1$ of NaBrO3 (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 $\cdot$ l$^{-1}$ is obtained.

$$
\begin{array}{cccc}
    \text{Table 1. Maximum concentration } \frac{c_{\text{BrO}_2, \text{max}}}{c_1} \text{ and ratio } \frac{c_{\text{BrO}_2, \text{max}}}{c_1} \text{ as a function of the initial concentration } c_1 \text{ of NaBrO}_3 \text{ for the procedure described in Figure 4. } C_{\text{BrO}_2} \text{ was calculated from the change of absorbance } \Delta A \text{ at 488 nm (spectral bandwidth 10 nm as in Fig. 4) on the basis of } \\
    \\ & c_1 & \frac{c_{\text{BrO}_2, \text{max}}}{c_1} & \frac{c_{\text{BrO}_2, \text{max}}}{c_1} \\
    \text{mole \cdot l}^{-1} & \text{mole \cdot l}^{-1} & \text{mole \cdot l}^{-1} \\
    \hline \\
    2.83 \cdot 10^{-4} & 4.60 \cdot 10^{-6} & 0.0163 \\
    1.50 \cdot 10^{-4} & 2.80 \cdot 10^{-6} & 0.0186 \\
    9.06 \cdot 10^{-5} & 2.67 \cdot 10^{-6} & 0.0295 \\
    6.00 \cdot 10^{-5} & 2.44 \cdot 10^{-6} & 0.0407 \\
    1.50 \cdot 10^{-6} & 1.83 \cdot 10^{-6} & 0.122 \\
    9.06 \cdot 10^{-6} & 1.76 \cdot 10^{-6} & 0.194 \\
    6.00 \cdot 10^{-6} & 1.42 \cdot 10^{-6} & 0.237 \\
    4.50 \cdot 10^{-6} & 1.35 \cdot 10^{-6} & 0.300 \\
    2.86 \cdot 10^{-6} & 1.14 \cdot 10^{-6} & 0.398 \\
    1.50 \cdot 10^{-6} & 6.76 \cdot 10^{-7} & 0.450 \\
    1.40 \cdot 10^{-6} & 7.47 \cdot 10^{-7} & 0.533 \\
    1.20 \cdot 10^{-6} & 6.27 \cdot 10^{-7} & 0.523 \\
    9.06 \cdot 10^{-7} & 5.99 \cdot 10^{-7} & 0.661 \\
    6.00 \cdot 10^{-7} & 4.07 \cdot 10^{-7} & 0.678 \\
    2.83 \cdot 10^{-7} & 2.42 \cdot 10^{-7} & 0.855 \\
    1.36 \cdot 10^{-7} & 1.38 \cdot 10^{-7} & 1.015 \\
    9.06 \cdot 10^{-8} & 1.05 \cdot 10^{-7} & 1.16 \\
    6.12 \cdot 10^{-8} & 7.88 \cdot 10^{-8} & 1.29 \\
    4.50 \cdot 10^{-8} & 6.04 \cdot 10^{-8} & 1.34 \\
    3.42 \cdot 10^{-8} & 4.19 \cdot 10^{-8} & 1.23 \\
    3.06 \cdot 10^{-8} & 4.22 \cdot 10^{-8} & 1.38 \\
\end{array}
$$

concentration of Br$^{4+}$-species

$$
    c_{\text{tot}} = c_{\text{BrO}_3} + 2 c_{\text{BrO}_4}
$$

is expected to be doubled when the first injection of NaBrO2 is followed by a second one:

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

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

$$
    K = \frac{(2 c_1^2 - c_2^2)}{(c_1 - c_1)}.
$$

Using the values given in Table 2 a mean value of $K = 1.5 \cdot 10^{-6}$ mole $\cdot$ 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:

$$
    c_{\text{tot, max}} = c_{\text{BrO}_2, \text{max}} + 2 c_{\text{BrO}_4, \text{max}}/K.
$$
c_{tot,max} is listed in Table 3 (column 4). The ratio $c_{tot,max}/c_I$ (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 $c_{tot,max}/c_I$ 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:

$$\frac{dc_{HBrO}}{dt} = -k_2 c_{BrO_2}c^2H^+ - 2k_4 c^2_{HBrO}, \quad (6)$$

$$\frac{dc_{tot}}{dt} = 2k_2 c_{BrO_2}c^2H^+ - c_{HBrO}. \quad (7)$$

These rate equations are easily solved using the initial conditions ($c_{HBrO}$)$_t=0 = c_I$ and ($c_{tot}$)$_t=0 = 0$. Replacing the expression $(k_2 \cdot c_{BrO_2} \cdot c_{H^+})$ by $k'_2$ the following equation for $c_{tot}$ is obtained [14]

$$c_{tot} = \frac{k'_2}{k_4} \ln \left[ 1 + \frac{2k_4}{k'_2} c_I \left(1 - \exp(-k'_2t)\right) \right]. \quad (8)$$

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

$$c_{tot,max} = \frac{k'_2}{k_4} \ln \left[ 1 + \frac{2k_4}{k'_2} c_I \right]. \quad (9)$$

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

$$\frac{c_{tot,max}}{c_I} = \frac{k'_2}{k_4} \frac{1}{c_I} \ln \left[ 1 + 2 \frac{k_4}{k'_2} c_I \right]. \quad (10a)$$

From this expression it is clear that the ratio $c_{tot,max}/c_I$ will be 2 in the limit $c_I \to 0$. 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

$$\frac{c_{tot,max}}{c_I} = F \frac{k'_2}{k_4} \frac{1}{c_I} \ln \left[ 1 + 2 \frac{k_4}{k'_2} c_I \right] \quad (10a)$$

regarding $F$ and $k'_2/k_4$ as adjustable parameters. A very good fit is obtained with values $F = 0.70$ and $k'_2/k_4 = 5.0 \cdot 10^{-6}$ mole $\cdot 1^{-1}$ (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 $2.81 \cdot 10^{-4}$ 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 $41 \cdot 1$ mole $\cdot 1^{-1}$ cm$^{-1}$ the HOBr concentration is calculated to be $1.41 \cdot 10^{-4}$ 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 HOBBr, 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 HOBBr 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), HOBBr must be formed simultaneously; since BrO\(_3^-\) is in large excess, small amounts of HOBBr 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 \(K = 1.5 \times 10^{-6}\) mole \(\text{l}^{-1}\). This value differs by 4 orders of magnitude from the value \(K = 1/19 \text{ mole } \text{l}^{-1} = 0.053 \text{ mole } \text{l}^{-1}\) 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 \(K = 5.3 \times 10^{-5}\) mole \(\text{l}^{-1}\) 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 \(c_{\text{tot, max}}/c_1\) is obtained if the value \(5.0 \times 10^{-6}\) mole \(\text{l}^{-1}\) is assigned to the ratio \(k_2^*/k_4\). In the theory of Field, Kőröös and Noyes, the values \(k_2 = 1 \times 10^4 \text{ m}^{-2} \text{s}^{-1}\) and \(k_4 = 4 \times 10^7 \text{ m}^{-1} \text{s}^{-1}\) are assumed [3, 15]; these values are leading to the ratio \(k_2^*/k_4 = k_2 c_{\text{BrO}_3^-} \cdot c_{\text{HBr}}/k_4 = 2.5 \times 10^{-4}\) mole \(\text{l}^{-1}\). 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\(^{3+}/\text{BrO}_3^-\)-reaction may be better understood: the autocalytic 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 \(c_{\text{tot, max}}\) (concentration of Br\(^{4+}\)-species formed including the dimer Br\(_2\)O\(_4\)) to \(c_1\) (initial concentration \(c_1\) of the NaBrO\(_2\) injected) does not exceed a value of 1.44 in the limit \(c_1 \to 0\) (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 \times 10^{-2} \text{ m} in 0.1 \text{ 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 50\%/ lower than assumed, and the ratios \(c_{\text{tot, max}}/c_1\) 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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