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Acid Hydrolysis of Tetrabromoplatinate(II) and Bromide Anation of Tribromoaquaplatinate(II)

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Dissociation constants at 25 and 35°C for the first and second aquations of $PtBr_4^{2-}$, rate constants at 15, 25, and 35°C, and activation parameters for the acid hydrolysis of $PtBr_4^{2-}$ and for the bromide anation of $PtBr_3H_2O^-$ have been determined spectrophotometrically at 268 nm. The kinetic measurements were performed in a medium, with bromide in excess in order to obtain first-order reactions and to suppress subsequent aquation. The acid hydrolysis is first order with respect to complex; the chloride anation is first order with respect to both complex and bromide. To suppress the protolysis of the aqua complexes, 0.50 M $HClO_4$ was chosen as the ionic medium. The results are given in Tables 3, 6, and 7.

Bromo-aqua complexes of Pt(II) are formed in aged solutions of K_2PtBr_4.[1-3] The equilibrium constants for the stepwise substitutions of bromide by water are defined by

$$K_n = [PtBr_{n-1}(H_2O)_{5-n}^{3-n}] \cdot [Br^-] \cdot [PtBr_n(H_2O)_{4-n}^{2-n}]^{-1};\ n = 1, 2, 3, 4 \qquad (1)$$

Grinberg and Shagisultanova [1,2] and Martin *et al.*[3] have previously calculated K_4 from titrations with sodium hydroxide of the acidic aqua complex formed. In these measurements, the subsequent acid hydrolyses to complexes containing more than one water were neglected, so the values of K_4 calculated may merely represent upper limits. The same authors have also determined indirectly the rate constant k_4 s^{-1} for the acid hydrolysis of $PtBr_4^{2-}$ from studies of the isotopic exchange of bromide [3,4] or from measurements of the base hydrolysis of $PtBr_4^{2-}$.[5] Both these reactions are supposed to proceed mainly through the formation of the aqua ion $PtBr_3H_2O^-$.

Spectrophotometric measurements [6] also offer a means to determine the stepwise equilibrium constants (1). Attempts to separate the anionic species of the equilibrium mixture from the neutral and cationic ones by means of anion exchangers (Dowex 1 × 4, 50 – 100 mesh) (*cf.* Ref. 7) have failed, because of reduction of the platinum by the resin. Nor has it been feasible to determine the concentration of free bromide of aged solutions potentiometrically, since

neither a bromide[7] membrane electrode (from Orion Research Inc.) nor silver-silver bromide electrodes [8] give stable emf's, probably because of precipitation of slightly soluble silver salts on the surface of the electrodes. The kinetics of the acid hydrolysis of $PtBr_4^{2-}$ and of the reverse reaction, *i.e.* the bromide anation of $PtBr_3H_2O^-$, may also be studied using spectrophotometric measurements as described previously for the corresponding chloro complexes.[9,10] The second aquation step and the equilibrium between *cis*- and *trans*-$PtBr_2(H_2O)_2$ may also be investigated spectrophotometrically.[11]

The experiments described in the present and subsequent [11] papers indicate that the reaction model given in Fig. 1 might be valid for the bromide system as well as for the chloride system.[10,12]

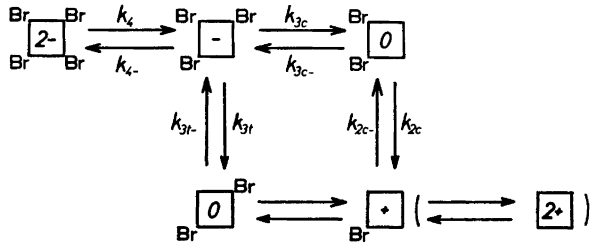

Fig. 1. Reaction model. The water ligands have been omitted. The acid hydrolyses are first order with respect to complex, the bromide anations are first order with respect to both complex and bromide.

EXPERIMENTAL

Chemicals. Potassium tetrabromoplatinate(II) prepared by Engelhard, USA, was used for the study of the rate of the acid hydrolysis of $PtBr_4^{2-}$. Coulometric analysis [13] showed that this preparation contained considerable amounts of the platinum as Pt(IV). This was reduced to Pt(II) by adding a stoichiometric quantity of hydrazinium sulphate to a solution of the salt. The salt was then recrystallized according to Shagisultanova.[14] The refined preparation was analysed for Pt both gravimetrically by reduction to metal with hydrazinium sulphate, and coulometrically according to Ginstrup.[13] Bromide was determined potentiometrically by titration with standard silver nitrate, using silver-silver bromide electrodes to indicate the point of equivalence. Result: Pt grav. (32.8 ± 0.2) %, coul. (32.8 ± 0.2) %; Br titr. (53.4 ± 0.2) %. Calc. for K_2PtBr_4: Pt 32.9 %, Br 53.9 %.

For the equilibrium measurements and the study of the bromide anation of $PtBr_3H_2O^-$, potassium tetrabromoplatinate(II)-dihydrate prepared by request by Degussa, Germany, was used without further purification. The absorption spectrum of this sample in 0.1 M hydrobromic acid was identical with that of Engelhard's recrystallized salt. The manufacturer's analysis: Pt 30.85 %. Analysis (as above): Pt grav. (31.4 ± 0.1) %, coul. (30.8 ± 0.2) %, Br titr. (50.7 ± 0.2) %. Calc. for $K_2PtBr_4 \cdot 2H_2O$: Pt 31.0 %, Br 50.8 %. To maintain constant water contents in the crystals, they were kept in a closed flask in a refrigerator.[15]

Perchloric acid (Baker's *p.a.*) and hydrobromic acid (Merck's *p.a.*) were used to prepare stock solutions. The hydrobromic acid was distilled immediately before use. All solutions were of ionic strength 0.50 M. The ionic medium was perchloric acid.

Apparatus. A Beckman DU spectrophotometer with a well thermostated cell compartment [9] was used. Absorption spectra were recorded by a Coleman Recording Spectrophotometer, Hitachi EPS-3T.

Selection of wavelength. Fig. 2 shows the change of spectrum caused by the stepwise acid hydrolyses. All measurements were performed at the peak at 268 nm. At this

wavelength, the absorptivity of free bromide ions may be neglected and the influence of traces of four-valent platinum is minimized, since the bromo complexes of Pt(IV) have minimum absorptivity.

Equilibrium measurements. Series of solutions of K_2PtBr_4, each with a constant total concentration of platinum, C_{Pt}, and varying total concentrations of bromide, C_{Br}, were prepared (Table 1). C_{Br} is given by $C_{Br}=4\cdot C_{Pt}+[Br^-]_0$ where $[Br^-]_0$ is the concentration of extra bromide added as hydrobromic acid. The concentration of platinum of the stock solutions used, determined coulometrically, agreed within the analytical errors with the concentration calculated from the weighing. The solutions were aged in the dark at (35.00 ± 0.02)°C for 5—8 days or at (25.00 ± 0.02)°C for 10—14 days. Kinetic experiments [11] indicate that equilibrium is established within these time intervals. The absorbances of the equilibrated solutions were measured in Quartz Suprasil cells with path lengths of 5, 2, 1, 0.5, 0.2, or 0.1 cm. No appreciable oxidation of the aged solutions to Pt(IV) was observed.

Acid hydrolysis of $PtBr_4^{2-}$. Stock solutions were mixed from 0.500 M HBr and 0.500 M $HClO_4$. They had the following concentrations of bromide: 5.00, 4.00, 3.00, 2.00, 1.25,

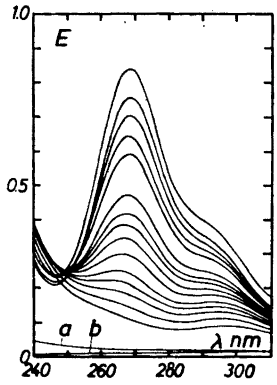

Fig. 2. Absorption spectra of solutions of K_2PtBr_4, equilibrated at 25°C, having $C_{Pt}=9.99\times10^{-5}$ (M) and the following total concentrations of bromide (from above): 100.4, 10.40, 6.40, 4.40, 3.40, 2.000, 1.600, 1.400, 1.200, 1.000, 0.800, 0.700, 0.600, 0.500, and 0.400 mM. The top curve represents approximately the spectrum of $PtBr_4^{2-}$ (98 % of the platinum is present as this species). The two bottom curves represent the absorbance of solutions containing (a) HBr (0.100 M) and $HClO_4$ (0.400 M) and (b) $HClO_4$ (0.500 M). The cell thickness was 1 cm. The blank contained 0.500 M $HClO_4$. Thus, the top curve should be corrected for the absorbance of free bromide.

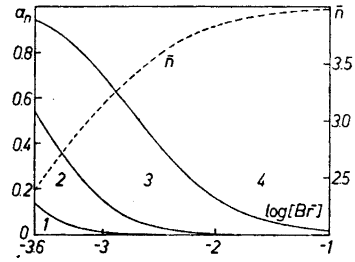

Fig. 3. The formation curve $\bar{n}(\log[Br^-])$ and the distribution of platinum between different species $PtBr_n(H_2O)_{4-n}^{2-n}$; $n=1, 2, 3, 4$, at 25°C. The constants K_4, K_3, and K_2 given in Table 3 were used for the calculation.

0.75, or 0.25 mM. Stock solutions of K_2PtBr_4 (5×10^{-3} or 10^{-2} M) containing HBr (0.1000 M) and of ionic strength 0.50 M were kept in the dark at room temperature. These solutions contain about 1.8 % of the platinum as $PtBr_3H_2O^-$ and 98 % as $PtBr_4^{2-}$ (*cf.* Fig. 3). They were analyzed for Pt coulometrically.[13]

The reaction was started by injecting 1.499 ml of the platinum stock solution with a calibrated syringe into a 250 ml flask, containing 200 ml bromide stock solution, thermo-

Table 1. Equilibrium measurements. Corresponding values of C_{Br} M and ε_{Pt} cm^{-1} M^{-1} at different values of C_{Pt} M.

$C_{Pt} \times 10^3$	$C_{Br} \times 10^3$, $\varepsilon_{Pt} \times 10^{-3}$									
	25°C									
1.557	7.63,	5.08	7.23,	4.81	6.63,	4.29	6.23,	3.92		
1.532	7.53,	5.04	7.13,	4.78	6.53,	4.28	6.13,	3.88		
1.512	7.45,	5.12	7.05,	4.77	6.45,	4.30	6.05,	3.89		
1.038	10.15,	6.87	8.15,	6.35	7.15,	5.98	6.15,	5.43	5.55,	4.90
	5.15,	4.57	4.75,	4.14	4.55,	3.94	4.35,	3.66	4.25,	3.53
	4.15,	3.39								
1.021	10.08,	6.92	8.08,	6.36	7.08,	5.93	6.08,	5.35	5.48,	4.89
	5.08,	4.52	4.68,	4.12	4.48,	3.91	4.28,	3.68	4.18,	3.50
	4.08,	3.41								
1.008	10.03,	6.87	8.03,	6.36	7.03,	5.96	6.03,	5.36	5.43,	4.87
	5.03,	4.59	4.63,	4.12	4.43,	3.90	4.23,	3.66	4.13,	3.50
	4.03,	3.39								
0.507	6.03,	6.19	5.03,	5.76	4.43,	5.46	4.03,	5.13	3.43,	4.59
	3.03,	4.13	2.63,	3.59	2.43,	3.21	2.23,	2.87	2.13,	2.68
	2.03,	2.48								
0.500	6.00,	6.31	5.00,	5.85	4.00,	5.23	3.40,	4.67	3.00,	4.17
	2.600,	3.61	2.400,	3.27	2.200,	2.878	2.100,	2.670	2.000,	2.468
0.2537	2.015,	3.88	1.815,	3.52	1.615,	3.14	1.415,	2.739	1.215,	2.255
	1.115,	2.014	1.015,	1.742						
0.2498	1.999,	3.88	1.799,	3.55	1.599,	3.19	1.399,	2.750	1.199,	2.250
	1.099,	1.990	0.999,	1.685						
0.1015	10.41,	7.35	6.41,	6.84	4.41,	6.19	3.41,	5.79	2.406,	5.04
	2.006,	4.59	1.606,	4.05	1.406,	3.70	1.206,	3.31	1.006,	2.856
	0.806,	2.314	0.706,	1.989	0.606,	1.694	0.506,	1.349	0.406,	0.989
0.0999	10.40,	7.39	6.40,	6.88	4.40,	6.32	3.40,	5.80	2.000,	4.60
	1.600,	4.05	1.400,	3.72	1.200,	3.32	1.000,	2.852	0.800,	2.326
	0.700,	2.001	0.600,	1.676	0.500,	1.320	0.400,	0.955		
0.0507	9.20,	7.28	8.20,	7.12	7.20,	6.97	6.20,	6.80	5.20,	6.58
	4.70,	6.42	4.20,	6.21	3.70,	6.00	3.20,	5.75	2.700,	5.44
	2.400,	5.18	2.200,	4.99	2.003,	4.78	1.803,	4.55	1.703,	4.44
	1.603,	4.28	1.503,	4.14	1.403,	3.99	1.303,	3.82	1.203,	3.63
	1.103,	3.43	1.003,	3.22	0.903,	2.984	0.803,	2.759	0.703,	2.440
	0.603,	2.128	0.503,	1.790	0.403,	1.423	0.303,	1.021		
0.0500	10.20,	7.42	9.20,	7.28	8.20,	7.22	7.20,	7.08	6.20,	6.89
	4.70,	6.48	4.20,	6.31	3.70,	6.08	3.20,	5.83	2.700,	5.48
	2.400,	5.24	2.200,	5.05	2.000,	4.82	1.800,	4.61	1.700,	4.48
	1.600,	4.34	1.500,	4.17	1.400,	4.02	1.300,	3.84	1.200,	3.66
	1.100,	3.48	1.000,	3.24	0.900,	2.984	0.800,	2.724	0.700,	2.436
	0.600,	2.116	0.500,	1.780	0.400,	1.408				
	35°C									
1.532	8.13,	5.13	7.53,	4.70	7.13,	4.42	6.53,	4.00	6.13,	3.60
1.512	8.05,	5.12	7.45,	4.75	7.05,	4.45	6.45,	3.96	6.05,	3.63
1.021	10.08,	6.55	8.08,	5.93	7.08,	5.54	6.08,	4.97	5.48,	4.52
	5.08,	4.22	4.68,	3.75	4.48,	3.56	4.28,	3.33	4.18,	3.21
	4.08,	3.11								
0.507	6.03,	5.89	5.03,	5.42	4.43,	4.97	4.03,	4.70	3.43,	4.18
	3.03,	3.71	2.628,	3.23	2.428,	2.897	2.228,	2.558	2.128,	2.371
	2.028,	2.237								
0.2528	2.011,	3.42	1.811,	3.16	1.611,	2.757	1.411,	2.409	1.211,	1.974
	1.111,	1.737	1.011,	1.531						

Table 1. Continued.

0.1014	6.41, 6.43	4.41, 5.76	4.01, 5.59	3.61, 5.35	3.01, 5.00
	2.410, 4.49	2.010, 4.04	1.606, 3.56	1.406, 3.15	1.206, 2.829
	1.006, 2.420	0.806, 1.980	0.706, 1.695	0.606, 1.429	0.506, 1.133
	0.406, 0.856				
0.0507	10.20, 6.94	9.20, 6.92	8.20, 6.78	7.20, 6.59	6.20, 6.37
	5.20, 6.12	4.70, 5.94	4.20, 5.78	3.70, 5.50	3.20, 5.25
	2.700, 4.87	2.400, 4.62	2.200, 4.43	2.000, 4.23	1.803, 3.98
	1.703, 3.87	1.603, 3.70	1.503, 3.61	1.403, 3.42	1.303, 3.28
	1.203, 3.10	1.103, 2.966	1.003, 2.731	0.903, 2.525	0.803, 2.264
	0.703, 2.071	0.603, 1.802	0.503, 1.491	0.403, 1.233	

stated at a temperature of 15.00, 25.00, or 35.00°C. The concentration of bromide of the resulting solution became 5.71, 4.72, 3.72, 2.73, 1.99, 1.49, or 0.99 mM, and that of platinum 7.5×10^{-5} or 3.8×10^{-5} M. Thus, free bromide was always present in great excess. Samples of the reacting solution were withdrawn with thermostated pipettes and the absorbance was measured in 1 or 2 cm cells.

Bromide anation of $PtBr_3H_2O^-$. Solutions of K_2PtBr_4 (0.553 mM at 15°C, 1.000 or 0.650 mM at 25°C, and 1.000 mM at 35°C) containing perchloric acid (0.500 M) but no extra bromide were aged at the pertinent temperature ±0.02°C for 1—15 h. Relatively small, but not negligible, concentrations of *trans*-$PtBr_2(H_2O)_2$ will be formed during this time.[11] 40 ml portions of these solutions were mixed with 160 ml of thermostated stock solutions containing hydrobromic acid and perchloric acid. The concentration of free bromide in the resulting solution became 2.00, 5.00, 10.00, 15.00, or 25.00 mM, and the total concentration of platinum was about 1×10^{-4} or 2×10^{-4} M. Thus, free bromide was present in excess. Samples were withdrawn with thermostated pipettes and the increase of absorbance was followed in 0.5 or 1 cm cells.

The infinity values of absorbance, E_∞, were measured after about 7 half-lives. They remained constant for several half-lives thereafter, but if observed during a very long time compared to the half-life of the reaction, a very slow, further increase of absorbance due to the bromide anation of *trans*-$PtBr_2(H_2O)_2$ could be noticed at the highest values of b. However, this reaction is much slower [11] than the bromide anation of $PtBr_3H_2O^-$, which has half-lives between 2 and 12 min at 35°C, so this drift of the values of E_∞ could be neglected.

RESULTS

Equilibrium measurements. The equilibrium constants were calculated using a computer and the least squares program "Letagrop Spek" (Sillén and Warnqvist [6,16]). The values used for the calculation are given in Table 1. The molar absorptivity of $PtBr_4^{2-}$, ε_4 cm^{-1} M^{-1}, given as a constant in these calculations, was determined from the kinetic measurements by extrapolation of the logarithmic plots for the acid hydrolysis to zero time.

The results are given in Table 2. Because of the slight dissociation of the complexes, the stability constant β_1 cannot be determined, and the value of β_2 calculated becomes very uncertain. A reasonable value of β_1 was given as a constant in the calculations. The values obtained for β_2, β_3, and β_4 will depend upon this value of β_1, whereas the ratios $K_n=\beta_{n-1}/\beta_n$; $n=2$, 3, 4, will be independent of it. Thus, K_4 and K_3 could be calculated, but the value of K_2 obtained will be very uncertain because of the large error in β_2.

A study [11] of the equilibrium between *cis*- and *trans*-$PtBr_2(H_2O)_2$ indicates approximate values for K_2 of about $(8\pm4)\times10^{-5}$ M at 25°C and about $(10\pm5)\times10^{-5}$ M at 35°C, which are of the same magnitude as those obtained

Table 2. Calculation of the equilibrium constants K_4, K_3, and K_2 M of eqn. (1) using the least squares program Letagrop Spek.[16] Parameters printed in italics were not varied. The stability constants, β_n, are given in M^{-n}, the molar absorptivities ε_n in cm^{-1} M^{-1}. $\varepsilon_4 = 8450$ cm^{-1} M^{-1} was given as a constant in the calculations. The errors are given as 1σ. U_{rel} is the error square sum and *sigy* is the standard deviation for the relative differences between experimental and calculated ε_{Pt}.

	25°C			35°C		
	1	2	3	1	2	3
$\beta_4 \times 10^{-14}$	31.0 ± 0.8	*31.0*	23 ± 3	5.44 ± 0.22	*5.44*	7.9 ± 0.8
$\beta_3 \times 10^{-12}$	5.64 ± 0.17	5.65 ± 0.07	4.2 ± 0.6	1.40 ± 0.06	1.40 ± 0.03	2.04 ± 0.22
$\beta_2 \times 10^{-8}$	*14*	13.9 ± 0.4	9.7 ± 1.7	*5*	5.19 ± 0.26	7.9 ± 1.0
$\beta_1 \times 10^{-4}$	*8*	*8*	*8*	*5*	*5*	*5*
$K_4 \times 10^3$	1.82 ± 0.07	1.82 ± 0.02	1.8 ± 0.4	2.57 ± 0.15	2.57 ± 0.05	2.6 ± 1.2
$K_3 \times 10^4$	2.48 ± 0.08	2.46 ± 0.08	2.3 ± 0.5	3.57 ± 0.15	3.71 ± 0.10	3.9 ± 1.8
$K_2 \times 10^5$	—	5.8 ± 0.2	8.2 ± 1.4	—	9.6 ± 0.5	6.3 ± 0.6
ε_3	1760 ± 10	1760 ± 10	1710 ± 10	2050 ± 20	2080 ± 20	2130 ± 20
ε_2	60 ± 40	50 ± 40	70 ± 40	90 ± 50	110 ± 50	60 ± 40
ε_1	500 ± 100	500 ± 100	430 ± 90	500 ± 100	500 ± 100	600 ± 100
$U_{rel} \times 10^2$	1.01	1.01	0.99	0.63	0.63	0.55
$sigy \times 10^3$	7.9	7.9	7.9	8.9	8.9	8.5

Table 3. Dissociation constants K_n M obtained from equilibrium measurements. The errors in K_4 and K_3 obtained in this paper are given as 3σ. The error in K_2 is an estimated maximum error.

Constant	25°C	35°C	Reference
$K_4 \times 10^3$	~3	—	Grinberg *et al.*[1,2]
$K_4 \times 10^3$	2.6 ± 0.3	—	Martin *et al.*[3]
$K_4 \times 10^3$	1.8 ± 0.2	2.6 ± 0.3	This paper
$K_3 \times 10^4$	2.5 ± 0.3	3.6 ± 0.3	This paper
$K_2 \times 10^5$	8 ± 4	10 ± 5	Subsequent paper[11]

in Table 2. The equilibrium constants are given in Table 3. The distribution of platinum between the different complexes and the formation function are given in Fig. 3.

Kinetic measurements. The method of calculation used previously [9,10] for the reactions of the analogous chloro complexes was improved to obtain a better correction for the second aquation step. First order reactions were obtained by having bromide in excess (b M). It appears from Fig. 3 that small concentrations of $PtBr_2(H_2O)_2$ (up to about 15 % of the platinum for $b = 10^{-3}$) will be present at equilibrium in the concentration range studied ($1 \times 10^{-3} < b < 25 \times 10^{-3}$). It follows from the values of the rate constants k_{3t}, $k_{3t\_}$, k_{3c} and $k_{3c\_}$ determined in the subsequent paper [11] that the following reaction scheme will be valid (*cf.* also Fig. 1):

$$\begin{array}{ccccc} & & trans\text{-}PtBr_2(H_2O)_2 & & \\ & & \Big\| \text{ negligibly slow} & & \\ & \overset{\text{slow}}{\rightleftharpoons} & \downarrow & \overset{\text{fast}}{\rightleftharpoons} & \\ PtBr_4^{2-} & & PtBr_3H_2O^- & & cis\text{-}PtBr_2(H_2O)_2 \\ C_{Pt}-x & & \alpha\cdot x & & (1-\alpha)\cdot x \end{array}$$

The concentrations of the complex species at time t are given in M. The constant $\alpha = b\cdot(K_{3c}+b)^{-1}$ may be calculated for each value of b from the values of the equilibrium constant K_{3c} given in Ref. 11, Table 5. The correction has only minor importance, since α is close to unity: $0.85<\alpha<1$.

Thus, both the rate of acid hydrolysis of $PtBr_4^{2-}$ and the rate of bromide anation of $PtBr_3H_2O^-$ may be described by the equation

$$dx/dt = k_4\cdot(C_{Pt}-x) - k_{4-}\,\alpha\, b\, x \qquad (3)$$

Intergrating and introducing absorptivities instead of concentrations, leads to

$$k_{exp}\ t = \ln\frac{e_0-e_\infty}{e-e_\infty} \qquad (4)$$

where

$$k_{exp} = k_4 + k_{4-}\,\alpha\, b \qquad (5)$$

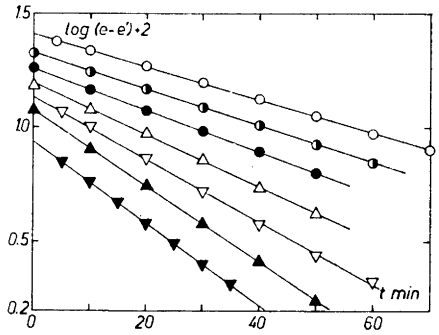

Fig. 4. Acid hydrolysis of $PtBr_4^{2-}$ at 25°C. Plots of log $(e-e')$ *vs.* t.[17] The concentration of free bromide was (from above): 0.99, 1.49, 2.00, 2.72, 3.72, 4.72, and 5.71 mM. The concentration of platinum, C_{Pt}, was (7.77, 7.77, 3.89, 3.89, 7.80, 7.77, and 7.80) $\times 10^{-5}$ M. The time interval used was 80, 70, 60, 60, 60, 60, and 35 min.

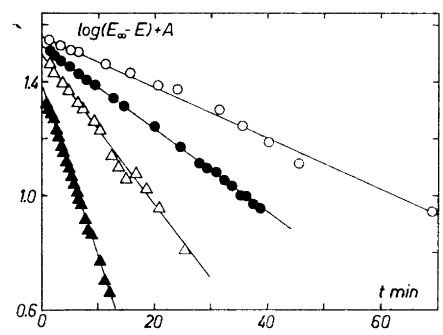

Fig. 5. Bromide anation of $PtBr_3H_2O^-$ at 25°C. Plots of log $(E_\infty-E)+A$ *vs.* t. The concentration of free bromide was 2.00 (○), 5.00 (●), 10.00 (△) and 25.00 (▲) mM. The term A added to the ordinates, was 2.3 (○), 2.0 (●, △) and 1.8 (▲). The total concentration of platinum was 0.20 (○, ●, △) and 0.13 (▲) mM. The solutions of K_2PtBr_4 used were aged for about 6 (○), 3 (●), 1 (△), and 4 (▲) hours. Cell: 0.501 cm.

For the acid hydrolysis, the rate constant k_{exp} s^{-1} was obtained from plots of $\log(e-e_\infty)$ *vs.* t, or according to Guggenheim,[17] from plots of $\log(e-e')$ *vs.* t. Fig. 4 gives some examples of such plots. Fig. 5 shows plots of $\log(e_\infty-e)$ *vs.* t for the reverse bromide anation.

Table 4. Acid hydrolysis of $PtBr_4^{2-}$. The rate constant k_{exp} s^{-1} of eqn. (5) at different concentrations of free bromide, b M. The total concentration of platinum was 7.5×10^{-5} M at 15°C, 7.8×10^{-5} or 3.9×10^{-5} M at 25°C, and 7.8×10^{-5} M at 35°C. The values given represent the mean of several experiments.

$b \times 10^3$	$k_{exp} \times 10^4$		
	15°C	25°C	35°C
0.993	0.95 ± 0.05	2.8 ± 0.2	7.8 ± 0.3
1.49	1.09 ± 0.05	3.0 ± 0.2	8.9 ± 0.4
2.00	1.28 ± 0.06	3.6 ± 0.2	10.0 ± 0.5
2.72	1.57 ± 0.08	4.3 ± 0.3	11.4 ± 0.6
3.00	—	4.5 ± 0.3	—
3.72	2.0 ± 0.1	5.3 ± 0.3	13.3 ± 0.8
4.72	2.3 ± 0.2	6.1 ± 0.4	15.9 ± 0.8
5.71	2.8 ± 0.2	6.9 ± 0.4	18 ± 1

Table 5. Bromide anation of $PtBr_3H_2O^-$. The rate constant k_{exp} s^{-1} of eqn. (5) at different concentrations of free bromide, b M. The total concentration of platinum was 1.1×10^{-4} M at 15°C, 2.0×10^{-4} or 1.3×10^{-4} M at 25°C, and 2.0×10^{-4} M at 35°C. Each value represents the mean of several experiments.

$b \times 10^3$	$k_{exp} \times 10^4$		
	15°C	25°C	35°C
2.00	1.20 ± 0.01	3.47 ± 0.04	9.8 ± 0.1
5.00	2.21 ± 0.03	5.68 ± 0.05	14.8 ± 0.1
10.00	3.89 ± 0.04	10.0 ± 0.1	24.2 ± 0.3
15.00	—	—	33.5 ± 0.3
25.00	9.0 ± 0.1	22.4 ± 0.3	51.8 ± 0.5

Table 6. The rate constants k_4 s^{-1} and k_{4-} s^{-1} M^{-1} for the acid hydrolysis of $PtBr_4^{2-}$ and for the chloride anation of $PtBr_3H_2O^-$. The errors were estimated from the graphs (Figs. 6 and 7). The equilibrium constants K_4 M, obtained as k_4/k_{4-} are also given.

Temperature °C	Acid hydrolysis of $PtBr_4^{2-}$		Chloride anation of $PtBr_3H_2O^-$		$K_4 \times 10^3$
	$k_4 \times 10^4$	$k_{4-} \times 10^2$	$k_4 \times 10^4$	$k_{4-} \times 10^2$	
15	0.55 ± 0.05	4.0 ± 0.4	0.55 ± 0.05	3.4 ± 0.1	1.6 ± 0.2
25	1.9 ± 0.2	9.1 ± 0.9	1.8 ± 0.2	8.3 ± 0.3	2.2 ± 0.3
35	6.1 ± 0.5	21 ± 2	6.3 ± 0.5	18.4 ± 0.6	3.4 ± 0.4

The results are given in Tables 4 and 5. In Table 6, the rate constants k_4 s^{-1} and k_{4-} s^{-1} M^{-1}, obtained from the linear plots of k_{exp} *vs.* $\alpha\, b$ (Figs. 6 and 7), are given.

The values of k_4 s^{-1} obtained by the two methods agree very well. The values of k_{4-} s^{-1} M^{-1} differ by about 10 – 15 %. The values obtained from the study of the bromide anation, however, are more accurate, since the concentration of bromide could be varied in a greater interval and the changes of absorptivity obtained at high b's were greater. The temperature dependence of the rate constants shown in Fig. 8 gave the activation parameters of Table 7.

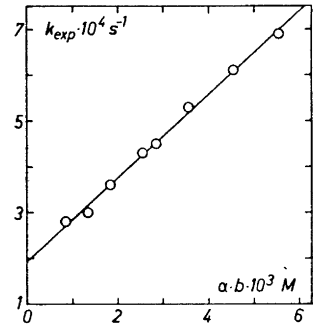

Fig. 6. Acid hydrolysis of $PtBr_4^{2-}$. The rate constant $k_{exp}=k_4+k_{4-}\alpha b$ (s^{-1}) as a function of αb at 25°C.

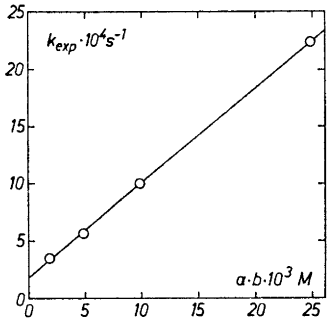

Fig. 7. Bromide anation of $PtBr_3H_2O^-$. The rate constant $k_{exp}=k_4+k_{4-}\alpha b$ (s^{-1}) as a function of αb at 25°C.

Table 7. Rate constants in s^{-1} and s^{-1} M^{-1}, respectively, activation enthalpies, $\Delta H^{\circ\ddagger}$ kcal mol^{-1}, and activation entropies, $\Delta S^{\circ\ddagger}$ cal K^{-1} mol^{-1}, at 25°C. Standard state of water: unit mole fraction, of complexes and bromide ligands: unit concentration (M).

Reaction	Rate constant	$\Delta H^{\circ\ddagger}$	$\Delta S^{\circ\ddagger}$	Ref.
$PtBr_4^{2-}+H_2O\rightarrow PtBr_3H_2O^-+Br^-$	$(1.9\pm0.2)\times10^{-4}$	21	− 6	This paper
	2.2×10^{-4}	19	−10	Martin *et al.*[3]
	1.75×10^{-4}	—	—	Grinberg *et al.*[5]
$PtBr_3H_2O^-+Br^-\rightarrow PtBr_4^{2-}+H_2O$	$(8.3\pm0.3)\times10^{-2}$	14	−15	This paper

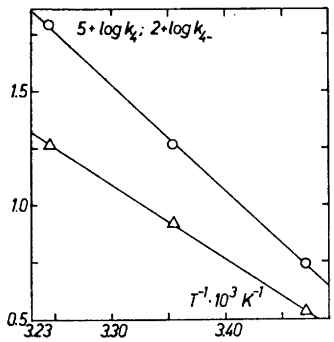

Fig. 8. Temperature dependence of the rate constants k_4 s^{-1} (○) and k_{4-} s^{-1} M^{-1} (△).

CONCLUSIONS

Martin and coworkers [3] have claimed that dinuclear species, *e.g.* $Pt_2Br_6^{2-}$ and $Pt_2Br_5H_2O^-$, exist in low concentrations in aged solutions of Rb_2PtBr_4. These species could be neglected in the present equilibrium measurements, since their total amount will not exceed about 1 % of the platinum(II) even in the most concentrated solutions used (*cf.* Ref. 3).

Martin *et al.*[3] have also shown that part of the exchange of the bromide ligands of $PtBr_4^{2-}$ occurs *via* the formation of a dimer transition state. The rate of this reaction could be written $R = k_d [PtBr_4^{2-}][PtBr_3H_2O^-]$, where the rate constant k_d was 0.2 s^{-1} M^{-1}. In the present measurements, the rate of disappearance of $PtBr_4^{2-}$ by this path of reaction will be negligible compared to the rate of the aquation, since the concentrations of the complexes were very small ($\sim 10^{-5}$ M).

The reproducibility of the equilibrium measurements was relatively poor compared to the measurements on the chloride system.[6,7] One reason for this is that the bromo complexes are stronger and therefore dissociate to a less extent. It might also be due to impurities in the salt used, which is difficult to recrystallize because of its high solubility.[14] Unfortunately, there has been no possibility to check the calculated constants by other equilibrium methods, for instance potentiometry or ion exchange (*vide supra*). The values of K_4 obtained from the kinetic measurements as k_4/k_{-4} (Table 7), are somewhat higher than those calculated from the equilibria, but the values coincide within the limits of error. The values found for K_4 by Grinberg,[1,2] Martin [3] and their coworkers (Table 3) are also somewhat higher but this may be explained by their neglect of the further aquation. The calculated values of the rate constant k_4 agree well with those obtained previously [3,5] from other methods of measurement (Table 7).

It appears from the activation enthalpies and entropies given in Table 7 that the enthalpy change for the first aquation step of $PtBr_4^{2-}$ is about 7 kcal mol^{-1} and the entropy change about 9 cal K^{-1} mol^{-1}. These quantities agree within the limits of error with the results from the equilibrium measurements, Table 3, which give (7 ± 3) kcal mol^{-1} for the enthalpy change and (10 ± 3) cal K^{-1} mol^{-1} for the entropy change. For the second aquation, the enthalpy change is (7 ± 3) kcal mol^{-1}, too.

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