Equilibria, Rates of Formation and Bromide Anations

of *cis*- and *trans*-Dibromodiaquaplatinum (II)

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Measurable concentrations of the species $PtBr_n(H_2O)_{4-n}{}^{2-n}$, $n = 1$, 2, 3, 4 have been demonstrated in aged dilute (<1 mM) solutions of K_2PtBr_4, 0.500 M in $HClO_4$ to suppress the protolysis of the aqua complexes. At equilibrium, about 2/3 of the neutral complex is present as the *cis*-isomer, 1/3 as the *trans*-isomer. Equilibrium constants are given in Table 5 for 25 and 35°C.

The bromide anation of $trans$-$PtBr_3(H_2O)_2$, cis-$PtBr_3(H_2O)_2$ and $PtBr(H_2O)_3{}^+$ have been studied spectrophotometrically. Rate constants and activation parameters for these reactions and for the reverse acid hydrolyses are given in Table 7.

E quilibrium measurements [1] indicate the formation of the species $PtBr_2(H_2O)_2$ in aged solutions of K_2PtBr_4. At equilibrium, this complex consists of a mixture of *cis*- and *trans*-isomers. The rates of formation of these isomers in aging solutions, their bromide anations and the equilibrium between them may be studied spectrophotometrically in the same manner as the reactions of the corresponding chloro complexes.[2,3] A reaction model, including notations for the rate constants used, has been given previously.[1]

EXPERIMENTAL

Chemicals and apparatus were the same as in Ref. 1. Potassium tetrabromo-platinate(II)-dihydrate prepared by Degussa was used. When not otherwise stated, all solutions had the ionic strength 0.500 M, obtained by means of added perchloric acid. For the study of rapid kinetic runs a Cary 15 Recording Recording Spectrophotom-eter, equipped with a specially built, thermostated holder for 1 cm cells, was employed.

Bromide anation of cis-$PtBr_2(H_2O)_2$. Stock solutions were made by mixing 1.000 M HBr and 1.000 M $HClO_4$. They had the following concentrations of free bromide: 0.0500, 0.0400, 0.02000, and 0.01000 M. The stock solutions of K_2PtBr_4 (5.87×10^{-4} M) contained sodium hydroxide (5×10^{-3} M). When aged for 12 to 20 h at 15, 25 or 35°C, they will contain relatively high concentrations of the complex cis-$PtBr_2(OH)_2{}^{2-}$ (*cf.* Ref. 2). 1.500 ml of these solutions were transferred into the 1 cm cell of the Cary Spectrophotom-eter and the recorder was started. 1.500 ml of one bromide stock solution was rapidly injected into the cell from a thermostated syringe. The hydroxo complex was then instantly converted to the corresponding aqua complex, cis-$PtBr_2(H_2O)_2$, and the ionic strength

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of the resulting solution became 0.500 M. The heat evolved by the neutralisation and dilution was negligible. The change of absorbance vs. time was recorded by the instrument at 251 nm. At this wavelength, the molar absorptivities of $PtBr_4^{2-}$ and $PtBr_3H_2O^-$ are both equal to 2810 cm^{-1} M^{-1} (cf. Ref. 1, Fig. 2). The recorded change of absorbance was
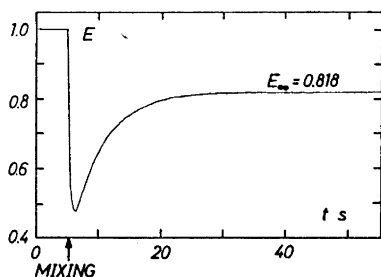
Fig. 1. Bromide anation of cis-$PtBr_2(H_2O)_2$. The curve was recorded at 35°C by the Cary spectrophotometer for a fast kinetic run having $C_{Pt}=2.94 \times 10^{-4}$ (M) and $b=2.50 \times 10^{-2}$ (M). 1 cm cell.

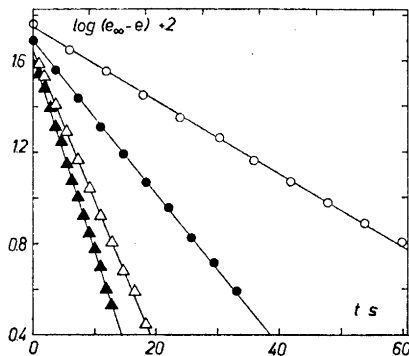**Fig. 2.** Bromide anation of cis-$PtBr_2(H_2O)_2$ at 35°C. Plots of log $(e_\infty-e)$ vs. t for kinetic runs having $C_{Pt}=2.94 \times 10^{-4}$(M), and the following concentrations of free bromide: 5.0×10^{-3} (O), 1.00×10^{-2} (●), 2.00×10^{-2} (△), and 2.50×10^{-2} (▲) M.

therefore due to reaction (1) exclusively, whereas the consecutive and slower [1] bromide anation of $PtBr_3H_2O^-$ caused no change. Kinetic runs having half-lives as low as 3.5 s were followed with good accuracy in this manner. Fig. 1 gives an example. The reverse reaction was suppressed, since the concentration of free bromide was greater than 5×10^{-3} M in all experiments. Then less than 2 % of the platinum was left as $PtBr_3(H_2O)_2$ at the final equilibrium (Ref. 1, Fig. 3). Since the concentration of bromide was much greater than the concentration of the complex, first order reactions were obtained.

Bromide anation of trans-$PtBr_2(H_2O)_2$. Solutions of K_2PtBr_4 (about 1.6×10^{-4} M) without extra bromide added were aged for 4 to 8 days at 25.00 or 35.00°C. At equilibrium, these solutions contained about 30 % of the platinum as trans-$PtBr_2(H_2O)_2$ and $PtBr(H_2O)_3^+$ at 35°C and about 26 % at 25°C. Stock solutions containing hydrobromic and perchloric acid having the following concentrations of free bromide: 0.500, 0.400, 0.2000, 0.1000, and 0.0500 M, were used. Equal volumes of these solutions and aged platinum solutions were mixed in flasks at the pertinent temperature ± 0.02°C, and the reaction was followed at 268 nm. The reverse reaction was suppressed, since the concentration of free bromide was greater than 25×10^{-3} M. First order reactions were obtained by having bromide in excess.

The equilibrium cis-/trans-$PtBr_2(H_2O)_2$. Solutions of K_2PtBr_4 (about 1.6×10^{-4} M) having varying concentrations of bromide (Table 3) were equilibrated for at least 3 days at 35.00°C and for at least 8 days at 25.00°C. These solutions were mixed with equal volumes of 0.500 M hydrobromic acid and the increase of absorbance at 268 nm due to the bromide anation of trans-$PtBr_2(H_2O)_2$ was followed (Fig. 7). Analysis of these kinetic runs gives the fraction of platinum, present as trans-$PtBr_2(H_2O)_2$ and $PtBr(H_2O)_3^+$, in the initial solution.[3]

Formation of trans-$PtBr_2(H_2O)_2$ *and* $PtBr(H_2O)_3^+$ *in aging solutions.* The rate of formation was studied at 25.00 and 35.00°C (i) from the decrease of absorbance at 268 nm of aging solutions of K_2PtBr_4 (Table 3), and (ii) by mixing samples of the aging solutions listed in Table 3 with equal volumes of 0.500 M HBr and following the bromide anation of trans-$PtBr_2(H_2O)_2$ (vide previous section and Ref. 3). The half-lives for the formation of the mixture of trans-$PtBr_2(H_2O)_2$ and $PtBr(H_2O)_3^+$ were about 15 h at 35°C and about 35 h at 25°C but occasionally, half-lives smaller than these were observed.

Table 1. Bromide anation of *cis*-PtBr$_2$(H$_2$O)$_2$. The rate constant $k_{exp} = k_{3c-}$ b (s^{-1}) at different concentrations of free bromide, b M. The total concentration of platinum was 2.94 × 10^{-4} M in all experiments. The error in k_{exp} was about 3 %.

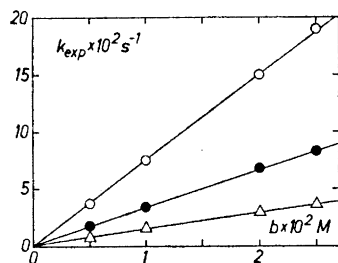| $b \times 10^3$	$k_{exp} \times 10^2$		
	15°C	25°C	35°C
5.0	0.79	1.77	3.7
10.0	1.54	3.4	7.5
20.0	2.90	6.8	15.0
25.0	3.6	8.3	19.0

Fig. 3. Bromide anation of *cis*-PtBr$_2$(H$_2$O)$_2$. The rate constant k_{exp} s^{-1} as a function of the concentration of free bromide at 15°C (△), 25°C (●), and 35°C (○).
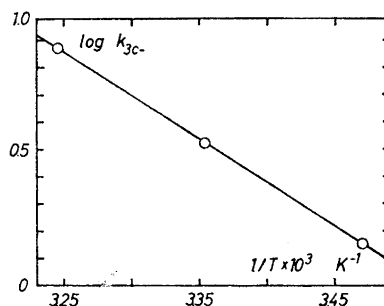
Fig. 4. Bromide anation of *cis*-PtBr$_2$(H$_2$O)$_2$. Temperature dependence of the rate constant k_{3c-} s^{-1}.

RESULTS

Bromide anation of cis-PtBr$_2$(H$_2$O)$_2$. The rate constant for the bromide anation

$$cis\text{-PtBr}_2(\text{H}_2\text{O})_2 + \text{Br}^- \longrightarrow \text{PtBr}_3\text{H}_2\text{O}^- + \text{H}_2\text{O} \tag{1}$$

may be written $k_{exp} = k_{3c-}$ b (s^{-1}), where b is the concentration of free bromide (*cf.* Ref. 2). The values of k_{exp} given in Table 1 were obtained from plots of log($e_\infty - e$) *vs. t* (Fig. 2). As for the chloride anation of *cis*-PtCl$_2$(H$_2$O)$_2$,[2] plots of k_{exp} *vs. b* give straight lines passing through the origin (Fig. 3). Reaction (1) is thus first order with respect to bromide. It is also first order with respect to complex, since k_{exp} was not influenced by the initial concentration of *cis*-PtBr$_2$(H$_2$O)$_2$, which varied with the time of aging for the platinum stock solutions. The values obtained for the rate constant k_{3c-} s^{-1} M^{-1} and the activation parameters, calculated from the temperature variation shown in Fig. 4, are given in Table 7.

Bromide anation of trans-$PtBr_2(H_2O)_2$ *and* $PtBr(H_2O)_3{}^+$. The aged solutions used contain an equilibrium mixture of *trans*-$PtBr_2(H_2O)_2$ and $PtBr(H_2O)_3{}^+$ (*cf.* Ref. 2). Using the same notation and method of calculation as for the corresponding chloro complexes described in Ref. 2, the rate constant

$$k_{exp} = k_{3t-}\, b + k_{2c-}\, K_{2t} \qquad (2)$$

Table 2. Bromide anation of *trans*-$PtBr_2(H_2O)_2$. The rate constant k_{exp} s^{-1} of eqn. (2) at different concentrations of bromide, b M. The values of k_{exp} given represent the mean of several experiments. C_{Pt} was 8×10^{-5}(M) for all experiments except those having $b = 99 \times 10^{-3}$, which had $C_{Pt} = 12.6 \times 10^{-5}$.

$b \times 10^3$	$k_{exp} \times 10^5$	
	25°C	35°C
25.0	0.70 ± 0.05	1.9 ± 0.1
50.0	1.17 ± 0.08	3.3 ± 0.2
99.0	2.0 ± 0.1	—
100.0	2.0 ± 0.1	6.2 ± 0.4
200.0	3.8 ± 0.2	12.0 ± 0.8
248.1	4.6 ± 0.3	—
250.0	4.7 ± 0.3	14 ± 1

Table 3. The equilibrium *cis-/trans*-$PtBr_2(H_2O)_2$. $(e_\infty - e_0)$ cm^{-1} and e_∞ cm^{-1} were obtained from kinetic runs (*vide* Fig. 7). α_1 and α_2 were calculated using the equilibrium constants K_4, K_3, and K_2 M, given in Table 5. Concentrations in M. The values given represent the mean of several experiments.

Temperature	$C_{Pt} \times 10^4$	$C_{Br} \times 10^3$	$e_\infty - e_0$ MEAN	e_∞ MEAN	α_{exp}	α_1	α_2	$K_{c/t}$ Eqn.(3)
	1.582	0.633	0.175	0.669	0.263	0.128	0.405	2.0
	1.574	0.729	0.133	0.661	0.201	0.088	0.359	2.2
	1.574	0.827	0.106	0.661	0.161	0.062	0.314	2.2
	1.574	0.926	0.088	0.661	0.133	0.044	0.274	2.1
25°C	1.574	1.024	0.071	0.661	0.108	0.034	0.241	2.3
	1.574	1.123	0.061	0.661	0.092	0.026	0.211	2.2
	1.574	1.320	0.046	0.661	0.069	0.016	0.167	2.2
							Mean:	2.2 ± 0.2
	1.611	0.644	0.199	0.662	0.301	0.158	0.454	2.2
	1.588	0.734	0.161	0.656	0.245	0.115	0.419	2.2
	1.588	0.832	0.132	0.656	0.201	0.085	0.381	2.3
	1.616	0.942	0.114	0.675	0.169	0.064	0.343	2.3
35°C	1.630	1.046	0.104	0.684	0.152	0.049	0.309	2.0
	1.630	1.145	0.090	0.684	0.132	0.039	0.280	2.0
	1.588	1.325	0.065	0.659	0.099	0.026	0.232	2.2
							Mean:	2.2 ± 0.2

Table 4. The equilibrium constant $K_{c/t}$ of eqn. (3) for different values of K_2 M at 25°C. The values of K_4 and K_3 used in the calculation are given in Table 5. C_{Pt} and C_{Br} in M.

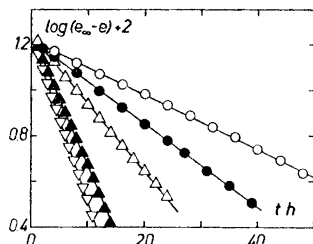| $C_{Pt} \times 10^4$	$C_{Br} \times 10^3$	$K_{c/t}$						
$K_2 \times 10^5 \longrightarrow$		0	3	6	7	8	9	12
1.582	0.633	0.9	1.1	1.6	1.8	2.0	2.3	3.1
1.574	0.729	1.0	1.3	1.8	2.0	2.2	2.4	3.3
1.574	0.827	1.1	1.4	1.8	2.0	2.2	2.4	3.1
1.574	0.926	1.2	1.4	1.8	1.9	2.1	2.3	2.9
1.574	1.024	1.3	1.6	1.9	2.1	2.3	2.4	3.0
1.574	1.123	1.4	1.6	1.9	2.0	2.2	2.3	2.9
1.574	1.320	1.5	1.7	1.9	2.1	2.2	2.3	2.7

Fig. 5. Bromide anation of *trans*-$PtBr_2(H_2O)_2$ at 25°C. Plots of log $(e_\infty - e)$ *vs. t* for kinetic runs having $C_{Pt} = 7.9 \times 10^{-5}$ and the following concentrations of free bromide: 0.0250 (O), 0.0500 (●), 0.1000 (△), 0.2000 (▲), and 0.2500 (▽) M.
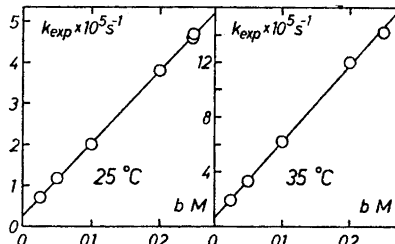
Fig. 6. Bromide anation of *trans*-$PtBr_2(H_2O)_2$. The rate constant k_{exp} s⁻¹ defined by eqn. (4) as a function of the concentration of free bromide, *b* M, at 25 and 35°C.

may be obtained from plots of $\log(e_\infty - e)$ *vs. t* (Fig. 5). Table 2 gives the values of k_{exp} calculated, and Fig. 6 shows the linear plots of k_{exp} *vs. b*. The values of $k_{3t\_}$ given in Table 7 were obtained from the slopes of these plots. The intercepts were approximately 2.5×10^{-6} s⁻¹ at 25°C and 5×10^{-6} s⁻¹ at 35°C. From these values and the equilibrium constant K_{2t} given in Table 5 approximate values of the rate constant $k_{2c\_}$ may be calculated (Table 7).

The equilibrium cis-/trans-$PtBr_2(H_2O)_2$. Using the notation and method of calculation described previously,[3] the equilibrium constant $K_{c/t}$ may be obtained as

$$K_{c/t} = [cis\text{-}PtBr_2(H_2O)_2] \, [trans\text{-}PtBr_2(H_2O)_2]^{-1} = \alpha_2(\alpha_{exp} - \alpha_1)^{-1} - 1 \qquad (3)$$

since, also in the bromide case $\varepsilon_{2t} \ll \varepsilon_4$ (*cf.* Ref. 3). α_{exp} could be obtained as $(e_\infty - e_0)/e_\infty$ from plots like those given in Fig. 7. In order to calculate α_2 and α_1, values of the stepwise dissociation constants K_4, K_3, and K_2 must be used. The two first mentioned have been calculated previously.[1] Approximate values of K_2 were also obtained from the previous measurements, but may also be determined from the present measurements by variation
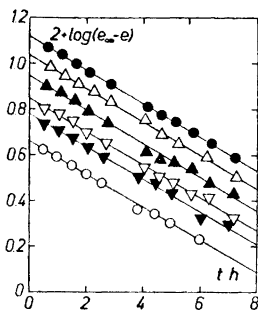
Fig. 7. log $(e_\infty - e)$ vs. t for kinetic runs used to determine $\alpha_{exp} = (e_\infty - e_0)/e_\infty$ at 25°C for equilibrated solutions of K_2PtBr_4 having $C_{Pt} = 1.574 \times 10^{-4}$ (M) and the following values of C_{Br} M (from above): 7.29×10^{-4}, 8.27×10^{-4}, 9.26×10^{-4}, 1.024×10^{-3}, 1.123×10^{-3}, and 1.320×10^{-3}. These solutions were mixed with equal volumes of 0.500 M HBr and the absorptivity e measured vs. time. The calculation of α_{exp} from the series shown is given in Table 3.
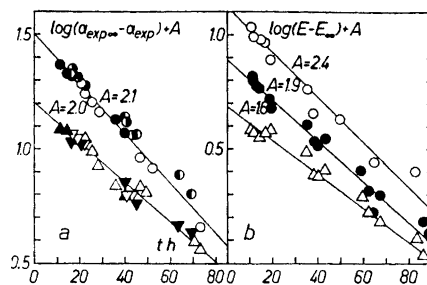
Fig. 8. Formation of trans-$PtBr_2(H_2O)_2$ and $PtBr(H_2O)_3^+$ at 25°C. a. Plots of log $(\alpha_{exp\infty} - \alpha_{exp})$ vs. t. Rings denote solutions having $C_{Pt} = 1.74 \times 10^{-4}$ (M) and no extra bromide added. Triangles denote solutions having $C_{Pt} = 1.76 \times 10^{-4}$ (M) and $[Br^-]_{added} = 2.00 \times 10^{-4}$ (M). b. Plots of log $(E - E\infty)$ vs. t. The solutions contain no extra bromide. C_{Pt} was 2.998×10^{-4} (O), 1.999×10^{-4} (●), and 0.999×10^{-4} (△) M.

of K_2 until a constant value of $K_{c/t}$ is obtained from eqn. (3) — vide Table 4. It appears from this table that if K_2 is equal to zero, a systematic change in the values of $K_{c/t}$ is obtained. This is indirect evidence for the presence of measurable concentrations of $PtBr(H_2O)_3^+$ in the solutions used. Values of $K_2 = (8 \pm 4) \times 10^{-5}$ at 25°C and $(10 \pm 5) \times 10^{-5}$ at 35°C give constant values of $K_{c/t}$. Table 3 gives the calculations of $K_{c/t}$ for these values of K_2. A summary of the equilibrium constants calculated for the system is given in Table 5. The constants K_{3c}, K_{3t}, K_{2c} and K_{2t} have been defined previously (Ref. 2, Fig. 1) for the chloride system.

The formation of trans-$PtBr_2(H_2O)_2$ and $PtBr(H_2O)_3^+$ in aging solutions. According to the method of calculation previously [3] described, a rate constant k_{exp}, defined by eqn. (16) in Ref. 3, may be obtained from plots like those given in Fig. 8. The calculation of the rate constant k_{2c-} from the experimental values of k_{exp} is given in Table 6. The approximation $b = $ constant used for the reactions of the chloro complexes, is also valid in this case. The rate constants k_{2c-} obtained from these measurements are of the same magnitude as the approximate values calculated for the reverse reaction from the intercepts of Fig. 6 (Table 7). Thus the reaction model used can account for both the forward reaction, i.e. the formation of trans-$PtBr_2(H_2O)_2$ and $PtBr(H_2O)_3^+$, and the reverse reaction, i.e. the bromide anations of these species.

DISCUSSION

The change of $K_{c/t}$ with the concentration of bromide for $K_2 = 0$ (Table 4) is a qualitative proof of the existence of small concentrations of $PtBr(H_2O)_3^+$ in the solutions used. The value of K_2 calculated from this

Table 5. Equilibrium constants at 25 and 35°C. All values are given in M except for $K_{c/t}$, defined by eqn. (3). Notations in Ref. 2, Fig. 1.

Constant	25°C	35°C
$K_4 \times 10^3$	1.8 ± 0.2^a	2.6 ± 0.3^a
$K_3 \times 10^4$	2.5 ± 0.3^a	3.6 ± 0.3^a
$K_{c/t}$	2.2 ± 0.2	2.2 ± 0.2
$K_{3c} \times 10^4$	1.7 ± 0.4	2.5 ± 0.5
$K_{3t} \times 10^4$	0.8 ± 0.2	1.1 ± 0.3
$K_2 \times 10^5$	8 ± 4	10 ± 5
$K_{2c} \times 10^4$	1.2 ± 0.6	1.4 ± 0.7
$K_{2t} \times 10^4$	2.6 ± 1.6	3.1 ± 1.5

[a] Ref. 1.

Table 6. Formation of *trans*-PtBr$_2$ and PtBr$^+$ in aging solutions of K$_2$PtBr$_4$. Concentrations are in M, k_{exp} in s^{-1} and k_{2c-} in s^{-1} M^{-1}.

Temperature	$C_{Pt} \times 10^4$	$C_{Br} \times 10^4$	$b \times 10^4$ Mean	$k_{exp} \times 10^6$	$k_{2c-} \times 10^2$	$k_{2c-} \times 10^2$ Mean
25°C	2.998	11.99	3.7	5.9^a	3.2	
	1.999	8.00	2.8	5.6^a	3.2	
	0.999	4.00	1.6	5.2^a	3.3	3.3 ± 0.5
	1.738	6.95	2.5	6.6^b	3.8	
	1.758	9.03	4.1	5.5^b	2.9	
35°C	3.00	12.00	4.1	13.0^a	5.7	
	2.003	8.01	3.0	12.8^a	6.0	
	1.001	4.00	1.7	12.4^a	6.5	6 ± 1
	1.860	7.44	2.8	12.9^b	6.1	
	1.790	9.16	4.4	15.6^b	6.8	

[a] From plots of $\log(E - E_\infty)$; [b] From plots of $\log(\alpha_{exp\infty} - \alpha_{exp})$.

Table 7. Bromide anation rate constants in s^{-1} M^{-1}, acid hydrolysis rate constants in s^{-1}, activation enthalpies, $\Delta H^{o\ddagger}$ kcal mol^{-1} and activation entropies, $\Delta S^{o\ddagger}$ cal K^{-1} mol^{-1} (standard state of water: unit mole fraction). The acid hydrolysis rate constants have been calculated from the equilibrium constants of Table 5 and the corresponding bromide anation constants. Notations in Ref. 1, Fig. 1.

Constant	15°C	25°C	35°C	$\Delta H^{o\ddagger}$	$\Delta S^{o\ddagger}$
k_{3c-}	1.42 ± 0.04	3.3 ± 0.1	7.4 ± 0.2	14	-9
$k_{3t-} \times 10^4$	—	1.8 ± 0.1	5.4 ± 0.2	20	-10
$k_{2c-} \times 10^{2a}$	—	~ 1	~ 2	—	—
$k_{2c-} \times 10^{2b}$	—	3.3 ± 0.5	6 ± 1	—	—
$k_{3c} \times 10^4$	1.6 ± 0.4	6 ± 1	19 ± 4	21	-3
$k_{3t} \times 10^8$	—	1.4 ± 0.4	6 ± 2	26	-8
$k_{2c} \times 10^{6a}$	—	~ 1	~ 3	—	—
$k_{2c} \times 10^{6b}$	—	4 ± 3	8 ± 6	—	—

[a] From the intercepts of Fig. 6a and b. [b] From experiments given in Table 6.

variation, however, might have a large error, since the concentration of free bromide could be varied only in a rather small interval $(6 \times 10^{-4} < [Br^-] < 13 \times 10^{-4})$. The uncertainties in the values of K_4 and K_3 used in the calculation will of course also influence the values of K_2 and $K_{c/t}$ obtained. The concentrations of $PtBr(H_2O)_3^+$ in the solutions used are too low to permit a determination of K_2 by means of cation exchange separation of $PtBr(H_2O)_3^+$ from the neutral and anionic species, a method which was used for the $PtCl(H_2O)_3^+$-ion.[4]

Consequently, the acid hydrolysis rate constants calculated from the relation $k_n = K_n\, k_{n-}$ (Table 7) will be rather uncertain. An attempt to describe these constants by the same type of equation, which has been proposed by Martin et al.[5] for the acid hydrolysis of chloro ammine complexes, and which has also been used by the present author for the acid hydrolysis rate constants of the chloride system,[3] leads to the following equation for k_4, k_{3c}, and k_{3t} at 25°C: $k/m = 4.6 \times 10^{-5} \times (3 \times 10^{-4})^{r \cdot 6^s}$. This equation gives a value of $k_{2c} = 2 \times 10^{-7}$ (s^{-1}) which differs by about one a power of ten from the experimental value, which is about 4×10^{-6} s^{-1}. This discrepancy might be due to the rather large experimental errors, especially in k_{2c}. A similar discrepancy has been observed for the ammoniation reactions of the platinum(II)-chloro ammine complexes.[6]

Although it has not been possible to investigate the bromide system as completely and accurately as the chloride system [2-4] because of experimental difficulties, it might be concluded that the stepwise substitution of bromide ligands by water in the tetrabromoplatinate(II) ion follows a reaction model (Ref. 1, Fig. 1) which is quite similar to that used for the tetrachloroplatinate(II) ion.[2,3]

REFERENCES

1. Elding, L. I. Acta Chem. Scand. 24 (1970) 2546.
2. Elding, L. I. Acta Chem. Scand. 24 (1970) 1341.
3. Elding, L. I. Acta Chem. Scand. 24 (1970) 1527.
4. Elding, L. I. Acta Chem. Scand. 24 (1970) 1331.
5. Tucker, M. A., Colvin, C. B. and Martin, D. S., Jr. Inorg. Chem. 3 (1964) 1373.
6. Colvin, C. B., Gunther, R. G., Hunter, L. D., Mc Lean, J. A., Tucker, M. A. and Martin, D. S., Jr. Inorg. Chim. Acta 2 (1968) 487.