Rate of the Bromous Acid – Bromide Reaction Measured in a Br_2–HOBr Buffer System in Sulfuric Acid Solution

Horst-Dieter Försterling, Szilvia Murányi *, and Helmut Schreiber
Fachbereich Physikalische Chemie, Philipps-Universität Marburg

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In the Belousov-Zhabotinsky system bromine species of oxidation states −1 to 5 are important for the start and for the inhibition of the autocatalytic reaction steps. Especially, the reaction of Br^- with $HBrO_2$ competes with the oxidation of Ce^{3+} by BrO_2 formed from $HBrO_2$ and $HBrO_3$. In our investigation the reaction of Br^- with $HBrO_2$ (solvent 1 M sulfuric acid) is followed spectroscopically in a mixture of bromine and hypobromous acid, which system works as a buffer for bromide. Including experiments on the hydrolysis of Br_2 and on the solubility product of AgBr in 1 M sulfuric acid solution direct information about the rate constant k_1 of the $Br^-/HBrO_2$ reaction is obtained ($k_1 = 2.5 \times 10^6\ M^{-2}\ s^{-1}$ at 20 °C and $4 \times 10^6\ M^{-2}\ s^{-1}$ at 25 °C, which values are valid in the range of 0.01 to 1 M sulfuric acid).

Key words: Belousov-Zhabotinsky reaction, Bromous acid, Bromide, Bromine hydrolysis, Bromate, Dual wavelength spectroscopy

Introduction

In the classical Belousov-Zhabotinsky (BZ) system [1] Ce^{4+} is reduced by malonic acid (process 1); the resulting Ce^{3+} is oxidized by bromate in several steps starting with a reaction of Ce^{3+} with BrO_2 radicals (process 2 [2, 3]). Process 2 is switched off by species reacting with BrO_2 directly (like malonyl radicals formed in process 1 [4]) or with $HBrO_2$ (like Br^- formed in a reaction of Ce^{4+} with bromomalonic acid [5, 6]). Process 2 is switched on again as soon as the concentration of the control intermediates is lower than a critical level, and oscillations can occur. For a quantitative understanding of the bromide control information about the rate of the bromide/bromous acid reaction

$$Br^- + HBrO_2 + H^+ \rightarrow 2\,HOBr \qquad (R\,1)$$

is needed. The rate of this reaction was investigated first by Noszticzius et al. [7] by following the potential of a bromide sensitive electrode; a rate constant $1 \times 10^6\ M^{-2}\ s^{-1} < k_1 < 4 \times 10^6\ M^{-2}\ s^{-1}$ was estimated from measurements in 1.5 M sulfuric acid solution. Ariese and Nagy [8] tried to follow this reaction spectroscopically using stopped flow technique. It turned out that the sensitivity of the method was not high enough to obtain reliable results; nevertheless a value $k_1 = 1.4 \times 10^6\ M^{-2}\ s^{-1}$ could be roughly estimated from measurements in a reaction medium of 0.01 M sulfuric acid. They also carried out electrochemical measurements using a bromide sensitive electrode like Noszticzius et al. They found that the reaction rate strongly depended on the acidity of the solution. For 1 M sulfuric acid solution they obtain $k_1\,[H^+] = 7 \times 10^5\ M^{-1}\ s^{-1}$. Taking into account thermodynamic data, Field and Försterling [2] proposed a value $k_1 = 3 \times 10^6\ M^{-2}\ s^{-1}$.

The aim of the present work is to investigate the rate of the $HBrO_2$–Br^- reaction spectroscopically in a reaction mixture of Br_2 and HOBr. Such a system works as a buffer for bromide; depending on the concentration of HOBr, the bromide concentration can be kept extremely low, and the rate of (R 1) can be made small enough to be followed in a conventional kinetic experiment. Such an experiment has already been described by Noszticzius et al. [7]; they used a silverbromide electrode as detecting system. That time it was not clear, however, if a direct reaction of Br_2 with $HBrO_2$ has to be taken into account. In a subsequent work Noszticzius et al. [6] were able to prove that $HBrO_2$ is not attacked by bromine directly. That means that the decay of bromine in a $Br_2/HBrO_2$ mixture is exclusively due to a consumption of Br^- via (R 1) and that the source of bromide is the hydrolysis

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* Permanent address: L. Eötvös University, Inst. Inorg. Anal. Chem., Budapest, Hungary.

Reprint requests to Prof. Dr. H. D. Försterling, Physikalische Chemie, Fb 14, Universität Marburg, Hans-Meerwein-Str., D-3550 Marburg, Fed. Rep. of Germany

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of bromine:

$$Br_2 + H_2O \rightleftarrows HOBr + Br^- + H^+ . \qquad (R\,2)$$

Similar experiments were carried out by Kshirsagar and Field [9], who measured the formation of HOBr during the reaction of bromate with bromine. As in the experiment of Noszticzius et al. [7], bromide is generated during the hydrolysis of bromine, and that bromide reacts directly with bromate,

$$Br^- + HBrO_3 + H^+ \rightarrow HBrO_2 + HOBr , \qquad (R\,3)$$

and with bromous acid, which is formed in (R 3). A second pathway for the disappearence of $HBrO_2$ is its disproportionation:

$$2\,HBrO_2 \rightarrow HOBr + HBrO_3 . \qquad (R\,4)$$

If the set of rate constants for reactions (R 1) to (R 4) from reference [2] is used, it turns out that the calculated rate of formation of HOBr is much higher than observed. In order to fit the calculations to their experiments Kshirsagar and Field assume that the equilibrium constant K_2 of the bromine hydrolysis,

$$K_2 = \frac{[HOBr]\,[Br^-]\,[H^+]}{[Br_2]} , \qquad (1)$$

has to be changed from $K_2 = 14 \times 10^{-9}$ M^2 [2] to $K_2 = 6.6 \times 10^{-10}$ M^2. The first value is based on direct measurements by Eigen and Kustin [10] and by Liebhafsky [11] with corrections for the activities in 1 M sulfuric acid solution calculated by Field, Körös and Noyes [5]. It seems to be strange that these corrections may be wrong by a factor of 20.

Another possibility for the difficulty in explaining the Kshirsagar-Field experiments may be the uncertainty in the value of the rate constant k_1. If that value is really lower than assumed in their calculations the overall rate of HOBr formation is expected to be lower too. This was already mentioned by Försterling and Schreiber [12].

Experiments

Chemicals

H_2SO_4 (96%), NaBr, $AgNO_3$ and Ag_2SO_4 (all Fluka pa.) were used without further purification. $NaBrO_3$ was recrystallized twice from hot water. $NaBrO_2$ was prepared following the procedure of Noszticzius et al. [7]. Solutions of HOBr in water were prepared using a method described by Betts and Mackenzie [13]; Ag_2SO_4 was added to a solution of bromine in water, the precipitate of AgBr was removed by filtration and the remaining solution was purified by vacuum distillation at about 30 °C.

The concentration of the aqueous HOBr solutions was calculated from the absorbance peak at 263 nm using $\varepsilon(HOBr) = 90$ M^{-1} cm^{-1}. That value was derived from a separate experiment in which HOBr was injected into 0.1 M NaOH solution; the concentration of NaOBr formed this way was calculated from its absorbance at 330 nm using the well known value $\varepsilon(NaOBr) = 303$ M^{-1} cm^{-1} at 330 nm reported by Lee and Lister [14]. $\varepsilon(HOBr)$ at 263 nm was found to be the same within 2% in 1 M H_2SO_4 and in water. For comparison, $\varepsilon(HOBr) = 87$ M^{-1} cm^{-1} at 265 nm is reported for a solution of HOBr in 1.66 M $HClO_4$ [13].

The concentration of the alkaline $NaBrO_2$ solutions was determined spectroscopically using the extinction coefficients reported by Lee and Lister [14]. From the ratio of the absorbances at 296 and 330 nm the contamination of $NaBrO_2$ by NaOBr was estimated to be less than 2%. If an $NaBrO_2$ solution was injected into 1 M sulfuric acid, a small amount of bromine was formed due to a reaction of traces of bromide with excess $HBrO_2$; from this measurement a 3% contamination of the $NaBrO_2$ stock solution by bromide was estimated.

Traces of bromine in sulfuric acid solutions of $NaBrO_3$ were removed by bubbling nitrogen gas through the solution; the remaining solution was checked spectroscopically for traces of HOBr impurities. All solutions were prepared from doubly distilled water.

Evaluation of experimental data and numerical methods

The analog signal of the measuring system was digitized by a 12 bit analog-digital converter, and the data were stored and evaluated in the memory of an Apple II computer connected with a Taxan plotter. The numerical integration of the kinetic differential equations was performed with the program DIFFGL, which is based on Gear's method [15], by using an IBM PS/2 personal computer.

Equilibrium constant K_2

For the evaluation of the kinetic data in the experiments presented here a reliable value of the equilibrium constant K_2 of the bromine hydrolysis reaction (R 2) in 1 M sulfuric acid medium is needed. The equilibrium concentration of bromide formed by the hydrolysis of Br_2 was measured by titration of the solution with Ag^+; the end point was detected by measuring the light scattering of AgBr particles in equilibrium with silver and bromide ions:

$$Ag^+ + Br^- \rightleftarrows AgBr_{solid} , \quad (R\,5)$$

$$L_{AgBr} = [Ag^+][Br^-] \quad (2)$$

(L_{AgBr} = solubility product of silverbromide). This way the equilibrium concentration of bromide in the bromine solution can be calculated according to

$$[Br^-] = L_{AgBr}/[Ag^+]_p \quad (3)$$

if $[Ag^+]_p$ is the concentration of added silver ions needed for the first appearance of AgBr precipitate.

Since the solubility product of AgBr will be different in 1 M sulfuric acid solution compared to neutral solution and no data in literature were available, the change of L_{AgBr} from neutral to acidic solution was measured first. In the actual procedure a 1×10^{-3} M solution of $AgNO_3$ in water was added in small aliquots to 140 ml of a 1×10^{-6} M Br^- solution in water; the sample cell (optical pathlength 10.7 cm) was illuminated by a tungsten lamp, and the absorbance A was recorded at a wavelength of 401 nm using a dual wavelength apparatus (reference wavelength 601 nm) as described earlier [16]. As soon as the concentration $[Ag^+]_p$ was reached, the absorbance of the solution increased rapidly, as can be seen in Fig. 1 (curve 1). From $[Ag^+]_p = 1 \times 10^{-6}$ M and $[Br^-] = 1 \times 10^{-6}$ M the solubility product $L_{AgBr} = 1 \times 10^{-12}$ M^2 was calculated according to (3). Additional data result in a mean value $L_{AgBr} = (1.0 \pm 0.1) \times 10^{-12}$ M^2 at a temperature of 22 °C.

The same procedure was applied with bromide and silver ions solved in 1 M H_2SO_4. From the experiment displayed in Figure 1 (curve 2) and from additional data the value $L_{AgBr} = (2.3 \pm 0.2) \times 10^{-12}$ M^2 is obtained. That means that L_{AgBr} is higher in 1 M sulfuric acid solution by a factor of about 2 compared to a solution in water.

In order to measure the equilibrium constant K_2, a solution of bromine was prepared by mixing hypobromous acid and bromide,

$$Br^- + HOBr + H^+ \rightleftarrows Br_2 + H_2O . \quad (R\text{-}2)$$

By such a procedure a much purer product was obtained compared to the direct dissolution of elementary bromine in 1 M sulfuric acid, which solution was not stable for a longer time. Ag^+ was added until the increase of absorbance indicated the end point of the titration. In the actual procedure 1.12 ml of a 0.01 M NaBr solution were added into 140 ml of a 1.5×10^{-4} M HOBr solution in 1 M sulfuric acid. The resulting Br_2 and HOBr initial concentrations were $[Br_2] = 0.80 \times 10^{-4}$ M and $[HOBr] = (1.50 - 0.80) \times 10^{-4}$ M $= 0.70 \times 10^{-4}$ M. The concentration of bromine was checked spectroscopically by its absorbance at 401 nm.

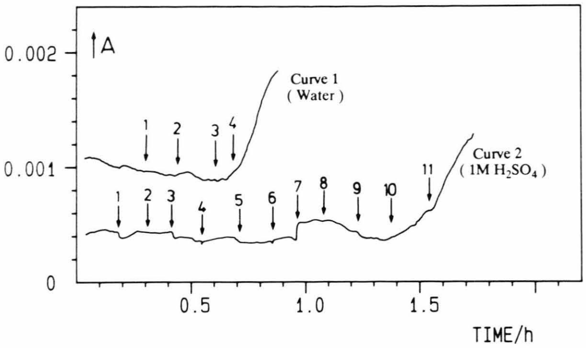

Fig. 1. Titration experiment in the Br^--system at 22 °C. Dual wavelength technique, wavelength 401 nm, reference wavelength 601 nm, optical pathlength 10.7 cm. Absorbance A of 140 ml of a 1×10^{-6} M NaBr solution as a function of time during the addition of small aliquots of a 1×10^{-3} M $AgNO_3$ solution. – *Curve 1:* NaBr solved in water; at points 1, 2, 3, 4 the volumes of added $AgNO_3$ solution were 50, 50, 20, 20 µl. The total volume of added solution is 0.140 ml, hence $[Ag^+]_p = 1 \times 10^{-6}$ M and $L_{AgBr} = 1 \times 10^{-12}$ M^2. – *Curve 2:* NaBr solved in 1 M H_2SO_4; at points 1, 2, ..., 11 the volumes of added $AgNO_3$ solution were 50, 50, 50, 30, 20, 20, 20, 20, 20, 20, 20 µl. The total volume of added solution is 0.320 ml, hence $[Ag^+]_p = 2.3 \times 10^{-6}$ M and $L_{AgBr} = 2.3 \times 10^{-12}$ M^2.

After that, the Br_2 absorbance was balanced and the absorbance A of the solution was followed at a much higher sensitivity in order to see the increase of absorbance due to the light scattering of AgBr particles. It turned out that in this case the best results were obtained with a single beam technique at a wavelength of 601 nm (instead of the dual wavelength technique used in the experiments described above). A 0.1 M solution of $AgNO_3$ was added in small aliquots, and the sharp increase of absorbance due to the light scattering of AgBr particles was observed (Figure 2). As a result, $[Ag^+]_p = 2.50 \times 10^{-4}$ M is obtained, and the bromide concentration is calculated according to (3) using the solubility product of AgBr determined above for 1 M sulfuric acid solution: $[Br^-] = 9.20 \times 10^{-9}$ M.

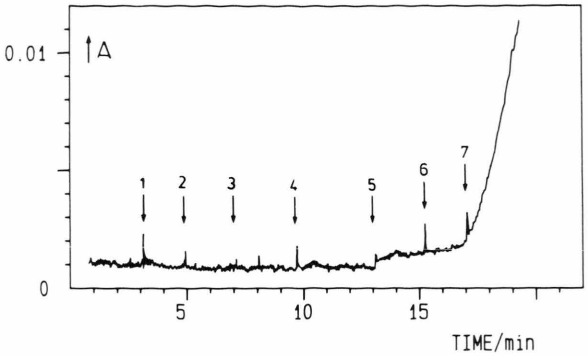

Fig. 2. Titration experiment in the Br_2/HOBr-system at 22 °C. Single beam technique, wavelength 601 nm, optical path length 10.7 cm, 1 M sulfuric acid as solvent. – Absorbance A of a 8.0×10^{-5} M bromine solution (prepared by injection of 1.12 ml of a 0.01 M NaBr solution into 140 ml of a 1.50×10^{-4} M HOBr solution) as a function of time during the addition of $AgNO_3$. At points 1 to 7 equal volumes of 50 µl of a 0.1 M $AgNO_3$ solution were added. The total volume added is 0.35 ml, hence $[Ag^+]_p = 2.50 \times 10^{-4}$ M.

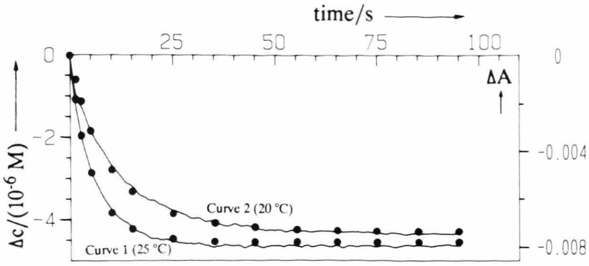

Fig. 3. Change of the absorbance ΔA (right hand scale) during the reaction of $HBrO_2$ (initial concentration 5×10^{-6} M) with Br_2 (initial concentration 1×10^{-4} M) in 1 M sulfuric acid solution containing HOBr (initial concentration 2×10^{-5} M). Curve 1: 25 °C, curve 2: 20 °C. The change Δc of the bromine concentration (left hand scale) was calculated as explained in the text. The experiments are compared to theory (dots) using the rate constants summarized in Table 2 ($[H^+] = 1.29$ M for 1 M sulfuric acid solution).

Table 1. Evaluation of the equilibrium constant K_2; the way of calculation is demonstrated in the text using run 11 as an example.

Run	$[HOBr]$ / 10^{-5} M	$[Br_2]$ / 10^{-5} M	$[Ag^+]_p$ / 10^{-4} M	$[Br^-]$ / 10^{-9} M	K_2 / 10^{-9} M
1	7.1	1.0	17.14	1.34	12.3
2	7.1	2.0	7.86	2.93	13.4
3	8.0	2.9	7.86	2.93	10.6
4	8.0	2.9	7.50	3.07	11.1
5	7.2	4.0	5.00	4.60	10.6
6	7.1	5.1	3.57	6.44	11.6
7	7.1	5.0	4.29	5.37	9.7
8	7.0	6.0	3.21	7.16	10.8
9	7.0	7.0	2.50	9.20	11.8
10	6.9	7.0	2.50	9.20	11.6
11	7.0	8.0	2.50	9.20	10.4
12	7.0	9.0	2.14	10.7	10.7
13	9.1	10.0	2.14	10.7	12.6
14	9.1	10.0	2.50	9.20	10.7

Now K_2 is calculated according to (1) with $[H^+] = 1.29$ M, the concentration of H^+ in 1 M sulfuric acid [17]:

$$K_2 = (9.20 \times 10^{-9}\ 7.0 \times 10^{-5}\ 1.29/0.80 \times 10^{-4})\ M^2$$
$$= 10.4 \times 10^{-9}\ M^2 .$$

The results of a series of similar experiments are collected in Table 1; from these experiments a mean value $K_2 = (11 \pm 1) \times 10^{-9}$ M² is obtained for a medium of 1 M sulfuric acid at a temperature of 22 °C.

Kinetic measurements

In order to follow the reaction of $HBrO_2$ with Br^- in a bromine buffer solution, a bromine solution in 1 M sulfuric acid was prepared from excess HOBr and Br^- as described above and thermostated at 25 °C; in a typical experiment the bromine and HOBr initial concentrations were $[Br]_2 = 1 \times 10^{-4}$ M and $[HOBr] = 2.0 \times 10^{-5}$ M. Into 140 ml of that solution 1.0 ml of a 7.0×10^{-4} M $NaBrO_2$ solution was injected, leading to a $HBrO_2$ initial concentration of 5.0×10^{-6} M. The $NaBrO_2$ was solved in a mixture of 0.01 M NaOH and 0.5 M Na_2SO_4, which solution has nearly the same index of refraction as 1 M sulfuric acid; this way Schlieren effects during the injection, which might disturb the measurement of the small absorbance changes significantly, could be avoided. The change ΔA of the absorbance due to the decay of bromine was followed using the dual wavelength technique (optical path length 10.7 cm, sample wavelength 401 nm, reference wavelength 601 nm); the result is displayed in Figure 3 (curve 1, right hand scale). It should be mentioned that even in the absence of added $HBrO_2$ a slow linear decrease of the absorbance A was observed, which is attributed to a slow decay of the bromine concentration. Within 100 s the decay was $\Delta A = 0.0004$, that is about 5% of the final absorbance change in Figure 3. The curves displayed in Figure 3 (and also in the following figures) are corrected for this small decay. The decay is less than 0.2% of the initial bromine concentration, hence no correction for this value is needed.

For comparison, the same experiment was repeated at a temperature of 20 °C (Fig. 3, curve 2). From the change ΔA of the absorbance we obtain the change Δc of the bromine concentration in the following way. If we combine (R 1) and (R 2) we find for the stoichiometry of the overall reaction of bromine with bromite

$$Br_2 + HBrO_2 + H_2O \rightarrow 3\,HOBr\,. \qquad (R\,2a)$$

That means that for each bromine molecule which disappears three HOBr molecules are formed. Hence

$$\begin{aligned}\Delta A &= d\,[\varepsilon(Br_2)\,\Delta c - \varepsilon(HOBr)\,3\,\Delta c]\\ &= d\,\Delta c\,[\varepsilon(Br_2) - 3\,\varepsilon(HOBr)]\,. \qquad (4)\end{aligned}$$

From the absorption spectra of Br_2 and HOBr we obtain the extinction coefficients $\varepsilon(Br_2) = 172\ M^{-1}\ cm^{-1}$ and $\varepsilon(HOBr) = 4\ M^{-1}\ cm^{-1}$ at $\lambda = 401$ nm; the optical path length d used in the experiments was $d = 10.7$ cm. This way the change Δc of the bromine concentration was calculated (Fig. 3, left hand scale). The final values of Δc are -4.6×10^{-6} and -4.3×10^{-6} M at 25 and 20 °C, respectively. The expected values for exclusive reaction of $HBrO_2$ with Br^- are 5×10^{-6} M in both cases. That means that only a small fraction of $HBrO_2$ disappears via the disproportionation reaction (R 4). This fraction is larger at 20 °C compared to 25 °C due to the smaller reaction rate of (R 1).

Additional measurements were performed with the same bromine concentration, but the initial concentration of HOBr was changed in the range from 2×10^{-5} M to 2×10^{-4} M (Fig. 4a, curves 1–4). By increasing the HOBr concentration the equilibrium (R 2) is shifted to the left hand side, and this way the rate of reaction (R 1) is slowed down. This can be clearly seen in the experiments; as a consequence, the disproportionation reaction becomes more and more important, and the final value Δc moves far away from the theoretical 5×10^{-6} M value.

In a third set of experiments, a 1 : 1 ratio of the bromine and HOBr initial concentrations was applied, but the absolute bromine concentration was changed by a factor of 20 from 1×10^{-4} M to 5×10^{-6} M (Figure 5a). The rate of bromine consumption decreases with decreasing initial concentrations.

Discussion

Equilibrium (R 2)

First we have to discuss the results obtained for L_{AgBr} and for K_2. The solubility product of AgBr in water was carefully measured at different temperatures by Gledhill and Malan [18] using a precise conductivity method; the value $5.08 \times 10^{-13}\ M^2$ was obtained at 25 °C. The value $1.0 \times 10^{-12}\ M^2$ found in our experiment in water solution is higher by a factor of 2. Apparently, this discrepancy must be due to some systematic error in the method used by us. One possibility might be that part of the AgBr formed during (R 5) in the experiment does not precipitate, but remains solved as $AgBr_{aq}$:

$$Ag^+ + Br^- \rightleftarrows AgBr_{aq}\,. \qquad (R\,5a)$$

Hence the amount of added Ag^+ at the first appearance of light scattering is larger than the amount required to exceed the solubility product. The equilibrium (R 5a) was investigated by Berne and Leden [19] using tracer methods. They report the value $K_{5a} = 1.4 \times 10^4\ M^{-1}$ at an ionic strength of 0.1 M (established by $NaClO_4$). Pulse radiolysis measurements performed by Schmidt et al. and by Meisel [20] lead to a value $K_{5a} = 3 \times 10^4\ M^{-1}$ in 1×10^{-4} M $HClO_4$. From (R 5a) we derive

$$[AgBr_{aq}] = K_{5a}\,[Ag^+]\,[Br^-] = K_{5a}\,L_{AgBr}\,. \qquad (5)$$

Even with the highest values of K_{5a} and of L_{AgBr} the concentration of solved AgBr does not exceed 6×10^{-8} M, that is less than 4% of the concentration of silver and bromide in the ionic state. Hence the discrepancy in our determination of the solubility product cannot be explained this way, unless supersaturation of the solution is taken into account.

It was not our aim, however, to measure an absolute value of L_{AgBr}, but to see the change, if the solvent water is replaced by the solvent 1 M sulfuric acid; in this case the systematic error should be very similar in both determinations. It turns out that L_{AgBr} is higher by a factor of 2.3 in 1 M sulfuric acid compared to a solution in water. Following the arguments of Field, Körös, and Noyes [5] concerning the activity coefficients in 1 M H_2SO_4, we have to write down the equation for the solubility product L^* of AgBr in terms of activities a:

$$(L_{AgBr})^* = a_{Ag^+}\,a_{Br^-} = f^2\,[Ag^+]\,[Br^-] = f^2\,L_{AgBr}\,. \qquad (6)$$

In water as a solvent the activity coefficients f are unity; if these activity coefficients are set equal to 0.7 for 1 M H_2SO_4 solution as proposed in [5], the solubility product is expected to be higher in 1 M sulfuric acid by a factor of two compared to a solution in water; this is nearly what we find in our experiment. A similar result was obtained by Berne and Leden

[19]; they find an increase of the solubility product of AgBr by a factor of 1.7 if the ionic strength is increased from 0 to 0.1 M ($NaClO_4$ solution).

In the bromine/HOBr experiment the amount of added silver ions up to the first appearance of light scattering will also be higher than expected for the first appearance of AgBr precipitate. In order to calculate the bromide concentration in equilibrium with bromide and HOBr it seems to be reasonable to use the value $L_{AgBr} = 2.3 \times 10^{-12}$ M^2 of the solubility product as determined in our experiments described above. This way the value $K_2 = 11 \times 10^{-9}$ M^2 was found for 1 M sulfuric acid solution at a temperature of 22 °C. The values 5.8×10^{-9} M^2 and 8.3×10^{-9} M^2 are reported by Liebhafsky [11] for the neutral solution at 25 and 30 °C, respectively. For better comparison we have to recalculate our value for these temperatures. We assume the validity of the thermodynamic relation between the equilibrium constant K_2 and the change of Gibb's energy ΔG^0 in the standard state:

$$\ln (K_2/M^2) = -\Delta G^0/(RT) . \qquad (7)$$

According to (7) our value $K_2 = 11 \times 10^{-9}$ M^2 changes into $K_2 = 10 \times 10^{-9}$ M^2 and 13×10^{-9} M^2, if we change the temperature from 22 °C to 20 °C and 25 °C, respectively; these values are higher by a factor of 2 compared to the corresponding Liebhafsky values.

If the same estimation of the activity coefficients is applied in the case of the hydrolysis reaction (R 2), we find for the hydrolysis constant $(K_2)^*$ in terms of activities

$$(K_2)^* = a_{HOBr}\, a_{Br^-}\, a_{H^+}/a_{Br_2} = f^2\, K_2 . \qquad (8)$$

With $f = 0.7$ for charged species in 1 M sulfuric acid solution [5] K_2 is expected to be larger by a factor of 2, just as obtained in our experiment.

In our opinion there is no doubt that K_2 increases from water as solvent to 1 M sulfuric acid by a factor of two as already calculated by Field, Körös, and Noyes [5]. The assumption of Kshirsagar and Field [9] that K_2 decreases by a factor of 20 is completely in disagreement with our experiments.

Bromide/bromite reaction in a bromine buffer system

First we discuss the experiments displayed in Figure 3. In this case the disproportionation reaction (R 4) is of minor importance for the kinetics compared to reactions (R 1) and (R 2). Since the value of the equilibrium constant K_2 is well established now we are able to deduce a rate constant for reaction (R 1). Since the HOBr concentration increases during the reaction, it is not possible to evaluate k_1 by an analytical procedure. Instead of this we performed numerical calculations treating k_1 as a parameter. From $K_2 = 13 \times 10^{-9}$ M^2 and the Eigen-Kustin value $k_{-2} = 8 \times 10^9$ M^{-2} s^{-1} [10] we deduce $k_2 = K_2 k_{-2} = 104$ s^{-1} at 25 °C. The rate constant for the disproportionation of $HBrO_2$ is $k_4 = 3000$ M^{-1} s^{-1} at 20 °C [2]. Similar measurements as described in [2] were carried out at 30 °C leading to $k_4 = 4000$ M^{-1} s^{-1}; interpolation for 25 °C gives $k_4 = 3500$ M^{-1} s^{-1}. The calculations were done with $[H^+] = 1.29$ M corresponding to 1 M sulfuric acid solution [17]. The best fit for curve 1 in Fig. 3 was obtained with $k_1 = 4 \times 10^6$ M^{-2} s^{-1} (Fig. 3, dots).

In the case of the 20 °C experiment $k_2 = 80$ s^{-1} is obtained from $K_2 = 10 \times 10^{-9}$ M^2 and $k_{-2} = 8 \times 10^9$ M^{-2} s^{-1}. With $k_4 = 3000$ M^{-1} s^{-1} the best fit of curve 2 in Fig. 3 is achieved with $k_1 = 2.5 \times 10^6$ M^{-2} s^{-1} (Fig. 3, dots).

The rate constants used in these calculations are summarized in Table 2. The value $k_1 = 2.5 \times 10^6$ M^{-2} s^{-1} determined from our experiments at 20 °C is in good agreement with the value 3×10^6 M^{-2} s^{-1} reported by Field and Försterling [2]; it is larger, however, by a factor of 6 than the value 0.4×10^6 M^{-2} s^{-1} deduced for 20 °C from the Ariese and Nagy value k_1 $[H^+] = 0.7 \times 10^6$ M^{-1} s^{-1} [8] (with $[H^+] = 1.29$ M and assuming the same temperature dependence as in our experiment) obtained from electrochemical measurements. With the same set of rate constants the kinetics of the curves in Figs. 4a and 5a are calculated and displayed in Figs. 4b and 5b. The main features of the experimental curves are very well modelled in the calculations. Systematic deviations occur in the final state of the reaction only, when the disproportionation of $HBrO_2$ becomes important (curves 2–4 in Figure 4). In these cases the experimental curves are higher in the final state than the calculated ones by about 20% indicating that the disproportionation of $HBrO_2$ is faster than assumed for a second order reaction. Such a behavior was already observed in the reaction of $HBrO_2$ with bromate if $HBrO_2$ is applied at concentrations lower than 3×10^{-6} M [2].

More information from Figs. 3 to 5 is obtained by comparing the initial slopes of the experimental curves to theory. In this case the disproportionation of $HBrO_2$, the decay of bromine and the increase of

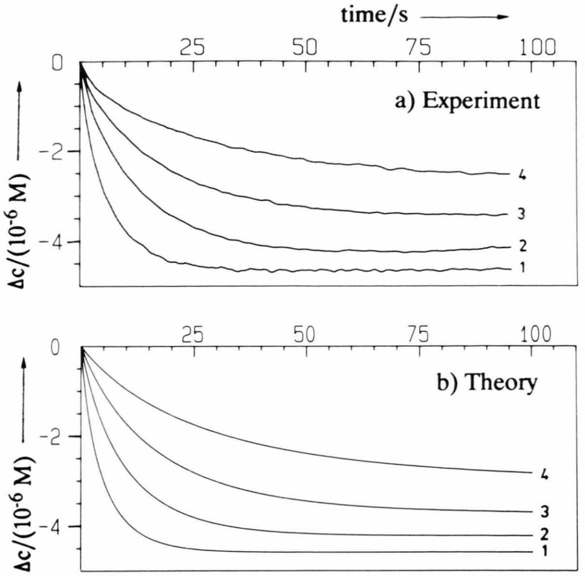

Fig. 4. Experiment as described in Fig. 3 at 25 °C with $[Br_2] = 1 \times 10^{-4}$ M and different HOBr-concentrations: 2×10^{-5} M (curve 1), 5×10^{-5} M (curve 2), 1×10^{-4} M (curve 3), 2×10^{-4} M (curve 4). a) experimental curves (25 °C), b) calculated curves (rate constants from Table 2, 25 °C, $[H^+] = 1.29$ M for 1 M sulfuric acid solution).

HOBr can be neglected. We only need equations (R 1) and (R 2) to calculate the initial slopes. Assuming a steady state for the bromide ions we find

$$[Br^-]_{stat} = k_2\,[Br_2]/(k_{-2}\,[HOBr]\,[H^+] + k_1\,[HBrO_2]\,[H^+])\,. \tag{9}$$

With the rate constants in Table 2, $[H^+] = 1.29$ M, $[HOBr] > 5 \times 10^{-6}$ M and $[HBrO_2] = 5 \times 10^{-6}$ M we find that the second term in the denominator of (9) can be completely neglected under the conditions of our experiments:

$$[Br^-]_{stat} = K_2\,\frac{[Br_2]}{[HOBr]\,[H^+]}\,. \tag{10}$$

The stationary bromide concentration depends on the ratio of the bromine and HOBr concentrations only and not on their absolute values. That means the system works as a buffer for bromide similar as a pH buffer solution works as a buffer for H^+. The rate of bromine consumption is equal to the rate of consumption of $HBrO_2$ via (R 1):

$$\frac{d[Br_2]}{dt} = \frac{d[HBrO_2]}{dt} = -k_1\,[Br^-]_{stat}\,[HBrO_2]\,[H^+] = -k_1\,K_2\,[HBrO_2]\,[Br_2]/[HOBr]\,. \tag{11}$$

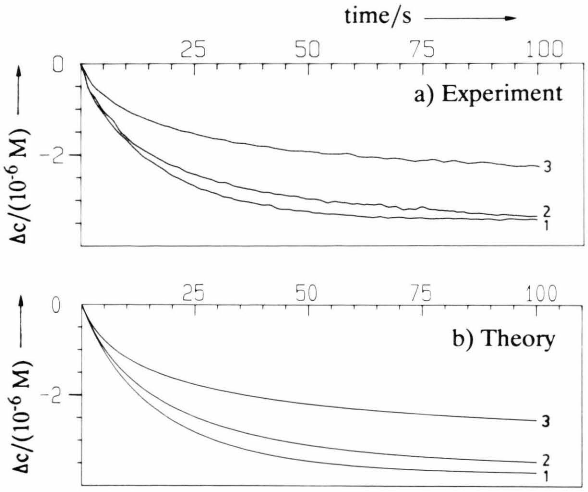

Fig. 5. Experiment as described in Fig. 3 at 25 °C with the ratio $[Br_2] : [HOBr] = 1 : 1$ at different HOBr- and Br_2 concentrations: 1×10^{-4} M (curve 1), 2×10^{-5} M (curve 2), 5×10^{-6} M (curve 3). a) experimental curves (25 °C), b) calculated curves (rate constants from Table 2, 25 °C, $[H^+] =$ 1.29 M for 1 M sulfuric acid solution).

Table 2. Rate constants k_1 to k_4 and equilibrium constant K_2 used in the calculations at 20 and 25 °C. a) Value determined here, b) value determined in [2].

Constants	$T = 20$ °C	$T = 25$ °C	Source
$k_1/(M^{-2}\,s^{-1})$	2.5×10^6	4×10^6	a)
$k_{-1}/(M^{-1}\,s^{-1})$	2×10^{-5}	2×10^{-5}	b)
$k_2(s^{-1})$	0.8×10^2	1.04×10^2	a)
$k_{-2}/(M^{-2}\,s^{-1})$	8×10^9	8×10^9	b)
$k_3/(M^{-2}\,s^{-1})$	1.6		a)
$k_{-3}(M^{-1}\,s^{-1})$	3.2	3.2	b)
$k_4/(M^{-1}\,s^{-1})$	3×10^3	3.5×10^3	a), b)
$k_{-4}/(M^{-1}\,s^{-1})$	1×10^{-8}	1×10^{-8}	b)
$K_2/(M^2)$	10×10^{-9}	13×10^{-9}	a)

Table 3. Initial slopes $d[Br_2]/dt$ of the experimental and theoretical curves displayed in Figs. 4–5 (initial concentrations $[Br_2]_0$ and $[HOBr]_0$). The theoretical values are calculated from (11), rate constant k_1 and equilibrium constant K_2 see Table 2 (25 °C), initial concentration of $HBrO_2$ is 5×10^{-6} M.

Curve	$[Br_2]_0$ / 10^{-6} M	$[HOBr]_0$ / 10^{-6} M	$(d[Br_2]/dt)_{t=0}$ / 10^{-6} M	
			Exper.	Theory
1 (Fig. 4)	100	20	1.3	1.30
2 (Fig. 4)	100	50	0.46	0.52
3 (Fig. 4)	100	100	0.30	0.26
4 (Fig. 4)	100	200	0.20	0.13
2 (Fig. 5)	20	20	0.30	0.26
3 (Fig. 5)	5	5	0.30	0.26

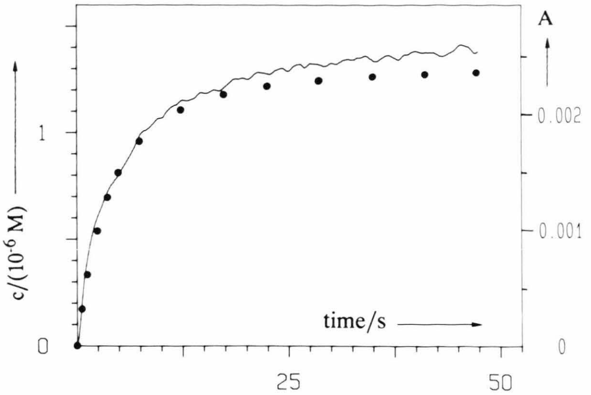

Fig. 6. Formation of Br_2 during the reaction of Br^- (initial concentration 3×10^{-6} M) with $HBrO_2$ (initial concentration 1×10^{-6} M) in 0.01 M sulfuric acid solution at 25 °C. *Solid line:* experimental curve. *Right hand scale:* absorbance A at 401 nm. *Left hand scale:* concentration c of Br_2 obtained from A with optical path length $d = 10.7$ cm and $\varepsilon(Br_2) = 172\ \mathrm{l\,mol^{-1}\,cm^{-1}}$. The dots are calculated bromine concentrations (k_1, k_{-1}, k_{-2}, and k_4 see Table 2, $k_2 = 46\ \mathrm{s^{-1}}$ according to the equilibrium constant $K_2 = 5.8 \times 10^{-9}\ \mathrm{M^2}$ valid in diluted sulfuric acid solution, $[H^+] = 0.016$ M).

It should be noted that the rate of consumption of bromine is expected to be independent of $[H^+]$. For the experiments displayed in Figs. 3–5 the experimental initial slopes $d[Br_2]/dt$ and the slopes calculated from (11) (with initial concentrations $[HBrO_2]_0$, $[Br_2]_0$, and $[HOBr]_0$) are compared in Table 3. It turns out that theory and experiment agree very well. Especially, the initial slopes of the curves in Fig. 5 are equal as predicted by theory (due to the same ratio $[Br_2]_0 : [HOBr]_0 = 1 : 1$).

Direct reaction of bromide and bromite in 0.01 M sulfuric acid

Although the results obtained in our experiments with bromine as a buffer for bromide ions are well consistent with the set of rate constants listed in Table 2, a direct experiment on (R 1) would be very helpful. From the electrochemical experiments of Ariese and Nagy [8] it is clear that reaction (R 1) cannot be followed directly at high sulfuric acid concentration. For this reason we performed an experiment in 0.01 M sulfuric acid solution at 25 °C. Into 140 ml of a 3×10^{-6} M solution of NaBr in 0.01 M H_2SO_4 875 µl of a 1.6×10^{-4} M $NaBrO_2$ solution were injected, resulting in an initial concentration $[HBrO_2]_0 = 1 \times 10^{-6}$ M. According to the 3 : 1 ratio of bromide and bromite a second order decay of bromide is expected; the final concentration of bromine formed during the reaction should be 2×10^{-6} M. In the actual experiment displayed in Fig. 6 a fast rise of the absorbance A is observed, which leads to a final absorbance $A = 0.0026$ corresponding to a final bromine concentration $0.0026/(10.7 \times 172)\ \mathrm{M} = 1.4 \times 10^{-6}$ M. This is 30% less than expected for complete reaction of Br^- with $HBrO_2$. In this experiment the initial $HBrO_2$ concentration is lower by a factor of 5 compared to the $HBrO_2$ concentrations used in the former experiments; it is most unprobable that the low yield of bromine is due to the disproportionation of bromous acid. On the other hand, we see from (1) that the fraction of bromide and hypobromous acid in equilibrium with bromine increases with decreasing H^+ concentration and with decreasing bromine initial concentration. In fact, the sulfuric acid concentration in our experiment is lower by a factor of 100 and the bromine concentration is lower by a factor of 2.5 compared to curve 3 in Figure 5. From (1) we calculate for the concentration of bromide formed by hydrolysis of bromine (initial concentration c_0):

$$[Br^-] = -K_2/(2[H^+]) + \sqrt{K_2 c_0/[H^+] + (K_2/(2[H^+]))^2}\,. \tag{12}$$

In [17] the concentration $[H^+]$ of sulfuric acid is listed down to $[H_2SO_4] = 0.1$ M; in this case $[H^+] = 0.138$ M is reported. Additional data [21] are available for $[H_2SO_4] = 0.005$ M; from the measured pH = 2.1 we calculate $[H^+] = 0.008$ M if we assume that there is no significant difference between activity and concentration. From this value we estimate $[H^+] = 0.016$ M at $[H_2SO_4] = 0.01$ M. On the other hand, for 0.01 M sulfuric acid medium the original Liebhafsky value $5.8 \times 10^{-9}\ \mathrm{M^2}$ should be better suited than our value $13 \times 10^{-9}\ \mathrm{M^2}$ derived for 1 M sulfuric acid solution. Inserting $c_0 = 2 \times 10^{-6}$ M, $[H^+] = 0.016$ M and $K_2 = 5.8 \times 10^{-9}\ \mathrm{M^2}$ into (12) we obtain $[Br^-] = 0.7 \times 10^{-6}$ M. That means that 35% of the bromine disappears, and the final concentration $[Br_2] = 1.3 \times 10^{-6}$ M is expected, which value is near to the measured 1.4×10^{-6} M. The calculated kinetics of the formation of bromine is compared to experiment in Figure 6 (dots). Regarding the uncertainties in our assumptions on K_2 and on $[H^+]$, experiment and theory agree well.

In the Ariese/Nagy experiments [8] a value $k_1[H^+] = 3 \times 10^4\ \mathrm{M^{-1}\,s^{-1}}$ is given for 0.02 M H_2SO_4; our experiment is modelled well by $k_1\ [H^+] = 4 \times 10^6$

$0.016 = 6.4 \times 10^4\ M^{-1}\ s^{-1}$; that value should be higher by a factor of two for 0.02 M sulfuric acid solution. This result indicates that in this case the k_1 value determined by electrochemical measurements is too low by a factor of about 4. We repeated the electrochemical experiments of Ariese and Nagy [8] at a sulfuric acid concentration of 0.01 M; within the limits of error the same result for k_1 as reported in [8] was obtained if the same way of evaluation of the experimental data was applied. From this point of view the results of the electrochemical method seem to be reliable. In our opinion, however, there is a systematic error in the interpretation of the experimental data. At $[H_2SO_4] = 0.01$ M and bromide concentration of about 1×10^{-6} M the hydrolysis of Br_2 is significantly shifted to the bromide side just as in our experiment displayed in Figure 6. That means that the bromide concentration decreases from an initial value c_0 to a value c_∞, which is about 30% of c_0 instead of zero as assumed in the evaluation by Ariese and Nagy. If that real c_∞ value would be used in the calculation, a significantly larger k_1 would be expected. The same argument is valid for higher sulfuric acid concentrations, since in these cases $[Br^-]_0$ was further reduced in order to decrease the rise time in the kinetic experiment. Moreover, the spectroscopic experiment performed by Ariese and Nagy [8] results in $k_1 = 1.4 \times 10^6\ M^{-2}\ s^{-1}$, which value is larger by a factor of two compared to their electrochemical experiments. In this case the initial bromide concentration was about 2 orders larger than in the electrochemical experiments; $[Br^-]_\infty$ is less than 1% of the initial concentration, and the evaluation of the data is correct in this case. k_1 obtained this way is still too low compared to our value by a factor 3, possibly due to problems with imperfect mixing during the stopped flow experiment as already mentioned by the authors.

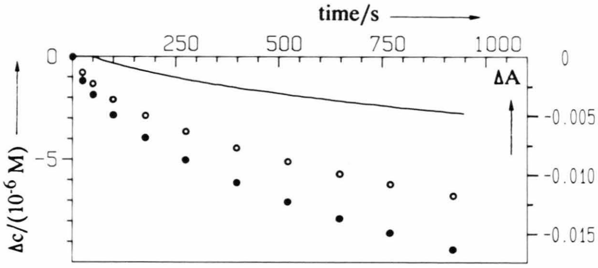

Fig. 7. Decay of bromine (initial concentration 5×10^{-5} M) in the reaction with bromate (0.1 M) in 1 M sulfuric acid at 20 °C. *Solid line:* experiment. The registration starts 50 s after the addition of NaBr. *Right hand scale:* change ΔA of the absorbance at 401 nm (dual wavelength method, reference 601 nm). *Left hand scale:* change Δc of the bromine concentration calculated from ΔA as described in the text. *Dots* and *circles:* Theory. The dots are calculated on the basis of the 20 °C rate constants listed in Table 2 ($[H^+] = 1.29$ M); the circles are calculated with $k_1 = 0$ (Reaction (R 1) neglected).

Reaction of bromine with bromate

Nevertheless the difficulties in explaining the low reaction rate during the reaction of bromine with excess bromate as reported by Kshirsagar and Field [9] are not yet resolved. On the basis of the experimental results presented here severe changes of K_2 as proposed in [9] cannot be justified. In order to obtain additional experimental data, we reexamined that reaction by using lower initial concentrations of bromine and by using a more sensitive method of detection. In our experiment 2 ml of a 8.8×10^{-3} M NaBr solution were added to 210 ml of a 0.1 M solution of $NaBrO_3$ in 1 M sulfuric acid at 20 °C. This way an initial concentration of $[Br_2] = 5 \times 10^{-5}$ M was obtained. The change ΔA of the absorbance at 401 nm (measured by the dual wavelength method, reference wavelength 601 nm) is displayed in Figure 7 (solid line; the registration of ΔA starts 50 s after the addition of NaBr). From ΔA the change Δc of bromine is calculated using a relation similar to (4); from the overall reaction

$$2\,Br_2 + HBrO_3 + 2\,H_2O \rightarrow 5\,HOBr \qquad (R\,6)$$

we conclude that 5 HOBr molecules are formed for two disappearing bromine molecules and the factor 3 in (4) has to be changed into 2.5. Δc was calculated using the 20 °C rate constants in Table 2. $k_3 = 1.6\ M^{-2}\ s^{-1}$ as measured by Lamberz [22] was preferred instead of the $2.5\ M^{-2}\ s^{-1}$ value given in [9], since the first value was obtained with bromate in excess as in the current experiment. The calculated curve is compared to experiment in Figure 7 (Dots). As in the Kshirsagar/Field experiment, the rate of bromine disappearance turns out to be smaller by a factor of about 3 compared to the calculations. In order to estimate the contribution of (R 1) a second calculation with $k_1 = 0$ was performed (Fig. 7, circles). In this case only one half of the bromine should disappear; nevertheless, the final value of Δc is reduced by less than 30% only. The reason is that in this case the HOBr production rate is smaller too and the hydrolysis reaction (R 2) is shifted more to the right hand

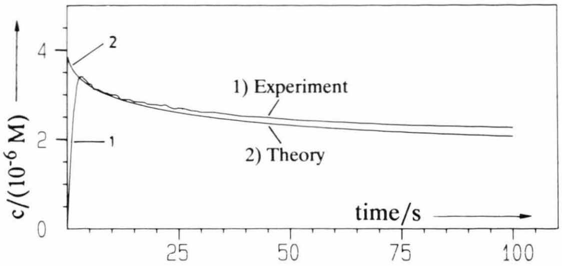

Fig. 8. Formation and decay of bromine during the reaction of bromide (initial concentration 5×10^{-6} M) with bromite (initial concentration 5×10^{-6} M) at 20 °C in 1 M sulfuric acid. *Curve 1:* experiment. The concentration *c* of bromine was calculated from the absorbance *A*; as in Figs. 3–5 the contribution of HOBr to *A* was taken into account. *Curve 2:* Theory. The calculation was started with an initial concentration 6×10^{-6} M of Br^- in order to obtain the same initial concentration of bromine as observed in the experiment. The rate constants used in the calculation are the 20 °C values in Table 2 ($[H^+] = 1.29$ M).

side. That means that reasonable changes in k_1 do not lead to significant changes in the overall reaction rate. Of course, it would be possible to model the experiment by assuming a K_2 value which is lower by a factor of 10 as proposed in [9]. In this case, however, $k_1 = 25 \times 10^6\ M^{-2}\ s^{-1}$ would be needed according to (11) to explain our experiment displayed in Figure 3; such a high value would be inconsistent with the direct experiment shown in Figure 6. Another possibility would be to decrease k_3 from $1.6\ M^{-2}\ s^{-1}$ to $0.16\ M^{-2}\ s^{-1}$ although this rate constant seems to be well established. It should be mentioned, however, that k_3 was measured with 1×10^{-4} M bromide solutions [22]; the bromide concentration in the actual experiment is lower by about two orders of magnitude. Moreover it is known that bromate in sulfuric acid solution is unstable; HOBr is formed slowly, which might shift the equilibrium (R 2) more to the left hand side than assumed. Anyway, additional experiments are required to solve the problem.

Bromide/bromite reaction with excess $HBrO_2$

The reaction of bromide with bromite in competition with silver ions was investigated by Försterling and Schreiber [12]. In these experiments $HBrO_2$ and NaBr solutions of equal concentrations were injected into 1 M sulfuric acid solution. A fast rise of the absorbance due to the formation of bromine is observed. After that process, excess $HBrO_2$ reacts with bromide, which is in equilibrium with bromine according to (1), and part of the bromine disappears (see Fig. 5a in [12]). In order to model the kinetics of the bromine decay it was necessary to use $k_1\ [H^+] = 5 \times 10^5\ M^{-1}\ s^{-1}$, which value is even less than the Ariese/Nagy value. According to the results obtained in the present investigation, such a procedure cannot be justified. For this reason the experiment was repeated, and the result was compared to calculations using the set of rate constants listed in Table 2. A typical run is displayed in Figure 8. Into 140 ml of a solution of 5×10^{-6} M NaBr in 1 M sulfuric acid thermostated at 20 °C 840 µl of a 8.4×10^{-4} M solution of $NaBrO_2$ were injected, leading to a $HBrO_2$ initial concentration 5×10^{-6} M. From the overall reaction

$$3\ Br^- + HBrO_2 + 3\ H^+ \rightarrow 2\ Br_2 + 2\ H_2O \qquad (R\,7)$$

a maximum bromine concentration of 3.3×10^{-6} M is expected; after that starting reaction an excess of 3.3×10^{-6} M $HBrO_2$ is present in the solution. Unfortunately, the maximum value of the experimental curve is reached not before 3 s due to the process of mixing and the rise time of the apparatus. The maximum value corresponds to a concentration of 3.3×10^{-6} M as expected, the zero time value, however, is larger and can be roughly extrapolated as 3.9×10^{-6} M, which value is higher by 18%. Part of this discrepancy can be attributed to some bromide and hypobromite impurities in the $NaBrO_2$ sample, but this way we cannot account for the whole effect. Anyway, a simulation of the kinetics has to start with that high value of bromide initial concentration. Using the set of rate constants valid for 20 °C and starting with a bromide initial concentration of 6×10^{-6} M (which value leads to 3.9×10^{-6} M bromine as obtained in the experiment) and a bromite initial concentration of 5×10^{-6} M, the calculated curve in Fig. 8 is obtained. Experiment and theory agree well, although the final bromine concentration is higher in the experiment; as already discussed in connection with Figs. 4 and 5, this may be due to a faster disproportionation process of $HBrO_2$ than expected for a clear second order reaction. We conclude that the high value of k_1 derived in the present work is compatible with this last experiment and that there is no need to use a lower value in the calculations. Of course, the conclusions drawn in [12] will be changed if a higher k_1 value is introduced. For example, the effective rate of bromide removal by silver ions will be increased by a factor of 5. These implications will be discussed separately.

Conclusions

We have proved that the bromine hydrolysis equilibrium (R 2) is shifted from water to 1 M sulfuric acid as solvent in practically the same way as originally predicted by Field, Körös, and Noyes [5]. There is a small difference between the Eigen and Kustin value $K_2 = 6.9 \times 10^{-9}$ M^2 (20 °C, ionic strength 0.1 M) [10] and the Liebhafsky value $K_2 = 4.2 \times 10^{-9}$ M^2 (extrapolated from the 25 °C value 5.8×10^{-9} M^2 to 20 °C, ionic strength 0) [11], which is most probably due to the change in ionic strength (the factor of 1.6 is practically the same as in the case of the solubility product of AgBr reported in [19]). We prefer the Liebhafsky value, because it is directly obtained from equilibrium experiments, and results at different temperatures are available. In our actual kinetic calculations we have maintained $k_{-2} = 8 \times 10^9$ M^{-2} s^{-1} [2]; k_2 was derived from K_2 and k_{-2} as can be seen from Table 2. This way $k_2 = 110$ s^{-1} as given in [5] has to be changed into 80 s^{-1} (20 °C) and 104 s^{-1} (25 °C). Perhaps it would be more reasonable to maintain k_2 and to adjust k_{-2}, but the results of our calculations depend on K_2 only and not at all on any arbitrary splitting into k_2 and k_{-2} provided that k_{-2} is in the order of 10^9 M^{-2} s^{-1}.

From our direct measurements at $[H_2SO_4] = 0.01$ M, and from our more indirect measurements in bromine buffer systems at $[H_2SO_4] = 1$ M, consistent values of the rate constant k_1 at 20 °C and 25 °C are derived. Our values $k_1 = 2.5 \times 10^6$ M^{-2} s^{-1} (at 20 °C) and $k_1 = 4 \times 10^6$ M^{-2} s^{-1} (at 25 °C) are larger by a factor of 6 compared to the rate constants obtained by Ariese and Nagy [8] from electrochemical measurements at different H_2SO_4 concentrations; on the other hand, our 20 °C value is very near to 3×10^6 M^{-2} s^{-1} as proposed in [2] on the basis of thermodynamic data on (R 1).

The unexpected low rate of the bromine-bromate reaction, as pointed out first by Kshirsagar and Field [9], could be proved in an independent experiment. An explanation of that discrepancy seems to be difficult, and further work is needed. Anyway, it can be excluded that the equilibrium (R 2) is much more shifted to the left hand side than assumed so far.

The result obtained with the reaction of excess bromite with bromide has implications on the conclusions drawn from a competition experiment with added silver ions [12], [23]. That competition experiment was modelled with the low k_1 value predicted in [8]; but it is clear now that the interpretation is also consistent with the high k_1 value established in the present investigation. One consequence will be that the rate constant for effective removal of bromide by silver ions has to be increased from 3×10^4 M^{-1} s^{-1} to 1.5×10^5 M^{-1} s^{-1}.

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