Formation of BrO_2 in the Belousov-Zhabotinsky-System Reaction of Aliphatic Alcohols with Bromate

H. D. Försterling, H. J. Lamberz, and H. Schreiber
Fachbereich Physikalische Chemie, Philipps-Universität, Marburg

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BrO_2 was found as an intermediate in the reaction of bromate with alcohols (e.g. methanol, isopropanol, allylalcohol) or ketones (e.g. acetone). This reaction may be important for the understanding of bromate driven oscillators.

Bromate driven chemical oscillators are widely used in the investigation of oscillating chemical reactions. So far three types of oscillators are known:

1) systems containing dicarbonic acids and inorganic redox couples (e.g. malonic acid and Ce^{3+}/Ce^{4+}) [1];

2) systems containing inorganic redox couples only (e.g. Ce^{3+}/Ce^{4+}) [2];

3) systems containing aromatic compounds (e.g. phenol) only [3]. In the latter case it is assumed that these compounds are involved in an autocatalytic reaction step including the species BrO_2.

Unfortunately, consecutive reactions following the phenol oxidation are leading to strongly coloured products making it impossible to detect BrO_2 spectroscopically. For this reason the reaction of aliphatic alcohols (instead of phenols) with bromate in sulfuric acid solution was studied in more detail.

Experiments

It is well known [4] that aliphatic alcohols (e.g. methanol) react with $HBrO_3$, if the alcohol is in excess; $HBrO_2$ is assumed to be a reaction product.

$$CH_3OH + HBrO_3 \rightarrow CH_2O + HBrO_2 + H_2O\,. \qquad (R\,1)$$

Since in all bromate driven oscillators bromate is in excess, the procedure was modified by injecting a small amount of CH_3OH (initial concentration in the range $4.2 \cdot 10^{-4}$ to $4.2 \cdot 10^{-3}$ m) into an excess of $HBrO_3$ (1 m solution of $NaBrO_3$ in 1 m sulfuric acid*). In this case the aldehyd formed in (R 1) will also react with $HBrO_3$, and formic acid is expected to be the final product, according to the overall reaction

$$CH_3OH + 2\,HBrO_3 \rightarrow HCOOH + 2\,HBrO_2 + H_2O\,. \qquad (R\,2)$$

On the other hand, it is well known [5, 6] that $HBrO_2$ reacts according to (R 3) – (R 5):

$$HBrO_2 + HBrO_3 \rightleftarrows Br_2O_4 + H_2O\,, \qquad (R\,3)$$

$$Br_2O_4 \rightleftarrows 2\,BrO_2\,, \qquad (R\,4)$$

$$2\,HBrO_2 \rightarrow HBrO_3 + HOBr\,. \qquad (R\,5)$$

Following the reaction scheme (R 2) to (R 5) BrO_2 is expected as an intermediate and HOBr as a final product. In order to detect HOBr and BrO_2 experimentally, the absorbance of the reaction mixture was measured at 330 nm (HOBr-absorbance ΔA_{330}) and at 550 nm (BrO_2-absorbance ΔA_{550}) simultaneously (Figure 1). It is to bee seen that ΔA_{330} increases monotonically, and that ΔA_{550} shows a maximum value. A spectrum of the solution was taken at the end of the reaction and compared in Fig. 2 to the absorption spectrum of HOBr [5, 8]. Evidently at least one additional compound beside HOBr must be present. If it is assumed that this compound is Br_2, the concentration $c_{Br_2} = 2 \cdot 10^{-5}$ mol l^{-1} is calculated from $\Delta A = 0.026$ and $\varepsilon_{Br_2} = 116$ l mol^{-1} cm^{-1} at 440 nm [5]. Taking this value and subtracting the Br_2-contribution from the spectrum of the solution, a fairly good agreement with the HOBr-spectrum is

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* $NaBrO_3$ (p.a. Fluke) was three times recrystallized from hot water. In all experiments oxygen was excluded by bubbling nitrogen through the stock solution for 30 min. The solution was transferred into the sample cell using a flow of N_2.

Reprint requests to Prof. Dr. H. D. Försterling, Fachbereich Physikalische Chemie, Hans-Meerwein-Straße, D-3550 Marburg.

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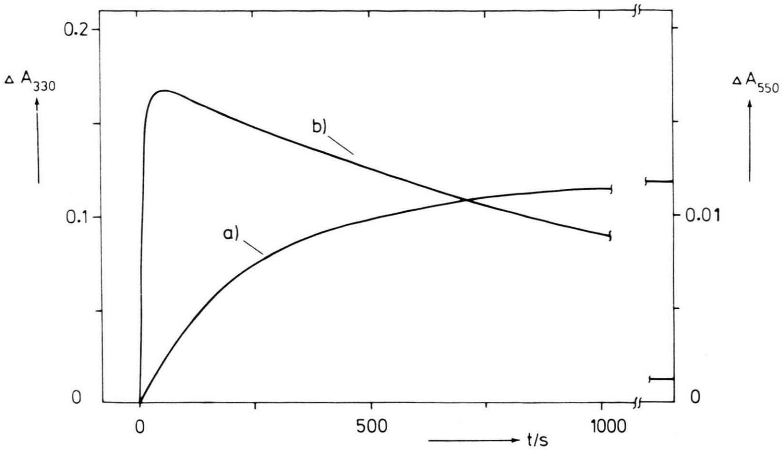

Fig. 1. Change of the absorbance ΔA in the reaction of CH_3OH (initial concentration $4.2 \cdot 10^{-4}$ mol l^{-1}) with bromate (1 m) in 1 m sulfuric acid solution. The solution was bubbled with nitrogen to exclude oxygen from the air. Temperature 20 °C, optical path length 10 cm. – Curve a) (left scale): monitoring wavelength 330 nm, double beam spectrophotometer Beckman M VI, reference 1 m $NaBrO_3$ in 1 m sulfuric acid. The final value $\Delta A_\infty = 0.12$ is reached at $t = 2000$ s. – Curve b) (right scale): monitoring wavelength 550 nm, dual wavelength spectrophotometer, reference wavelength 670 nm [7]. The final value $\Delta A_\infty = 0.001$ is reached at $t = 2500$ s.

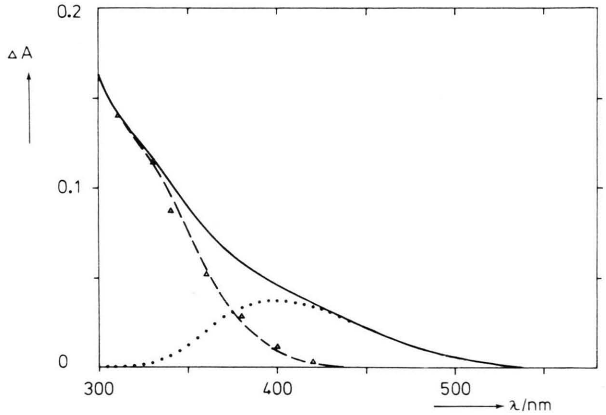

Fig. 2. Absorption spectrum of the reaction mixture in Fig. 1 at the end of the reaction (solid line) compared to the spectrum of HOBr (dashed line). If the contribution of Br_2 (dotted line) is subtracted from the total absorbance, the triangles are obtained. Optical path length 10 cm, reference 1 m $NaBrO_3$ in 1 m sulfuric acid.

obtained (Fig. 2, triangles). From the final value $\Delta A_{330,\infty} = 0.12$ and $\varepsilon_{HOBr} = 32$ l mol^{-1} cm^{-1} the final concentration of HOBr ($c_{HOBr,\infty}$) was calculated and compared to the initial concentration of CH_3OH (c_0); Table 1 shows that the ratio $c_{HOBr,\infty}/c_0$ is about 90% of the value expected from (R2) to (R5). From this experiment it is concluded that HOBr is the main reaction product, and that only a small amount of Br_2 is formed in a side reaction.

A second spectrum was taken 30 to 110 s after starting the reaction (according to Fig. 1, ΔA_{550} is constant within 2% during this time). This spectrum (triangles in Fig. 3) turned out to be identical with the BrO_2 spectrum reported by Buxton and Dainton [9].

Table 1. Absorbance change $\Delta A_{330,\infty}$ and final concentration $c_{HOBr,\infty}$ of HOBr in the reaction of CH_3OH with bromate for different initial concentrations c_0 of CH_3OH (all concentrations in mol l^{-1}). Optical path length 10 cm.

c_0	$\Delta A_{330,\infty}$	$c_{HOBr,\infty}$	$c_{HOBr,\infty}/c_0$
$4.2 \cdot 10^{-4}$	0.12	$3.8 \cdot 10^{-4}$	0.90
$2.1 \cdot 10^{-3}$	0.57	$1.8 \cdot 10^{-3}$	0.86
$4.2 \cdot 10^{-3}$	1.16	$3.6 \cdot 10^{-3}$	0.86

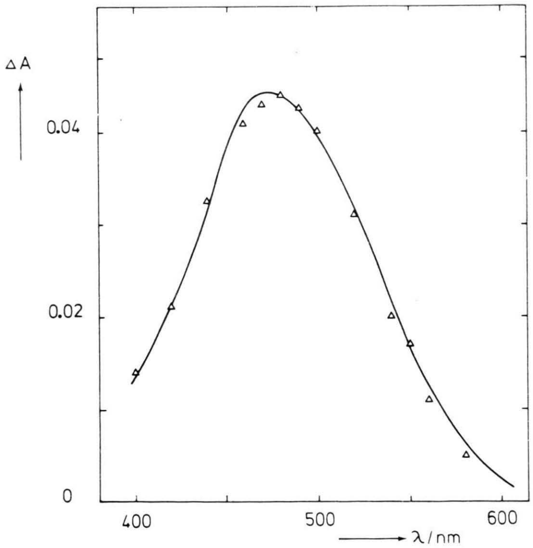

Fig. 3. Absorption spectrum of the reaction mixture in Fig. 1 taken 30 to 110 s after starting the reaction (triangles) compared to the absorption spectrum of BrO_2 (solid line). The values from 400 to 450 nm had to be slightly corrected for the absorption of HOBr formed during the run of the spectrum. Optical path length 10 cm, reference 1 m $NaBrO_3$ in 1 m sulfuric acid.

Formation of HOBr

The maximum absorbance of BrO_2 in Fig. 1 is 0.0165; taking $\varepsilon_{BrO_2} = 367\ \mathrm{mol^{-1}\,cm^{-1}}$ [9] the maximum BrO_2 concentration is calculated to be $4.4 \cdot 10^{-6}$ m. This is about 1% of $c_{HOBr,\infty}$ only; consequently, the reactions (R3) and (R4) may be omitted when the stoichiometry of the overall reaction

$$CH_3OH + HBrO_3 \rightarrow HCOOH + HOBr + H_2O \quad \text{(R6)}$$

is under consideration, and HOBr is expected to be formed according to a first order kinetics:

$$\frac{\mathrm{d}c_{HOBr}}{\mathrm{d}t} = -\frac{\mathrm{d}c_{CH_3OH}}{\mathrm{d}t} = k_6\, c_{HBrO_3}\, c_{CH_3OH} = k_6'\, c_{CH_3OH} \qquad (1)$$

($k_6' = k_6\, c_{HBrO_3}$). Indeed, from a first order plot of the experimental HOBr-curve in Fig. 1, a first order rate constant $k_6' = 3.8 \cdot 10^{-3}\ \mathrm{s^{-1}}$ is obtained (Figure 4). This value is in agreement with the value given in [4].

Formation of BrO_2

Since the concentration of BrO_2 is small compared to the HOBr concentration, the maximum BrO_2 concentration may easily be estimated by using the stationary state approximation. From R2 to R5 the following differential equations are derived ($k_3' = k_3\, c_{HBrO_3}$):

$$\frac{\mathrm{d}c_{HBrO_2}}{\mathrm{d}t} = 2\,k_6'\, c_{CH_3OH} - 2\,k_5\, c^2_{HBrO_2} - k_3'\, c_{HBrO_2} + k_{-3}\, c_{Br_2O_4}, \qquad (2)$$

$$\frac{\mathrm{d}c_{Br_2O_4}}{\mathrm{d}t} = k_3'\, c_{HBrO_2} - k_{-3}\, c_{Br_2O_4} - k_4\, c_{Br_2O_4} + k_{-4}\, c^2_{BrO_2}, \qquad (3)$$

$$\frac{\mathrm{d}c_{BrO_2}}{\mathrm{d}t} = 2\,k_4\, c_{Br_2O_4} - 2\,k_{-4}\, c^2_{BrO_2}. \qquad (4)$$

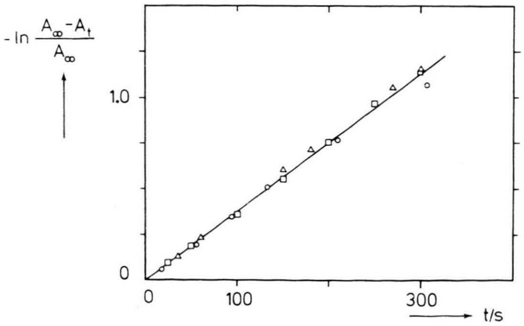

Fig. 4. First order plot of the HOBr-absorbance in the reaction of CH_3OH with bromate (initial concentrations of CH_3OH $4.2 \cdot 10^{-4}$ m (circles), $2.1 \cdot 10^{-3}$ m (squares) and $4.2 \cdot 10^{-3}$ m (triangles).

In the stationary state the time derivatives of $HBrO_2$, Br_2O_4 and BrO_2 are zero. Indicating stationary state concentrations with the index *s* and treating (R4) as a fast equilibrium, the expressions

$$c_{HBrO_2,s} = \sqrt{\frac{k_6'}{k_5}} \cdot \sqrt{c_{CH_3OH}}, \qquad (5)$$

$$c_{BrO_2,s} = \sqrt{\sqrt{k_6'} \cdot \frac{k_4}{k_{-4}} \cdot \frac{k_3'}{k_5} \cdot \frac{\sqrt{k_5}}{k_{-3}}} \cdot \sqrt[4]{c_{CH_3OH}}, \qquad (6)$$

$$c_{Br_2O_4,s} = \frac{k_{-4}}{k_4} \cdot c^2_{BrO_2,s} \qquad (7)$$

are obtained.

According to Fig. 1 the maximum concentration of BrO_2 is reached 30 s after starting the reaction, and c_{CH_3OH} may be replaced by the initial concentration c_0. For numerical evaluation, the values of the rate constants must be known. k_6' was obtained as described above ($3.8 \cdot 10^{-3}\ \mathrm{s^{-1}}$). In a preceding paper [5] the ratios $k_4/k_{-4} = 1.5 \cdot 10^{-6}\ \mathrm{mol\,l^{-1}}$ and $k_3/k_5 = 5 \cdot 10^{-6}\ \mathrm{mol\,l^{-1}}$ were determined from experiments on the reaction of bromous acid with bromate. From the same kind of experiments $k_{-3} = 5\ \mathrm{s^{-1}}$ was obtained [6], if the value $k_5 = 4 \cdot 10^7\ \mathrm{l\,mol^{-1}\,s^{-1}}$ given by Field, Kőrös and Noyes [1] was used. Inserting these values into the expressions (5) to (7), stationary state concentrations were calculated and compared to the experimental value for BrO_2 (Table 2). Nearly the same values were obtained if the rate equations (1) to (4) were solved numerically. Fig. 1 shows that ΔA_{550} reaches the final value 0.001 instead of zero as expected from the reaction scheme. This difference is due to the absorbance of Br_2 formed in the side reaction.

Table 2. Calculated stationary state concentrations of $HBrO_2$, BrO_2 and Br_2O_4 and experimental values for BrO_2 for different initial concentrations c_0 of CH_3OH (all concentrations in $\mathrm{mol\,l^{-1}}$).

c_0	Calculated (5) to (7)			Experimental c_{BrO_2}
	c_{HBrO_2}	c_{BrO_2}	$c_{Br_2O_4}$	
$4.2 \cdot 10^{-4}$	$2.0 \cdot 10^{-7}$	$3.5 \cdot 10^{-6}$	$8.2 \cdot 10^{-6}$	$4.4 \cdot 10^{-6}$
$2.1 \cdot 10^{-3}$	$4.5 \cdot 10^{-7}$	$5.2 \cdot 10^{-6}$	$1.8 \cdot 10^{-5}$	$7.2 \cdot 10^{-6}$
$4.2 \cdot 10^{-3}$	$6.3 \cdot 10^{-7}$	$6.2 \cdot 10^{-6}$	$2.6 \cdot 10^{-5}$	$8.2 \cdot 10^{-6}$

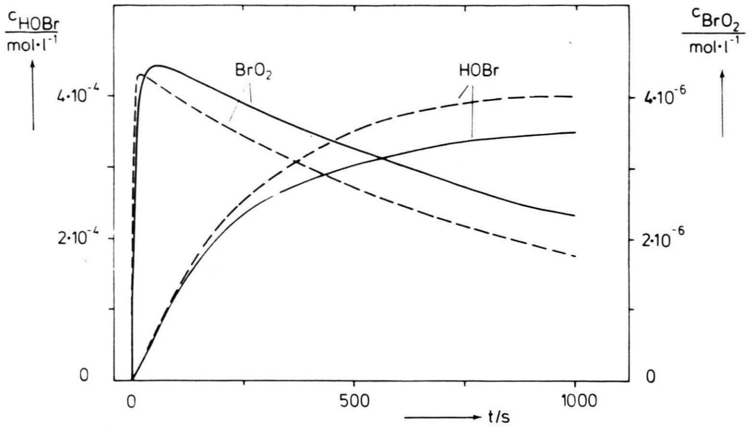

Fig. 5. Kinetics of the formation of HOBr and BrO_2 in the reaction of CH_3OH ($c_0 = 4.2 \cdot 10^{-4}$ mol l^{-1}) with bromate (1 m) in 1 m sulfuric acid solution. Solid line: experiment (temperature 20 °C). Dashed line: computer simulation based on (R2) to (R5) with $k_5 = 4 \cdot 10^8$ l mol^{-1} s^{-1} and $k_{-3} = 10$ s^{-1}. – The calculated curve for HOBr is about 10% higher than experiment in agreement with Table 1. The calculated curve for BrO_2 reaches its maximum value about 40 s earlier than experiment. The reason for this difference is not yet clear.

Discussion

From Table 1 it is to be seen that the amount of HOBr formed in the reaction is about 90% of the value expected from (R2) to (R5). This result indicates that (R2) to (R5) is the main reaction path, accompanied by minor side reactions which were not investigated in more detail. The maximum BrO_2 concentrations calculated in Table 2 are about 25% smaller than the experimental values. This result may be due to the uncertainty in the value of the rate constant k_5. If k_5 is assumed to be larger by a factor of ten (in this case k_{-3} must be increased to 10 s^{-1} [10]) the maximum BrO_2 concentration and the overall kinetics are in a fair agreement with theory (Figure 5). If k_5 is assumed to be smaller by a factor of ten, the discrepancy between experiment and theory is significantly increased (BrO_2 concentration 50% smaller than experiment) indicating that (R5) must be much faster than recently concluded by Noszticzius [11] from potential measurements using ion sensitive electrodes. The first order formation of HOBr over a wide range of initial concentrations indicates that the main reaction step is the direct attack of CH_3OH on $HBrO_3$. In the case of an autocatalytic mechanism (direct attack of BrO_2 [3]) the reaction rate is expected to increase with increasing CH_3OH initial concentration, contrary to our experiments.

It turned out that the reaction scheme (R1) – (R5) is not restricted to methanol as a reducing agent. Similar kinetics are observed if methanol is replaced by isopropanol, allylalcohol or acetone. In the latter case this result may be important if in the Belousov-Zhabotinsky system malonic acid is replaced by oxalic acid and acetone is used to eliminate Br_2 from the solution [12].

By the procedure described above nearly constant steady state concentrations of BrO_2 are obtained for at least 100 s. In this way fast reactions of BrO_2 with reducing or oxidizing agents may be easily investigated. Results on the reaction of BrO_2 with Ce^{3+} will be reported in a subsequent paper.

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