HBrO₂/Ce⁴⁺ Reaction and HBrO₂ Disproportionation Measured in Sulfuric Acid Solution at Different Acidities

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The rate of the reaction of bromous acid with Ce⁴⁺, which is responsible for the slowing down of the autocatalytic oxidation of Ce³⁺ by bromate in the Belousov–Zhabotinsky reaction, is measured directly by spectroscopic methods in sulfuric acid medium at different acidities. BrO₂ radicals are identified as primary reaction products. The rate constant decreases from 40 000 M⁻¹ s¹ in 0.3 M H₂SO₄ to 1000 M⁻¹ s⁻¹ in 3 M H₂SO₄. The reaction is slowed down upon the addition of NaClO₄. The observations are discussed on the assumption that the active cerium species are sulfato complexes with one or two sulfato groups; the equilibrium constants for the complex formation increase with increasing ionic strength leading to smaller concentrations of the active sulfato complexes. Additionally, the disproportionation reaction of HBrO₂ was investigated in the same range of acidities. The rate of this reaction increases from 1300 M⁻¹ s⁻¹ in 0.3 M H₂SO₄ to 12 000 M⁻¹ s⁻¹ in 3.0 M H₂SO₄. We suggest that the rate-determining step is a reaction of a protonated with an unprotonated HBrO₂ by Ce⁴⁺. These results are important for the understanding of the autocatalytic process in the Belousov–Zhabotinsky reaction, especially at high sulfuric acid concentrations, and for the study of nonbromide controlled oscillations.

1. Introduction

The autocatalytic oxidation of Ce^{3+} by acidic bromate constitutes an essential part of the Belousov–Zhabotinsky (BZ) system. This reaction proceeds in the following steps¹⁻⁴ (numbering of the reactions according to ref 2; for rate constants, see Table I):

$$2HBrO_2 \rightleftharpoons HOBr + HBrO_3$$
 (R4)

$$HBrO_{2} + BrO_{3}^{-} + H^{+} \rightleftharpoons Br_{2}O_{4} + H_{2}O \qquad (R5')$$

$$Br_2O_4 \rightleftharpoons 2BrO_2$$
 (R5")

$$Ce^{3+} + BrO_2 + H^+ \Rightarrow Ce^{4+} + HBrO_2$$
 (R6)

It must be pointed out that for reaction R6 only the forward rate constant k_6 was obtained from a direct experiment.⁵ The reverse rate constant k_{-6} as given in ref 2, however, was deduced from indirect thermodynamic data only.

The first investigators who followed (R-6) in a direct kinetic experiment (stopped flow technique) were Sullivan and Thompson.⁶ Since Schlieren effects occurred during the mixing of the components (due to the different refractive indices of the solutions), measurements in sulfuric acid medium above $[H_2SO_4] = 0.3$ M, the concentration range typical for the Belousov-Zhabotinsky reaction,⁷ were not possible.

From these considerations it is necessary to reexamine (R-6) by an experimental technique in which Schlieren effects can be avoided. This was done first by Lamberz.⁸ In his experiments a small volume of NaBrO₂ solved in 0.1 M NaOH was injected into a large volume of a solution of Ce(SO₄)₂ in 1 M sulfuric acid. Ce⁴⁺ was in excess compared to NaBrO₂, and the small change of [Ce⁴⁺] was measured (dual wavelength technique). From this experiment it was evident that (R-6) proceeds fast enough even in 1 M sulfuric acid medium. The interpretation of Lamberz's results was difficult, however, since he believed that (R4), the disproportionation of bromous acid, is very fast. In the meantime, the rate of this reaction was measured directly by Noszticzius et al.⁹ and by Ariese and Ungvárai-Nagy.¹⁰ From their results it is clear that (R4) cannot affect the measurements of (R-6) as strongly as was assumed by Lamberz.

TABLE I:	Rate	Con	stants	k3 t	0 <i>k</i> 6	for	the	Autocatalyti	c
Oxidation	of Ce ³⁺	by	Broma	ıte"				•	

forward	reverse
$k_4 = 3 \times 10^3 \mathrm{M}^{-1} \mathrm{s}^{-1}$	$k_{-4} = 1 \times 10^{-8} \mathrm{M}^{-2} \mathrm{s}^{-1}$
$k_{5'} = 33 \text{ M}^{-2} \text{ s}^{-1}$	$k_{-5'} = 2.2 \times 10^3 \mathrm{s}^{-1}$
$k_{5''} = 7.4 \times 10^4 \mathrm{s}^{-1}$	$k_{-5''} = 1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$
$k_6 = 6.2 \times 10^4 \mathrm{M}^{-2} \mathrm{s}^{-1}$	$k_{-6} = 8.9 \times 10^3 \mathrm{M}^{-1} \mathrm{s}^{-1}$

^a The values refer to a temperature of 20 °C [3], [4]. $k_{-6} = 8.9 \times 10^3$ M⁻¹ s⁻¹ is the value originally suggested in [2].

2. Chemicals and Experimental Methods

H₂SO₄ (96%), NaOH, Na₂SO₄, Ce(SO₄)₂·4H₂O, Ce₂(SO₄)₃ (all Fluka pa.) were used without further purification. NaBrO₂ was prepared following the procedure of Noszticzius et al.;9 the purity of the product was checked spectroscopically as described in ref 11. The NaBrO₂ solution was used only if the ratio $\epsilon_{296nm}/$ ϵ_{330nm} was in the range from 1.29 to 1.31. The concentration of the stock solution was $[NaBrO_2] = 0.042 \text{ M}$; 500 μ L of the stock solution was diluted by 9.5 mL of a solution containing 0.02 M NaOH and different concentrations of Na₂SO₄ (resulting sodium bromite concentration 0.0021 M); by changing [Na₂SO₄] from 0.5 to 1.5 M, the refractive index of this solution could be adjusted to the refractive index of sulfuric acid solutions in the concentration range from 0.5 to 2.0 M. This way Schlieren effects after the mixing of the compounds, which would disturb the optical measurement, can be avoided; since only a small volume of the alkaline NaBrO₂ solution (about 1 mL) is injected into a large volume of a Ce4+-H₂SO₄ mixture (about 140 mL), no significant change of the sulfato concentration occurs. All solutions were prepared from doubly distilled water. The measurements were carried out at 20 °C (±0.1 °C).

The absorption spectra were measured with a Hewlett-Packard HP8452A diode-array spectrophotometer; the kinetics were followed using the same spectrophotometer or a homemade dual wavelength fiber optics spectrophotometer.¹² The homemade spectrophotometer was used when high sensitivities were needed (e.g. Figure 7b, measured absorbances below 5×10^{-4}); this spectrometer was equipped with two dual wavelength channels. The spectrophotometers were equipped with homemade cell holders for cells up to 10.8-cm path length. The solutions in the cells were mixed by a magnetic stirrer, the temperature was

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Figure 1. Absorption spectrum of HBrO₂ in 0.5 M sulfuric acid. The spectrum was taken 3 s after the injection of 700 μ L of a 0.002 M solution of NaBrO₂ (solved in a mixture of 0.01 M NaOH and 0.5 M Na₂SO₄) into 140 mL of a well-stirred solution of 0.5 M H₂SO₄ (initial concentration of HBrO₂ after mixing, 1×10^{-5} M) and multiplied by a factor of 1.08 to extrapolate to zero time. The scan time was 1 s; the optical path length was 10.8 cm. From A = 0.076 at 240 nm we calculate the extinction coefficient $\epsilon_{240} = 700$ M⁻¹ cm⁻¹.

controlled electronically. The data were stored and evaluated in the memory of an IBM PS/2 computer. The numerical integration of the kinetic differential equations was performed with the program DIFFGL, which is based on Gear's method.¹³

3. Disproportionation of HBrO₂ at Low Initial Concentrations and at Different Acidities

In the experiments of Ariese and Ungvárai-Nagy¹⁰ reaction R4, the disproportionation of HBrO2, was studied spectrophotometrically at high HBrO₂ initial concentrations (2×10^{-5} to 2×10^{-3} M) in 0.5 M sulfuric acid. We extended these experiments to initial concentrations of HBrO2 in the range from 2×10^{-6} to 2×10^{-5} M (a similar range was used in the electrochemical experiments by Noszticzius et al.9) and to sulfuric acid concentrations in the range from 0.5 to 2 M. In Figure 1 an absorption spectrum of HBrO₂ is displayed. As already outlined in ref 10, the best wavelength to follow the disproportionation reaction is 240 nm. For the detection of the absorbance change of HBrO₂ during the disproportionation reaction the sensitive dual wavelength technique¹² (HP8452A spectrophotometer) was used. Alkaline solutions of NaBrO2 were injected into sulfuric acid solutions, and the change of the absorbance A at 240 nm was recorded. A typical result for the initial concentration $[NaBrO_2]_0 = 2 \times 10^{-5} M \text{ in } 1 M H_2SO_4 \text{ is displayed}$ in Figure 2a. A sudden increase and a slow decay of A are observed. The final value A_{∞} corresponds to the absorbance of the reaction products HOBr and HBrO₃. From the measured absorbance we calculate the concentration of $HBrO_2$ by

$$[HBrO_{2}] = [HBrO_{2}]_{0}(A - A_{\infty})/(A_{0} - A_{\infty})$$
(1)

with A, A_0 , and A_{∞} = absorbances at time t, at zero time, and at infinite time and $[HBrO_2]_0$ = initial concentration of HBrO₂. For the experiment in Figure 2 the concentration c of HBrO₂ is displayed in Figure 3 (solid line).

If (R4) is treated as a second-order reaction

$$\frac{\mathrm{d}[\mathrm{HBrO}_2]}{\mathrm{d}t} = -2k_4[\mathrm{HBrO}_2]^2 \tag{2}$$

we expect

$$\frac{1}{[\text{HBrO}_2]} = \frac{1}{[\text{HBrO}_2]_1} + 2k_4(t - t_1)$$
(3)

 $([HBrO_2]_1 = \text{concentration of } HBrO_2 \text{ at time } t_1 \text{ when the evaluation of the kinetic data is started}). From (1), (2), and (3)$



Figure 2. Measured absorbance A at $\lambda = 240$ nm (dual wavelength technique, reference wavelength 400 nm, diode array spectrometer) during the disproportionation of HBrO₂ in 1 M sulfuric acid solution as a function of time (curve a, left-hand scale) at 20 °C and a check for a second-order reaction by plotting the quantity G in eq 4 as a function of time (curve b, right-hand scale). The vertical bars indicate the deviation from the straight line in different measurements. The initial concentration of HBrO₂ was 2×10^{-5} M (0.815 mL of a 3.44 $\times 10^{-3}$ M NaBrO₂ solution in a mixture of 0.01 M NaOH and 0.5 M Na₂SO₄ were injected into 140 mL of a well-stirred solution of 1 M H₂SO₄). The optical path length of the cell was 10.8 cm. The values used for plotting the straight line (b) and for the evaluation of the rate constant k_4 are $A_0 = 0.151$ (calculated from [HBrO₂]₀ = 2×10^{-5} M, d = 10.8 cm, and $e_{240} = 700$ M⁻¹ cm⁻¹), $A_1 = 0.105$ at $t_1 = 2.4$ s, and $A_{\infty} = 0.019$.



Figure 3. Decay of HBrO₂ (initial concentration 2×10^{-5} M, 1 M sulfuric acid) at 20 °C: solid line, concentration c of HBrO₂ obtained from the measured absorbance A (Figure 2), using eq 1 with $A_0 = 0.151$ (calculated as in Figure 1) and $A_{\infty} = 0.017$; dots, concentration c calculated from the second-order rate law (3). The rate constant k_4 was adjusted to k_4 = 4.5×10^3 M⁻¹ s⁻¹ to fit the experimental curve; this value is larger by 20% compared to the value obtained from the straight line in Figure 2.

we get

$$G = \frac{A_1 - A_{\infty}}{A - A_{\infty}} - 1 = 2k_4 [HBrO_2]_0 \frac{A_1 - A_{\infty}}{A_0 - A_{\infty}} (t - t_1) \quad (4)$$

 $G = (A_1 - A_{\infty})/(A - A_{\infty}) - 1$ is plotted in Figure 2b as a function of time. From the slope 0.095 s⁻¹ of the straight line and the additional data given in the legend of Figure 2 we calculate k_4 = 3700 M⁻¹ s⁻¹. This value is comparable to the Noszticzius et al.⁹ value of 3800 M⁻¹ s⁻¹ measured at 25 °C in 1.5 M H₂SO₄ and larger than the Ariese-Ungvárai-Nagy¹⁰ value of 2200 M⁻¹ s⁻¹ measured in 0.5 M H₂SO₄ at 24 °C.

During the evaluation of the data it turned out that the quality and the slope of the straight lines according to (4) were very sensitive to small changes in the final value A_{∞} . It was more reliable to compare the measured concentration curves directly to the curves calculated from the second-order rate law (3) with k_4 adjusted to give the best fit. The result for 1 M H₂SO₄ can be seen in Figure 3 (dots). The best fit for k_4 is 4500 M⁻¹ s⁻¹; this is about 20% more than obtained from the straight line in Figure 2b.

Similar measurements were performed with the same initial concentration of $HBrO_2$, but at different acidities, ranging from 0.5 to 2.0 M sulfuric acid. The results are displayed in Figure 4a; the rate constants k_4 are summarized in Table II, column 4.



Figure 4. Comparison of measured (a) and calculated (b) kinetics of the decay of bromous acid at 20 °C and at different acidities: sulfuric acid concentrations of 0.5 (1), 1.0 (2), 1.5 (3), and 2.0 M (4). The initial concentration of bromous acid is 1×10^{-5} M. The concentration *c* is the total concentration of bromous acid. The experimental HBrO₂ concentrations were obtained from the measured absorbances using the final value $A_{\rm m} = 0.0084$. This is just the value expected from the absorbances of the final products HOBr ($\epsilon_{240} = 70$ M⁻¹ cm⁻¹) and HBrO₃ ($\epsilon_{240} = 85$ M⁻¹ cm⁻¹). The calculated concentrations were obtained from reactions R4a and R4b, using the values $K_{4a} = 0.02$ M⁻¹ and $k_{4b} = 1.7 \times 10^5$ M⁻¹ s⁻¹. In the actual numerical simulation (R4a) was treated as a fast reaction with $k_{4a} = 2 \times 10^6$ M⁻¹ s⁻¹ and $k_{-4a} = 1 \times 10^8$ M⁻¹ s⁻¹.

TABLE II: Experimental Rate Constant k_4 (Values from Curve Fit) and Acidity Function C (Calculation from (10) with $K_{4a} = 0.02 \text{ M}^{-1}$) at Different Sulfuric Acid Concentrations

$[H_2SO_4]/M$	[H+]/M	С	$k_4/M^{-1} s^{-1}$
0.3	0.38	0.0075	(1300)
0.5	0.644	0.0126	2200
1.0	1.29	0.0245	4500
1.5	1.93	0.0358	6500
2.0	2.65	0.0478	8000
2.5	3.32	0.0584	(10000)
3.0	4.00	0.0686	(12000)

^a The H⁺ concentrations are taken from the data of Robertson and Dunford.¹⁵ Values in brackets: k_4 extrapolated from (11) with $k_{4b} = 1.7 \times 10^5$ M⁻¹ s⁻¹.

Surprisingly, the values obtained for k_4 increase from 2200 $M^{-1} s^{-1}$ in 0.5 M H₂SO₄ to 8000 $M^{-1} s^{-1}$ in 2.0 M H₂SO₄. A similar result was found by Noszticzius et al.,⁹ who followed the disproportionation reaction electrochemically in 0.15 and 1.5 M sulfuric acid solutions. That means the disproportionation reaction of HBrO₂ involves at least one protonation step. The only possible reaction path explaining the dependence on the acidity is the formation of the protonated species H₂BrO₂⁺ as a reactive compound;¹⁴

$$HBrO_2 + H^+ \rightleftharpoons H_2BrO_2^+$$
 (R4a)

$$HBrO_2 + H_2BrO_2^+ \rightarrow HOBr + BrO_3^- + 2H^+ \qquad (R4b)$$

(R4a) is treated as a fast equilibrium:

$$K_{4a} = \frac{[H_2 BrO_2^+]}{[HBrO_2][H^+]}$$
(5)

From (R4b) and (5) we can deduce the rate law

$$\frac{d[HOBr]}{dt} = k_{4b}[HBrO_2]^2 K_{4a}[H^+]$$
(6)



Figure 5. Experimental rate constant k_4 as a function of the acidity function C, where $C = K_{4a}[H^+]/(1 + K_{4a}[H^+])^2$, with $K_{4a} = 0.02 M^{-1}$ at different sulfuric acid concentrations. For numerical data, see Table II.

With

$$[HBrO_2]_{tot} = [HBrO_2] + [H_2BrO_2^+] =$$

 $[HBrO_2](1 + K_{4a}[H^+])$ (7)

 $([HBrO_2]_{tot} = total concentration of bromous acid) and the stoichiometry$

$$[HBrO_2]_{tot} + 2[HOBr] = [HBrO_2]_0$$
(8)

we obtain from (6)

$$\frac{\mathrm{d}[\mathrm{HBrO}_2]_{\mathrm{tot}}}{\mathrm{d}t} = -2k_{4b}C([\mathrm{HBrO}_2]_{\mathrm{tot}})^2 \tag{9}$$

with the abbreviation

$$C = \frac{K_{4a}[\mathrm{H}^+]}{(1 + K_{4a}[\mathrm{H}^+])^2}$$
(10)

We assume that the extinction coefficients of the protonated and unprotonated bromous acid are essentially the same (we could not detect a measurable difference when we determined the extinction coefficient of bromous acid solutions at different acidities), so the measured absorbance A can be attributed to the total concentration $[HBrO_2]_{tot}$. This way the experimental rate constant k_4 as defined in (2) can be expressed by

$$k_4 = k_{4b}C \tag{11}$$

From (11) we expect that the experimental k_4 values increase linearily with C, which expression depends on the acidity of the solution. In Figure 5 the experimental k_4 values are plotted as a function of C for $K_{4a} = 0.02 \text{ M}^{-1}$ (K_{4a} treated as an adjustable parameter; numerical data in Table II; [H⁺] calculated from the sulfuric acid concentration using the data from Robertson and Dunford¹⁵). From the slope of the straight line in Figure 5 we calculate $k_{4b} = 1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. Using this value and $K_{4a} =$ 0.02 M^{-1} , the kinetics for the decay of HBrO₂ was calculated for different acidities and compared to the experimental curves in Figure 4b. Calculated and measured curves agree very well.

Unfortunately, the agreement is worse if the initial concentration of the bromous acid is further decreased. This is demonstrated in Figure 6 for an initial concentration 2×10^{-6} M and $[H_2SO_4] = 0.5$ M. Immediately after the injection of NaBrO₂ into the sulfuric acid solution the concentration decreases much faster than expected from the calculation; later on, the experimental curve is nearly parallel to the calculated one. The reason for this discrepancy (which also occurs during the reaction of HBrO₂ with bromate at low bromite initial concentrations²) is not yet clear. In ref 10 it is mentioned that a slow increase of *A* after the end of the reaction is observed, which behavior could



Figure 6. Comparison of measured (a) and calculated (b) kinetics of the decay of bromous acid in 0.5 M sulfuric acid solution at 20 °C. The initial concentration of bromous acid is 2×10^{-6} M. The concentration *c* is the total concentration of bromous acid calculated from the measured absorbances.



Figure 7. Change ΔA of the absorbance at 400 nm (a) and of the absorbance A at 550 nm (b) measured simultaneously during the reaction of HBrO₂ with Ce⁴⁺ in 1 M sulfuric acid solution at 20 °C. The initial concentration of Ce⁴⁺ was 5×10^{-5} M. A 700- μ L aliquot of a 0.001 M NaBrO₂ solution (solved in a mixture of 0.01 M NaOH and 0.5 M Na₂SO₄) was injected into 140 mL of the Ce⁴⁺ solution, resulting in an initial concentration [HBrO₂]₀ = 5×10^{-6} M. The optical path length was 10.8 cm. The dual wavelength method¹² was used. The measurement was done with a homemade fiber optics instrument, with a reference wavelength 600 nm in case a and 670 nm in case b. In particular, in case b a high sensitivity was needed to measure absorbances below 5×10^{-4} .

not be understood by the authors; in our experiments such a behavior did not appear if the $NaBrO_2$ solution was pure enough.

4. Reaction of Ce4+ with HBrO2 at Different Acidities

To follow reaction R-6 by a stopped-flow technique Sullivan and Thompson⁶ applied an excess of $HBrO_2$ compared to Ce⁴⁺.

$$Ce^{4+} + HBrO_2 \rightarrow Ce^{3+} + BrO_2 + H^+ \qquad (R-6)$$

From first-order plots of $[Ce^{4+}]$ the rate constant k_{-6} was obtained, assuming $[HBrO_2] = [HBrO_2]_0$ and neglecting the disproportionation of HBrO₂ completely. From the preceding chapter it is clear, however, that the disproportionation of HBrO₂ can be a serious side reaction, at least at high acidities. For this reason we designed an experiment with Ce⁴⁺ in excess compared to HBrO₂ and followed the small decay of the Ce⁴⁺ absorbance. As an example, initial concentrations $[Ce^{4+}]_0 = 5 \times 10^{-5}$ M and $[HBrO_2]_0 = 5 \times 10^{-6}$ M were used (1 M sulfuric acid). The change, ΔA_{400} , of the absorbance at $\lambda = 400$ nm was monitored (Figure 7a); this change is essentially due to the change of the Ce⁴⁺ concentration. Simultaneously, the absorbance A_{550} at λ = 550 nm was recorded (Figure 7b); this absorbance is essentially due to the absorbance of BrO₂ (absorption maximum of BrO₂ at 490 nm⁴).



Figure 8. Change of the concentration $\Delta c = \Delta [Ce^{4+}]$ (a) and of the concentration $c = [BrO_2]$ (b): solid lines, evaluation of the experimental curves in Figure 7 using the relations (12) and (13), where the extinction coefficients are taken from ref 12 [ϵ (Ce⁴⁺,400) = 800 M⁻¹ cm⁻¹, ϵ (Ce⁴⁺, 550) = 0.7 M⁻¹ cm⁻¹, ϵ (BrO₂,400) = 400 M⁻¹ cm⁻¹, ϵ (BrO₂,550) = 387 M⁻¹ cm⁻¹]; dots, simulated values. The simulation was done with the reactions (R4a), (R4b), (R5'), (R5''), and (R6). The rate constants used in the simulation are the values listed in Table I for (R5'), (R5'') and (R6); the values for (R4a) and (R4b) are the same as in Figure 4; $k_{-6} = 12\ 000\ M^{-1}\ s^{-1}\ for\ 1\ M\ H_2SO_4$ (Table III, column 6).

The measured absorbances are connected to Δ [Ce⁴⁺] (change of the Ce⁴⁺ concentration = [Ce⁴⁺] - [Ce⁴⁺]₀) and [BrO₂] (concentration of BrO₂) in the following way:

 $\Delta A_{400}/d = \Delta [\text{Ce}^{4+}] \epsilon (\text{Ce}^{4+}, 400) + [\text{BrO}_2] \epsilon (\text{BrO}_2, 400)$ (12)

$$A_{550}/d = \Delta [\text{Ce}^{4+}] \epsilon (\text{Ce}^{4+}, 550) + [\text{BrO}_2] \epsilon (\text{BrO}_2, 550)$$
(13)

From (12) and (13) we can calculate Δ [Ce⁴⁺] and [BrO₂]. Using the extinction coefficients derived in ref 12 the kinetics of Δ [Ce⁴⁺] and [BrO₂] was calculated (Figure 8, solid lines). We observe a decay of Ce⁴⁺ and the formation and decay of BrO₂ (maximum BrO₂ concentration of 1.4×10^{-7} M). From Figure 8a we read the final value Δ [Ce⁴⁺]_w = -8.8×10^{-6} M; that means that the change of the Ce⁴⁺ concentration is about twice the initial concentration of the bromous acid.

This surprising result can be explained by the fast disproportionation of BrO_2 (formed in (R-6)) into bromite and bromate according to (R-5') and (R-5"). Since [HBrO₃] is nearly zero in our experiment, the reaction (R-5') is practically irreversible, and one molecule of HBrO₂ is formed from 2 molecules of BrO₂. By combining (R-6), (R-5'), and (R-5") we obtain the following for the overall reaction between Ce⁴⁺ and HBrO₂ (disproportionation reaction of HBrO₂ neglected):

$$2Ce^{4+} + HBrO_2 + H_2O \rightarrow 2Ce^{3+} + HBrO_3 + 2H^+$$
 (R7)

This means that 1×10^{-5} M of Ce⁴⁺ disappears if the initial concentration of the injected HBrO₂ is 5×10^{-6} M. This is nearly what we observe in the experiment.

Kinetics of ΔCe^{4+} in 1 M H₂SO₄. Because of the regeneration of HBrO₂ in steps R-5' and R-5" the rate of consumption of HBrO₂ in the overall reaction is half of the rate calculated from step R-6, if the disproportionation of HBrO₂ is neglected completely:

$$\frac{d[HBrO_2]}{dt} = -\frac{1}{2}k_{-6}[Ce^{4+}][HBrO_2]$$
(14)

From the stoichiometry

$$^{1}/_{2}\Delta[Ce^{4+}] = [HBrO_{2}] - [HBrO_{2}]_{0}$$
 (15)



Figure 9. Logarithmic plots of the curves in Figure 8: curve a, $-\ln B = -\ln (\Delta [Ce^{4+}] - \Delta [Ce^{4+}]_{\infty})$ versus time t; curve b, $-\ln B = -\ln ([BrO_2]/[BrO_2]_{max})$ versus time t.

$$^{1}/_{2}\Delta[Ce^{4+}]_{\infty} = -[HBrO_{2}]_{0}$$
 (16)

 $(\Delta [Ce^{4+}]_{\infty} = change of [Ce^{4+}] at infinite time) we obtain the rate law for the change <math>\Delta [Ce^{4+}]$ of the Ce⁴⁺ concentration:

$$\frac{\mathrm{d}\Delta[\mathrm{Ce}^{4+}]}{\mathrm{d}t} = -\frac{1}{2}k_{-6}[\mathrm{Ce}^{4+}](\Delta[\mathrm{Ce}^{4+}] - \Delta[\mathrm{Ce}^{4+}]_{\infty}) \quad (17)$$

In our experiment described above, the concentration of Ce⁴⁺ decreases by 20%. In a first approximation we treat the Ce⁴⁺ concentration in (17) as constant ($[Ce^{4+}] = [Ce^{4+}]_0$); in this case we derive from (17)

$$-\ln\left[\frac{\Delta[Ce^{4+}] - \Delta[Ce^{4+}]_{\infty}}{-\Delta[Ce^{4+}]_{\infty}}\right] = (k_{-6})'t \qquad (18)$$

with

$$(\mathbf{k}_{-6})' = \frac{1}{2}k_{-6}[\mathrm{Ce}^{4+}]_0$$
(19)

In Figure 9 (curve a) the left-hand side of (18) is plotted as a function of time for the measurement displayed in Figure 8a. An approximately straight line with an average slope $k'_{-6} = 0.27 \text{ s}^{-1}$ is obtained leading to $k_{-6} = 11 \text{ 000 M}^{-1} \text{ s}^{-1}$. A closer inspection, however, reveals that the slope of the logarithmic curve decreases from the starting point to the end of the curve. This is mainly because the Ce⁴⁺ concentration is not really constant during the reaction.

Kinetics of BrO_2 in 1 M H₂SO₄. During the reaction of Ce⁴⁺ with HBrO₂ the intermediate BrO₂ is formed as can be seen in Figure 8b (the rise time of about 2 s up to the maximum value is due to the time constant of 1 s of the measuring system); the decay of BrO₂ is slower than the decay of Ce⁴⁺. If we apply a steady-state approximation for BrO₂ and Br₂O₄ we are able to calculate the steady-state concentration of BrO₂ from the reactions R-6, R5', and R5'':

$$[BrO2]2 = (const)[HBrO2]$$
(20)

with

const =
$$\frac{(k_{-6})'}{(k_{-5})''}(1 + (k_5)''/(k_{-5})')$$
 (21)

For $[BrO_2]$ we get from (14) and (20) (for $[Ce^{4+}] = [Ce^{4+}]_0$)

$$-\ln\left[\frac{[\text{BrO}_2]}{[\text{BrO}_2]_{\text{max}}}\right] = \frac{1}{2}(k_{-6})'t$$
(22)

with

$$[BrO_2]_{max} = [(const)[HBrO_2]_0]^{1/2}$$
 (23)

In Figure 9 (curve b) $-\ln ([BrO_2]/[BrO_2]_{max})$ is plotted as a function of time. An approximately straight line is obtained with the initial slope 0.15 s⁻¹ which is about half of the initial slope



Figure 10. Kinetics of $\Delta c = \Delta [Ce^{4+}]$ during the reaction of Ce⁴⁺ with HBrO₂ at different acidities at 20 °C: (a) experiment; (b) simulation. [H₂SO₄] = 0.5, 1.0, 1.5, and 2.0 M for curves 1–4. The initial concentrations are $[Ce^{4+}]_0 = 5 \times 10^{-5}$ M, $[HBrO_2]_0 = 5 \times 10^{-6}$ M. For the experimental conditions and for the rate constants used in the simulations, see the caption to Figure 8. In the simulation small corrections for the initial concentrations of HBrO₂ were applied to take account for the fast consumption of some HBrO₂ during the mixing process (corrections 0%, 5%, 10%, and 15% at acidities 0.5, 1.0, 1.5, and 2.0 M H₂SO₄).



Figure 11. Kinetics of BrO_2 during the reaction of Ce^{4+} with $HBrO_2$ at different acidities: (a) experimental curves; (b) simulation curves with the same assumptions as made in Figure 10. $[H_2SO_4] = 0.5$, 1.0, 1.5, and 2.0 M for curves 1-4. It must be admitted that there is some contribution of $HBrO_2$ to the absorbance at 550 nm which was not taken into account in the evaluation of the BrO_2 concentration from the measured absorbances. Actually the measured BrO_2 concentrations are lower than reported in this figure by approximately 10% at 1 M H₂SO₄ and about 20% at 2 M H₂SO₄.

found for the Ce⁴⁺ decay (as expected from (18) and (22)). With the rate constants $(k_5)'$, $(k_{-5})'$ and $(k_{-5})''$ from Table I, $(k_6)' =$ 0.27 s^{-1} , and $[\text{HBrO}_2]_0 = 5 \times 10^{-6} \text{ M}$, we calculate from (23) $[\text{BrO}_2]_{\text{max}} = 1.7 \times 10^{-7} \text{ M}$. This is what we get in Figure 8b by extrapolation of the measured BrO₂ concentration to zero time.

Dependence of k_{-6} on Acidity. The experiments on the Ce⁴⁺/ HBrO₂ reaction were repeated at different acidities (0.5–3.0 M H₂SO₄) and for different initial concentrations of Ce⁴⁺ ((2–10) × 10⁻⁵ M) and of HBrO₂ (2 × 10⁻⁶ to 1 × 10⁻⁵ M). The results are displayed in Figure 10a for Δ Ce⁴⁺ and in Figure 11a for BrO₂.

$[H_2SO_4]/M$	$[Ce^{4+}]_0/10^{-5}$ M	[HBrO ₂] ₀ /10 ⁻⁶ M	slope v/10 ⁻⁶ M s ⁻¹	convrn/%	$k_{-6}/10^4 \text{ M}^{-1} \text{ s}^{-1}$	μ/M
0.5	5	5	-5.9	99	2.4	0.8
1.0	2	2	-0.5	92	1.2	1.6
	2.5	5	-1.6	82		
	5	5	-3.0	88		
	5	7	-4.3	82		
	5	10	-5.8	84		
+ 1.0 M NaClO ₄	5	6.7	-2.2	76	0.6	2.6
1.5	5	5	-1.7	65	0.7	2.4
	5	10	-3.4	70		
+ 1.5 M NaClO ₄	5	5	0.6	23	0.3	3.9
2.0	5	5	-1.1	42	0.4	3.3
	5	10	-2.1	43		
2.5	5	5	-0.6	18	0.3	4.1
3.0	10	5	-0.5	11	0.1	5.0
		Sullivan-Thor	npson-experiment ^b			
0.3	0.54	19.1			4.0	0.5

TABLE III: Experimental Results for the Reaction of Ce⁴⁺ with HBrO₂ at Different Sulfuric Acid Concentrations and Different Initial Concentrations of Ce⁴⁺ and HBrO₂ at 20 °C^a

^a The slopes $v = (d\Delta[Ce^{4+}]/dt)_0$ are the initial slopes of the measured Ce⁴⁺ curves (see Figure 10a). A conversion of 100% means that the final value of $\Delta[Ce^{4+}]$ is equal to two times the initial concentration [HBrO₂]₀. The rate constant k_{-6} in column 6 is obtained from the slope v using eq 24. Additionally, the ionic strengths μ for the different measurements are displayed in column 7: $\mu = 1/2([H^+] + [HSO_4^{-}] + 4[SO_4^{2-}] + [Na^+] + [CIO_4^{-}])$. For the different sulfuric acid concentrations [H⁺], [HSO_4^{-}], and [SO_4^{2-}] are taken from ref 15. In two experiments NaClO₄ was added to the reaction mixture. ^b Data obtained by Sulivan and Thompson.⁶ They report a value $k_{-6} = 6.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 25 °C; assuming a temperature factor for k_{-6} of 1.5 from 20 to 25 °C, we estimate $k_{-6} = 4.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C.

Because of the consumption of Ce⁴⁺ and of the disproportionation reaction, the rate constant $k_{-6} = 11\ 000\ M^{-1}\ s^{-1}$ derived from the straight line in Figure 9 for 1 M H₂SO₄ cannot be completely correct. To get a more realistic value for k_{-6} the initial slopes $v = (d\Delta[Ce^{4+}]/dt)_0$ of the directly measured Ce⁴⁺ curves (Figures 8a, 10a) were evaluated (Table III, column 4). From (14) and (15) we calculate the rate constant k_{-6} according to

$$k_{-6} = \frac{-v}{[Ce^{4+}]_0[HBrO_2]_0}$$
(24)

([Ce⁴⁺]₀, [HBrO₂]₀ = initial concentrations of Ce⁴⁺ and HBrO₂). For 1 M H₂SO₄ we get $k_{-6} = 12 000 \text{ M}^{-1} \text{ s}^{-1}$ instead of 11 000 M⁻¹ s⁻¹ obtained in the approximation used above. The rate constants for 0.5 to 3.0 M H₂SO₄ are collected in Table III, column 6. It can be seen that the reaction rate decreases by a factor of 24 in going from 0.5 to 3.0 M sulfuric acid solution. At the same time the conversion of Ce⁴⁺ into Ce³⁺ during the reaction decreases from nearly 100% in 0.5 M H₂SO₄ to about 10% in 3 M H₂SO₄ (100% conversion means that the total change of the Ce⁴⁺ concentration is equal to two times the initial bromous acid concentration). The decrease of the conversion is due to a decrease of the rate of (R-6) and to the above measured increase of the rate of the disproportionation reaction (R4).

In Figures 8 (dots), 10b, and 11b numerical calculations including those for reactions R4–R6 are displayed. The curves for ΔCe^{4+} and BrO₂ are fairly in agreement with the measured ones.

Including the Back-Reaction (R6). In an additional experiment we investigated the reaction of Ce⁴⁺ with HBrO₂ in the presence of added Ce³⁺. From (R6) we expect that the BrO₂ formed in reaction R-6 will be reduced again by Ce³⁺ present in the solution. This way reaction R-6 will be slowed down with increasing Ce³⁺ concentration. This effect can be seen in Figure 12 for Ce³⁺ concentrations of 0, 1×10^{-4} M and 2×10^{-4} M.

5. Discussion

So far the rate of the $Ce^{4+}/HBrO_2$ reaction was directly measured at sulfuric acid concentrations up to 0.3 M.⁶ The rate



Figure 12. Change $\Delta c = \Delta [Ce^{4+}]$ during the reaction of Ce⁴⁺ with HBrO₂ at different initial concentrations of Ce³⁺ at 20 °C in 1 M H₂SO₄: solid lines, experiment; squares, triangles, and dots, simulation. Initial concentrations: $[Ce^{4+}]_0 = 5 \times 10^{-5}$ M; $[HBrO_2]_0 = 5 \times 10^{-6}$ M; $[Ce^{3+}]_0$ = 0 (curve 1), 1 × 10⁻⁴ (curve 2), 2 × 10⁻⁴ M (curve 3). For the experimental conditions and for the rate constants used in the simulations see the caption to Figure 8.

of the disproportionation reaction of HBrO₂ was measured for sulfuric acid concentrations from 0.15 to 1.5 $M^{.9,10}$ In the experiments presented here we extended the range of the sulfuric acid concentration up to 3 M. As can be seen from Table II, k_4 increases from 1300 M⁻¹ s⁻¹ at 0.3 M H₂SO₄ to 12 000 M⁻¹ s⁻¹ at 3.0 M H₂SO₄; k_{-6} decreases from 40 000 M⁻¹ s⁻¹ to 1000 M⁻¹ s⁻¹ in the same range of acidity (Table III).

In the case of k_{-6} this is a change by a factor of 40. Sullivan and Thompson⁶ already realized a strong dependence of k_{-6} on the acidity, but they had to add NaClO₄ in a high concentration to avoid Schlieren effects above $[H_2SO_4] = 0.3$ M. For this reason they could not distinguish between the acidity effect and an effect of the added NaClO₄. On the other hand, they found that k_{-6} is larger by a factor of about 15 if sulfuric acid is exchanged by perchloric acid. They assume that in the sulfuric acid system not all of the different Ce(IV)-sulfato complexes are reactive with HBrO₂. They suggest that only the species Ce(SO₄)²⁺ and Ce(SO₄)₂ are reactive and that (Ce(SO₄)₃)²⁻ is completely unreactive.

Support for their assumption is given by Hanna et al.,¹⁶ who find a very strong dependence of the distribution of the different sulfato complexes on the acidity in a range from $[H^+] = 0$ to



Figure 13. Experimental rate constant k_{-6} versus ionic strength μ of the solution. The data are taken from Table III: dots, measurements in sulfuric acid; triangles, measurements in 1:1 mixtures of sulfuric acid and NaClO₄.

 $[H^+] = 2.0$ M. In these experiments, however, the sulfate concentration was kept constant and the acidity was changed by the addition of perchloric acid. In our case the situation is different: with increasing sulfuric acid concentration the sulfate concentration increases as well as the $[H^+]$ concentration. Using the data of Hardwick and Robertson¹⁷ and Robertson and Dunford,¹⁵ we calculated the ratios $[Ce^{4+}]/c_0$, $[CeSO_4^{2+}]/c_0$, $[Ce(SO_4)_2]/c_0$ and $[Ce(SO_4)_3^{2-}]/c_0$ in the range 0.5–2.0 M sulfuric acid. Surprisingly these ratios are essentially constant in the considered range of the acidity, although with increasing acidity the $Ce(SO_4)_3^{2-}$ complex should be favored.

A closer inspection of the Robertson and Dunford values¹⁵ of $[H^+]$, $[HSO_4^-]$, and $[SO_4^{2-}]$ reveals that the equilibrium constant K_H for the equilibrium

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$$
(R8)

$$K_{\rm H} = \frac{[{\rm H}^+][{\rm SO}_4^{2-}]}{[{\rm H}{\rm SO}_4^{-}]}$$
(25)

increases from 0.26 M for 0.5 M sulfuric acid to 1.28 M for 2 M sulfuric acid. This is reasonable, since charged particles are involved in the reaction and (25) is written in terms of concentrations instead of activities in spite of the high ionic strength. Consequently, we cannot expect that the equilibrium constants for the different sulfato complexes are really constants in the range of the acidity used in our experiments; also, in this case, charged species at high ionic strength are involved. Unfortunately, there are no data for these equilibrium constants available in the literature except for ionic strength 2.0 M.

We performed additional measurements for k_{-6} by adding NaClO₄ (same concentration as for H_2SO_4) to the reaction mixture (Table III); in these cases k_{-6} decreased by 50%. Additionally, for all the measurements listed in Table III, the ionic strength μ was calculated (Table III, column 7). In Figure 13 the measured k_{-6} values are plotted as a function of μ . It turns out that the points corresponding to the NaClO₄ additions fit well into the curve. From this result we conclude that the equilibrium constants for the sulfato complexes increase with increasing ionic strength leading to a decrease of the concentrations of the reactive Ce^{4+} -sulfato complexes $CeSO_4^{2+}$ and $Ce(SO_4)_2$ and to a decrease of k_{-6} . Of course, a direct effect of the ionic strength on the rate of the reaction of HBrO₂ with the active cerium species cannot be ruled out completely; this effect will be small, however, because the reactant HBrO₂ is an uncharged molecule.

6. Conclusions

Our results are important for the understanding of the autocatalytic reaction and for the negative feed back loop in the

Belousov-Zhabotinsky system. So far, both rate constants k_4 and k_{-6} were assumed to be independent of acidity.² The rate constants commonly used for 1 M H₂SO₄ solutions ($k_4 = 3000$ M⁻¹ s⁻¹, $k_{-6} = 8900$ M⁻¹ s⁻¹) are not far away from the values obtained in this work ($k_4 = 4500$ M⁻¹ s⁻¹, $k_{-6} = 12000$ M⁻¹ s¹), although k_{-6} as given in ref 2 was not the result of a direct experiment; difficulties arose in simulations for high acidity systems, where radical-controlled oscillations can be observed.^{18,19} It turned out that the autocatalytic reaction was faster in 3 M H₂SO₄ than expected from theory. This discrepancy is mainly caused by a too large value for k_{-6} used in those simulations; decreasing k_{-6} by a factor of 12 (from 1 to 3 M sulfuric acid solution) will have a significant speeding up effect on the autocatalytic process.

In this work it is directly proved that BrO₂ radicals are the primary reaction products in (R-6). The observed concentrations of BrO_2 are in good agreement with the simulations. This is important for the interpretation of previous experiments²⁰ on the reaction of BrO₂ radicals with malonyl radicals MA[•] in 1 M H_2SO_4 solutions. In these experiments BrO_2 radicals were produced by (R-6) and consumed up by malonyl radicals. It turned out that the BrO₂/MA[•] reaction can work as a second negative feed back loop in the Belousov-Zhabotinsky reaction (Radicalator model^{18,19}). According to the results obtained in this work the BrO_2 radical production by (R-6) is less efficient at the high acidities needed for these investigations (Figure 11); the BrO₂ concentration, however, turns out to be still large enough to extend previous ESR experiments²⁰ from 1 to 3 M sulfuric acid. Also the generation of BrO_2 by (R-6) is an efficient method to evaluate the rate of the reaction of the Ru(II)-tris(bipyridyl) complex with BrO_2^{21} in a direct experiment.

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