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Platinum(IV) Bromo Aqua Complexes. Acid Hydrolysis Equilibria and Kinetics of Bromide Anation

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The stepwise stability constants, K_n *for the bromo aqua complexes* $PtBr_{n-1}(H_2O)_{7-n}^{5-n}$; $n=4, 5, 6$, *formed in the successive acid hydrolyses of* $PtBr_6^{2-}$, *have been determined to be* $K_6=(1.9\pm0.1)\times10^3\ M^{-1}$, $K_5=(1.0\pm0.2)\times10^4\ M^{-1}$ *and* $K_4=(1.1\pm0.2)\times10^5\ M^{-1}$. *A bromide assisted mechanism is proposed for the bromide anations of* $PtBr_4(H_2O)_2$ *and* $PtBr_5H_2O^-$. *Both these reactions are found to be first order with respect to platinum complex. The dependence of the observed rate constant on the bromide concentration can be described by the eqn.*

$$k_{exp}=k'[Br^-]+k''[Br^-]^2$$

The last term is probably due to a reaction path via *a bromide associated outer sphere complex, which might also be involved in the path described by the first term. A spectrophotometric method has been used. To suppress the protolysis of the aqua complexes, 0.50* M *perchloric acid was used as the ionic medium. The temperature was 25.0°C.*

Introduction

A variety of reactions of platinum(IV) halide complexes has been studied during the last ten years, for instance ligand substitutions,[1-13] isotopic exchanges of platinum or of halide ligands,[14-19] reductions,[20-23] and acid and base hydrolyses.[16,24-34] Several mechanisms have been proposed for these reactions. For instance, many of them have been observed to be accelerated by light,[16,17,19,24,25,32,35,36] and the primary photochemical process has been suggested to involve either the formation of platinum in lower oxidation states[16,17,35,36] or a weakening of the bonding between the central ion and the ligands.[32] Also, oxidizing and reducing substances and platinum(II) affect the rate of many of these reactions.[1-5,10-19,23,26,27,32,33,43] This indicates that platinum in lower oxidation states or bridged intermediates, such as Pt^{IV}–X–Pt^{II}, (X = halide), may be involved in the reaction mechanisms.

Qualitative studies of the hydrolyses of $PtCl_6^{2-}$ and $PtBr_6^{2-}$ were published as early as about 1920 by Archibald *et al.*[24,25] In the nineteen sixties, Dreyer and coworkers[27] investigated the influence of catalysts and light upon these reactions. A detailed study of the photochemistry of $PtBr_6^{2-}$ has been published by Balzani *et al.*[32] However, quantitative data on the uncatalyzed, thermal hydrolysis reactions of platinum(IV) bromo complexes are meagre. Except for recent investigations by Skinner and Jones[33,34] on the base hydrolysis of $Pt(CN)_4Br_2^{2-}$ and the bromide anation of $Pt(CN)_4BrH_2O^-$, no studies of the kinetics of the thermal reactions of bromo aqua complexes have been published. Only two investigations on the hydrolysis equilibria of $PtBr_6^{2-}$ have been found in the literature.[29,30] These are both restricted to the first hydrolysis step:

$$PtBr_6^{2-}+H_2O\rightleftarrows PtBr_5H_2O^-+Br^-$$

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We have studied the stepwise acid hydrolysis equilibria of the hexabromoplatinate(IV) ion spectrophotometrically and determined the stepwise stability constants K_4, K_5, and K_6, defined by

$$K_n = \frac{[\mathrm{PtBr}_n(\mathrm{H_2O})_{6-n}{}^{4-n}]}{[\mathrm{PtBr}_{n-1}(\mathrm{H_2O})_{7-n}{}^{5-n}][\mathrm{Br}^-]}; \quad n=4,\ 5,\ 6; \qquad (1)$$

We have also investigated spectrophotometrically the kinetics of the two bromide anations:

$$\mathrm{PtBr_5H_2O^-} + \mathrm{Br^-} \rightarrow \mathrm{PtBr_6}^{2-} + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{PtBr_4(H_2O)_2} + \mathrm{Br^-} \rightarrow \mathrm{PtBr_5H_2O^-} + \mathrm{H_2O} \qquad (3)$$

The thermal acid hydrolyses of $PtBr_6^{2-}$ and $PtBr_5H_2O^-$, *i. e.* the reverse of reactions (2) and (3), were found to be very slow. No reproducible rate parameters could be obtained for these reactions.

Experimental Section

Materials. Potassium hexabromoplatinate(IV) (Heraeus) was recrystallized from a 50 m*M* solution of hydrobromic acid. This preparation was analysed for platinum gravimetrically by reduction to metal with hydrazine sulphate in sodium hydrogen carbonate solution. Bromide was determined potentiometrically. The salt was also analysed for Pt^{IV} and Pt^{II} by a coulometric method.[37]

Calcd for K_2PtBr_6: Pt, 25.93; Br, 63.71%. Found: Pt, grav. (25.96±0.08); Pt, coul. (26.1±0.3); Br, titr. (63.23±0.05)%.

The coulometric analysis indicated that less than 0.02% of the platinum was present as Pt^{II}. The hydrobromic acid (Merck's *p. a.*) was distilled immediately before preparing the solutions in order to remove free bromine. The perchloric acid was Baker's *p.a.*

Apparatus. Spectra were recorded by a Cary 15 Recording Spectrophotometer. A Beckman Quarz Spectrophotometer Model DU was used for the equilibrium measurements and a Zeiss Quarz Spectrophotometer Model PMQ II equipped with a Goerz compensation recorder for the kinetic studies. All solutions were kept in water thermostats at (25.00± 0.02) °C.

Selection of Wavelength. Figure 1 shows spectra of equilibrated solutions of K_2PtBr_6 containing varying concentrations of hydrogen bromide. The peak at 315 nm ($\varepsilon_6 = 1.86 \times 10^4$ cm^{-1} M^{-1}) decreases as the hexabromoplatinate(IV) ion is hydrolysed, while the absorbance at about 260 nm increases. There are two isosbestic points, one at 238 nm and another at 283 nm, where $\varepsilon_6 = \varepsilon_5$. The equilibrium measurements were performed at 315 nm, the kinetic measurements at 315 or 238 nm.

Equilibrium Measurements. Series of solutions listed in Table I, each having a constant total concentration of platinum, C_{Pt}, and varying total concentrations of bromide, C_{Br}, were equilibrated. The ionic strength was kept at 0.50 *M* by perchloric acid. The time for equilibration in the dark was two or three months at 25°C. In order to accelerate the equilibration, most of the solutions were irradiated for one to three hours with light from an UV-lamp or with sunshine before thermostating to 25°C in the dark. This speeded up the equilibration several factors of ten (*cf.* Ref. 32) but did not influence the final equilibrium. Thus irradiated solutions gave the same equilibrium absorbances as those aged in the dark. Equilibrated solutions were protected from illumination. All handling was performed using red light (*vide infra*).

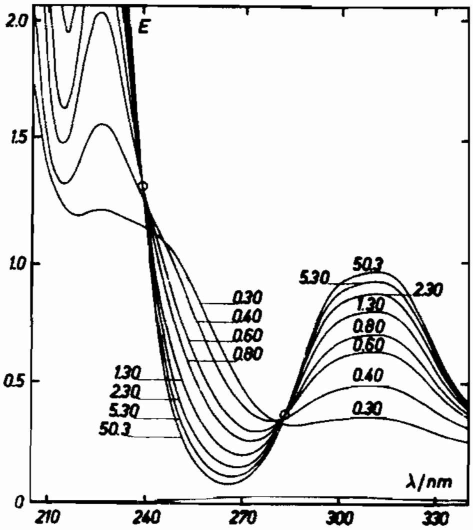


Figure 1. Absorption spectra of aged solutions at different concentrations of hydrogen bromide. $C_{Pt} = 5.00 \times 10^{-5}$ *M*. The numbers in the figure denote C_{Br} in m*M*. Path length = 1.000 cm.

Halide Anation of $PtBr_5H_2O^-$. Solutions containing hydrobromic acid of various concentrations and perchloric acid to maintain a constant concentration of hydrogen ion of 0.50 *M*, were thermostated at (25.00±0.02) °C. The reactions were started by adding to these solutions aged platinum stock solutions. At intervals of time, samples were taken from the reacting solutions and the absorbance was measured at 315 nm.

The dominating species in the aged platinum solutions used was $PtBr_4(H_2O)_2$. Since the bromide anation of $PtBr_4(H_2O)_2$ is faster than that of $PtBr_5H_2O^-$ by a factor of about ten, the former reaction will not disturb the latter after the first few minutes.

The total concentration of platinum in the kinetic runs was usually about 4×10^{-5} *M*. Some experiments were made with $C_{Pt} = 1 \times 10^{-5}$ *M* or 9×10^{-5} *M* in order to check the first order dependence with respect to platinum. The concentration of bromide was varied within the interval $0.0250\,M \leqslant [\mathrm{Br}^-] \leqslant 0.400$ *M*. Thus, bromide was always present in large enough excess, compared to platinum, to obtain pseudo first order kinetics.

Light was found to accelerate the rates of these kinetic runs, especially the slow ones, having low con-

Table I. Equilibrium measurements.

$C_{Pt}\times10^3/M$	$C_{Br}\times10^3/M$, $\varepsilon_{Pt}\times10^{-3}/\mathrm{cm}^{-1}M^{-1}$;
0.01919	0.115, 4.95; 0.155, 6.47; 0.175, 7.37; 0.175, 7.48; 0.175, 7.22; 0.195, 7.87; 0.235, 8.66; 0.255, 9.17; 0.275, 9.59; 0.475, 12.14; 0.535, 12.66; 0.575, 12.87; 0.615, 13.18; 1.115, 15.01; 2.115, 16.31; 3.12, 16.88; 4.12, 17.20;
0.01921	0.115, 4.91; 0.135, 5.99; 0.155, 6.62; 0.175, 7.20; 0.190, 7.81; 0.190, 7.65; 0.195, 7.86; 0.210, 8.17; 0.215, 8.33; 0.215, 8.38; 0.230, 8.64; 0.230, 8.90; 0.235, 8.87; 0.250, 9.11; 0.250, 9.32; 0.255, 9.31; 0.270, 9.73; 0.275, 9.76; 0.290, 9.89; 0.290, 10.05; 0.295, 10.17; 0.315, 10.48; 0.315, 10.21; 0.330, 10.46; 0.330, 10.67; 0.335, 10.74; 0.365, 11.16; 0.370, 11.04; 0.370, 11.24; 0.410, 11.71; 0.415, 11.73; 0.440, 11.71; 0.440, 12.02; 0.465, 12.23; 0.490, 12.23; 0.490, 12.49; 0.515, 12.62; 0.515, 12.76; 0.540, 12.55; 0.540, 12.81; 0.590, 12.81; 0.590, 13.12; 0.615, 13.35; 0.690, 13.27; 0.690, 13.79; 0.715, 13.92; 0.715, 13.96; 0.790, 19.79; 0.790, 14.16; 0.815, 14.41; 0.815, 14.58; 0.890, 14.32; 0.890, 14.52; 0.915, 14.83; 0.990, 14.78; 0.990, 14.94; 1.015, 15.14; 1.115, 15.38; 1.190, 15.30; 1.190, 15.46; 1.215, 15.52; 1.315, 15.83; 1.390, 15.72; 1.390, 15.77; 1.415, 16.04; 1.515, 16.15; 1.590, 15.98; 1.590, 15.98; 1.615, 16.25; 1.615, 16.19; 1.715, 16.41; 1.790, 16.35; 1.790, 16.24; 1.815, 16.56; 1.915, 16.61; 1.990, 16.50; 2.015, 16.51; 2.115, 16.77; 2.115, 16.76; 2.315, 17.03; 2.390, 16.81; 2.390, 16.87; 2.515, 17.14; 2.715, 17.29; 2.790, 16.97; 2.915, 17.34; 3.12, 17.50; 3.12, 17.23; 3.32, 17,55; 3.52, 17.60; 3.72, 17.66; 3.92, 17.76; 4.12, 17.81; 4.62, 17.86; 5.12, 18.02; 5.62, 18.13; 6.12, 18.18; 7.12, 18.28; 8.12, 18.33; 10.12, 18.44;
0.01922	0.865, 14.41; 0.965, 14.83; 0.965, 14.78; 1.065, 15.04; 1.165, 15.19; 1.165, 15.24; 1.365, 15.45; 1.365, 15.71; 1.615, 15.92; 1.865, 16.13; 1.865, 16.29; 2.065, 16.49; 2.465, 16.75; 2.465, 16.70; 2.865, 17.07; 2.865, 16.96; 3.37, 17.22; 3.37, 17.17; 3.87, 17.48; 3.87, 17.27; 4.87, 17.53; 5.87, 17.69; 6.87, 17.79;
0.01923	0.215, 8.29; 0.315, 10.19; 0.415, 11.51; 0.515, 12.48; 0.615, 13.21; 0.865, 14.35; 1.115, 15.13; 1.615, 15.91; 2.115, 16.33; 3.12, 17.06; 3.12, 17.11; 4.12, 17.37; 4.12, 17,42; 5,12, 17.47; 5.12, 17.63; 7.62, 17.73; 7.62, 17.89;
0.0500	0.300, 6.76; 0.330, 7.66; 0.340, 7.94; 0.360, 8.38; 0.375, 8.46; 0.375, 8.64; 0.380, 8.80; 0.395, 9.00; 0.395, 9.06; 0.400, 9.26; 0.415, 9.38; 0.415, 9.66; 0.420, 9.66; 0.420, 9.46; 0.445, 9.96; 0.445, 9.94; 0.450, 10.06; 0.495, 10.58; 0.495, 10.70; 0.500, 10.66; 0.525, 11.02; 0.525, 11.06; 0.550, 11.32; 0.575, 11.62; 0.575, 11.58; 0.600, 11.88; 0.600, 11.84; 0.625, 12.12; 0.625, 12.18; 0.650, 12.44; 0.650, 12.36; 0,675, 12.44; 0.675, 12.58;
0.1000	0.600, 8.57; 0.640, 9.10; 0.660, 9.42; 0.700, 10.10; 0.750, 10.76; 0.750, 10.66; 0.750, 10.68; 0.800, 11.38; 0.800, 11.22; 0.800, 11.30; 0.850, 11.94; 0.850, 11.66; 0.850, 11.84; 0.900, 12.18; 0.900, 12.30; 1.000, 12.93; 1.000, 13.07; 1.100, 13.59; 1.100, 13.41; 1.100, 13.53; 1.200, 13.93; 1.200, 14.07; 1.300, 14.51; 1.350, 14.41; 1.350, 14.61; 1.400, 14.79; 1.450, 14.73; 1.450, 14.97; 1.600, 15.35; 1.650, 15.33;
0.2500	1.500, 10.64; 1.500, 10.63; 1.500, 10.52; 1.600, 11.63; 1.600, 11.60; 1.600, 11.72; 1.700, 12.39; 1.700, 12.32; 1.700, 12.44; 1.800, 13.16; 1.800, 13.20; 1.900, 13.80; 1.900, 13.76; 2.000, 14.24; 2.000, 14.28; 2.100, 14.55; 2.100, 14.64; 2.200, 14.83; 2.200, 14.96; 2.400, 15.35; 2.400, 15.43; 2.400, 15.48; 2.600, 15.67; 2.600, 15.79; 2.600, 15,92; 2.800, 16.03; 2.800, 16.19; 2.800, 16.20; 3.00, 16.39; 3.00, 16.60; 3.20, 16.59; 3.40, 16.79; 3.50, 16.99; 3.50, 16.92; 3.60, 16.94; 3.80, 17.11; 4.00, 17.23; 4.00, 17.31; 4.00, 17.24; 4.50, 17.44; 5.00, 17.63; 5.00, 17.64; 5.50, 17.71; 6.00, 17.84; 6.50, 17.91;
0.500	3.00, 12.02; 3.00, 11.90; 3.00, 11.98; 3.10, 12.56; 3.10, 12.49; 3.10, 12.64; 3.20, 13.07; 3.20, 12.90; 3.20, 13.12; 3.40, 14.00; 3.40, 13.82; 3.40, 14.00; 3.60, 14.57; 3.60, 14.42; 3.60, 14.88; 3.60, 14.64; 3.80, 15.46; 3.80, 15.14; 4.00, 15.94; 4.00, 15.70; 4.00, 15.82; 4.00, 15.56; 4.40, 16.40; 4.40, 16.22; 4.40, 16.52; 5.00, 16.92; 5.00, 16.76; 5.00, 17.00; 5.40, 17.18; 5.40, 17.26; 6.00, 17.54; 6.00, 17.50; 6.00, 17.62; 7.00, 17.90; 7.00, 17.66; 7.00, 17.74; 8.00, 18.04; 9.00, 18.12;
1.000	6.00, 13.69; 6.20, 14.49; 6.40, 14.88; 6.60, 15.33; 6.80, 15.66; 7.00, 16.05; 7.20, 16.20; 7.40; 16.40; 7.60, 16.60;

centrations of bromide. Therefore, the solutions were protected from illumination as far as possible. They were kept in covered thermostats, and all the handling was performed using red light, which was found to have a minimum influence on the rates.

Halide Anation of $PtBr_4(H_2O)_2$. Measurements were performed at 315 and 238 nm. At 238 nm, the molar absorptivities of $PtBr_6^{2-}$ and $PtBr_5H_2O^-$ are equal (*cf.* Figure 1), so the change of absorbance at this wavelength is due to reaction (3) exclusively, whereas the consecutive and about ten times slower bromide anation of $PtBr_5H_2O^-$ causes no change. For kinetic runs at 238 nm, solutions were mixed in the same way as described for reaction (2). They were protected from illumination. The total concentration of platinum was about $3\times10^{-5}\,M$, and the concentration of bromide was $0.0100\,M \leqslant [Br^-] \leqslant 0.0750\,M$. Thus, the concentration of bromide was large enough to remain essentially constant during the runs and to cause reaction (3) to go to completion.

For the measurements at 315, thermostated hydrobromic acid solutions and platinum stock solutions were mixed directly in the cell using thermostated syringes. The absorbance was recorded *vs.* time using the recorder of the Zeiss spectrophotometer. The total concentration of platinum was about $4\times10^{-5}\,M$ and that of bromide $0.0400\,M \leqslant [Br^-] \leqslant 0.300\,M$.

Since these series were followed directly in the thermostated cell, the solutions were continously illuminated by 315 nm light. This did not accelerate these rapid bromide anations, however. Table IV shows that the observed rate constants calculated from the measurements at this wavelength were the same as those obtained from the measurements at 238 nm, using solutions kept in dark thermostats.

Catalysis. Since oxidizing and reducing substances and Pt^{II} have often been found to affect the rates of reactions of Pt^{IV} complexes, solutions containing Ir^{III} Fe^{II} Fe^{III}, Br_2 and $PtBr_4^{2-}$ were used for some kinetic runs. The concentration of the added species was generally about 10% of the concentration of Pt^{IV}. As indicated by Table III these added substances had no effect on the reaction rates at the concentrations used.

Table II. Stepwise stability constants K_n defined by eqn. (1). The errors are given as 1σ for the constants calculated by the least squares method. Other errors have been estimated graphically.

Constant	This paper Graphical 25.0 °C	This paper Least squares 25.0 °C	Ref 29. 25 - 55 °C	Ref. 30. 50 °C
$K_6\times10^{-3}/M^{-1}$	1.09±0.2	1.87±0.10	0.25±0.15	0.71
$K_5\times10^{-4}M^{-1}$	1.0±0.2	1.03±0.17	—	—
$K_4\times10^{-5}/M^{-1}$	—	1.1 ±0.17	—	—

Results

Equilibria. The stepwise stability constants, K_n, were calculated graphically by the method of corresponding solutions[38-40] and numerically using a computer and a least squares programme « Letagrop Spek ».[41]

Figure 2 gives the molar absorptivities, ε_{Pt}, as a function of C_{Br} for the different C_{Pt}'s used. The values of $\bar{n}([Br^-])$ obtained by cutting these plots by lines parallel to the C_{Br}–axis are given in Figure 3a. Since always $C_{Br}\geqslant6\times C_{Pt}$ for these solutions of K_2PtBr_6, the regions of concentration below the dashed line of Figure 2 will not be accessible for measurement. Hence, for small ε_{Pt}'s, the values of C_{Pt} will be restricted to a very small interval, which might give erroneous values of the mean ligand number, $\bar{n}$, in this region. Therefore, only K_6 and K_5 could be calculated by this method (Table II).

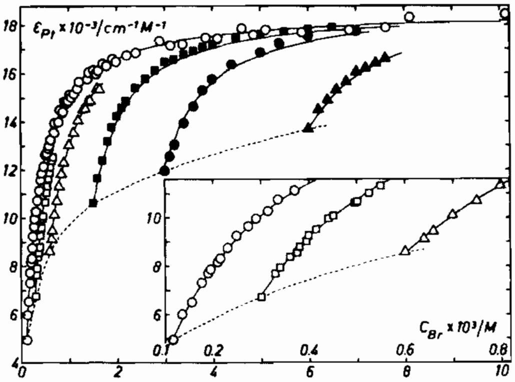


Figure 2. Equilibrium measurements. ε_{Pt} as a function of C_{Br} at the following concentrations of platinum in mM: 0.0192 (○), 0.0500 (□), 0.1000 (△), 0.2500 (■), 0.500 (●), and 1.000 (▲). The full-drawn curves are calculated by the computer from the values of K_n and ε_n obtained by the least squares method (Table II). The dashed curve represents solutions in which $C_{Br}=6\times C_{Pt}$.

The calculations using the least squares programme[41] gave the molar absorptivities at 315 nm of the complexes ($\varepsilon_6=18600\pm100$ cm^{-1} M^{-1}; $\varepsilon_5=10000\pm100$ cm^{-1} M^{-1}; $\varepsilon_4=3600\pm200$ cm^{-1} M^{-1}) and the stepwise stability constants K_6, K_5, and K_4 of Table II. The input data for these calculations are given in Table I (*cf.* Ref. 42).

Halide Anation of $PtBr_5H_2O^-$. This reaction is first order with respect to platinum, so the rate can be expressed by

$$-\frac{d[PtBr_5H_2O^-]}{dt}=k_{6exp}[PtBr_5H_2O^-] \tag{4}$$

for kinetic runs, having excess bromide. Integration and introduction of the absorptivities, given by

$$e=[PtBr_5(H_2O)^-]\varepsilon_5+[PtBr_6{}^{2-}]\varepsilon_6$$

$$e_\infty=([PtBr_5(H_2O)^-]_0+[PtBr_6{}^{2-}]_0)\varepsilon_6$$

leads to

$$\ln\frac{e_\infty-e}{e_\infty-e_0}=-k_{6exp}t \tag{5}$$

The rate constant k_{6exp} was obtained from ordinary first order plots. The results are summarized in Table III. The observed rate constant is a function of the concentration of bromide, as shown by Figure 4. Plotting $k_{6exp}/[Br^-]$ *vs.* $[Br^-]$ gives a straight line corresponding to the following relationship:

$$k_{6exp}=k'_6[Br^-]+k_6''[Br^-]^2 \tag{6}$$

Thus, the experiments indicate that the bromide anation of $PtBr_5H_2O^-$ proceeds *via* two pathways, one being first order with respect to bromide and complex, and the other being second order in bromide and first order in complex. The second term of eq. (6) dominates the rate expression for the highest concentrations of bromide used, but for lower concen-

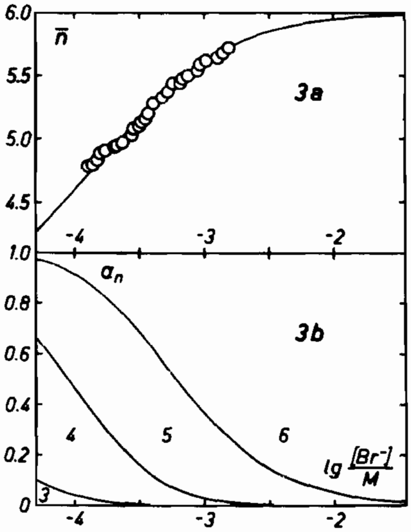


Figure 3. *a.* The formation curve calculated from the constants K_6, K_5 and K_4 obtained by the least squares method (Table II). The values of $\bar{n}(\log[Br^-])$ (○), obtained by the method of corresponding solutions are also given. *b.* The distribution of platinum between different species.

Table III. Bromide anation of $PtBr_5(H_2O)^-$. The rate constant k_{6exp} defined by eqn. (6). The errors are given as 1σ.

$C_{Pt}\times 10^5/M$	$[Br^-]\times 10^3/M$	$k_{6exp}\times 10^4/s^{-1}$	Added substance
4	25.0	0.89±0.03	—
4	50.0	1.91±0.06	—
4	50.0	1.88	K_2PtBr_4
4	75.0	3.92±0.15	—
4	75.0	3.73	K_2PtBr_4
4	100.0	6.58±0.13	—
4	125.0	8.95±0.08	—
4	150.0	12.13±0.10	—
4	175.0	16.3 ±0.4	—
4	200	20.90±0.12	—
4	250	33.2 ±0.2	—
1.1	250	31.4 ±0.4	—
8.8	250	35 ±1	—
4	250	33.6	K_2PtBr_4
4	250	35.3	Br_2
4	250	35.4	$IrCl_3$
4	250	33.8	$FeCl_2$
4	250	34.3	$FeCl_3$
4	300	45.9 ±0.3	—
4	350	61.6 ±0.6	—
4	400	79.7 ±1.4	—

Table IV. Bromide anation of $PtBr_4(H_2O)_2$. The rate constant k_{5exp} defined by eqn. (8). The errors are given as 1σ.

$C_{Pt}\times 10^5/M$	$[Br^-]\times 10^3/M$	$k_{5exp}\times 10^2/s^{-1}$	λ/nm
3	10.0	0.040±0.003	238
3	15.0	0.056±0.003	238
3	25.0	0.094±0.002	238
4	40.0	0.190±0.005	315
3	50.0	0.25 ±0.01	238
4	50.0	0.26 ±0.01	315
3	75.0	0.50 ±0.01	238
4	75.0	0.44 ±0.01	315
4	100.0	0.77 ±0.01	315
4	150.0	1.33 ±0.02	315
4	200	2.11 ±0.05	315
4	250	3.3 ±0.1	315
4	300	4.6 ±0.2	315

trations, the first term becomes increasingly important. From a least squares calculation, the rate constants k_6' and k_6'' were obtained with their standard deviations as:

$$k_6'=(1.8\pm0.2)\,.\,10^{-3}\ s^{-1}M^{-1}$$

$$k_6''=(4.5\pm0.1)\,.\,10^{-2}\ s^{-1}M^{-2}$$

Halide Anation of $PtBr_4(H_2O)_2$. The rate law is analogous to that of reaction (2). The absorbance at the end of the reaction was not measurable at 315 nm, because of the subsequent, about ten times slower halide anation of $PtBr_5H_2O^-$, and was inaccurate at 238 nm because of the steep slope of the spectra at the isosbestic point (*cf.* Figure 1). Therefore, the rate constant k_{5exp}, defined by

$$-\frac{d[PtBr_4(H_2O)_2]}{dt}=k_{5exp}[PtBr_4(H_2O)_2] \qquad (7)$$

was calculated from Guggenheim plots of log(*e'*—*e*) *vs. t*. The results are given in Table IV. As indicated by Figure 5, k_{5exp} varies with the concentration of bromide in the same way as k_{6exp}:

$$k_{5exp}=k_5'[Br^-]+k_5''[Br^-]^2 \qquad (8)$$

The rate constants with their standard deviations were obtained from a least squares calculation as:

$$k_5'=(3.2\pm0.1)\,.\,10^{-2}\ s^{-1}M^{-1}$$

$$k_5''=(4.0\pm0.1)\,.\,10^{-1}\ s^{-1}M^{-2}$$

Discussion

Equilibria. The two methods used to calculate K_6 and K_5 give accordant results. The least squares method also gives a value of K_4. Values of K_5 and K_4 have not been found in the literature. The value of K_6 agrees rather well with that determined by Davidson and Jameson,[30] if allowance is made for the difference in temperature (Table II). But the value of K_6 calculated by Nikolaeva and Pastukhova[29] is about one factor of ten smaller than that found in this study. The method used by these authors—titrations with hydroxide of the monobasic acid $PtBr_5H_2O^-$—may give erroneous results, however, since hydroxide will be consumed also by $PtBr_4(H_2O)_2$. If the titrations are not performed very rapidly, exchange between hydroxide and bromide ligands of the complex will also occur during the titrations, causing an overconsumption of hydroxide ions.

Kinetics. The kinetic measurements indicate two parallel reaction paths for both halide anations studied, one first order and the other second order with respect to bromide. No catalytic effects could be observed (*vide* Table III). Therefore, mechanisms involving labile Pt^{III} or bridged Pt^{II}–Br–Pt^{IV} intermediates can be rejected as causing the rates studied.

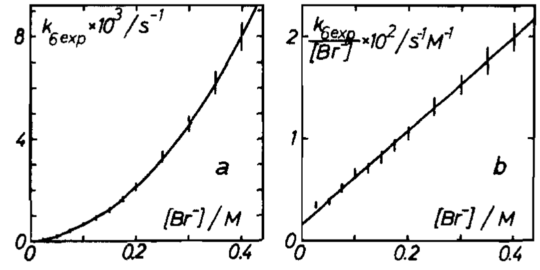


Figure 4. Bromide anation of $PtBr_5H_2O^-$. *a.* The observed rate constant k_{6exp} as a function of the concentration of bromide. *b.* $k_{6exp}/[Br^-]$ as a function of the concentration of bromide.

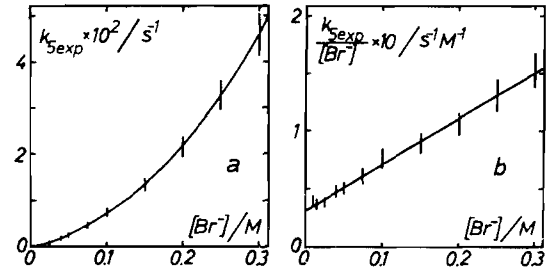


Figure 5. Bromide anation of $PtBr_4(H_2O)_2$. *a.* The observed rate constant as a function of the concentration of bromide. *b.* $k_{5exp}/[Br^-]$ as a function of the concentration of bromide.

An experimental rate law of the same form as that found for the present reactions was recently described by Skinner and Jones[34] for the bromide anation of $Pt(CN)_4BrH_2O^-$. They proposed a mechanism, involving an association of bromide to the negatively charged complex.

In order to examine a possible association between $PtBr_6^{2-}$ and bromide, some spectra of solutions having high concentrations of free bromide (C_{Br}: 0.30, 0.90, 1.50, 2.10, and 3.00 *M*; C_{Pt}: 4.10^{-5} *M*) and the ionic strength 3.0 *M* ($HClO_4$) were recorded (Figure 6). The change of absorbance of these solutions was directly proportional to the concentration of bromide. Since the equilibrium measurements indicate that the concentrations of aqua complexes are negligible if $[Br^-]$ is greater than about 0.1 *M*, this change might be attributed either to an association between $PtBr_6^{2-}$ and Br^- in these solutions or to a medium effect, or to both of these factors. If the medium effect is supposed to be negligible, an association constant $[PtBr_6 \ldots Br^{3-}]/[PtBr_6^{2-}] . [Br^-]$ can be estimated to be of the magnitude of about 10^{-2} M^{-1}. A similar change has been observed by Poë and coworkers[8] and by Skinner and Jones[33] when excess of bromide was added to solutions of *trans*–$Pt(CN)_4Br_2^{2-}$. Poë attributed this change, which was also proportional to the concentration of bromide, to an association between bromide and the platinum complex. This might be surprising in view of the negative charge of both ions, but since Pt^{IV} is very electronegative and since bromide is a soft ligand some association between an inner sphere and an outer sphere bromide might occur. Poë estimated the association constant for $Pt(CN)_4Br_2 \ldots Br^{3-}$ to be less than about 0.1 *M i.e.* a value of the same order of magnitude as that estimated for $PtBr_6 \ldots Br^{3-}$ from our measurements.

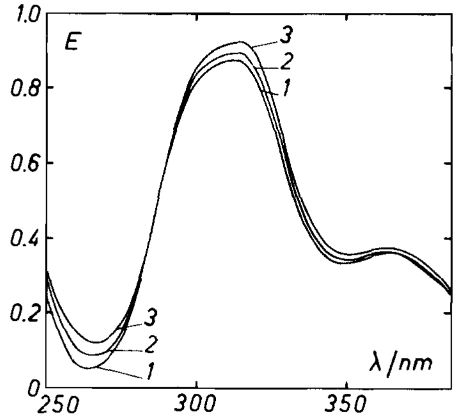
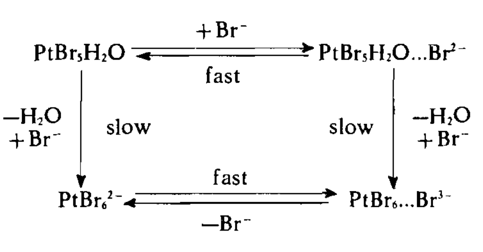


Figure 6. The change of spectrum when great concentrations of bromide is added to solutions containing $PtBr_6^{2-}$. C_{Br}/M: 1, 0.30; 2, 1.50; 3, 3.00. The spectra for C_{Br} 0.90 and 2.10 *M* have been ommitted for clarity. $C_{Pt}=5\times10^{-5}$ *M*. The blank contained hydrobromic acid of the same concentration as the respective solutions.

Thus, association between anionic platinum(IV) complexes and bromide might occur. Because of the less negative ionic charges of $PtBr_5H_2O^-$ and $PtBr_4(H_2O)_2$, such an association of bromide to these complexes might be stronger.

The following reaction scheme is consistent with the experimental rate laws (6) and (8). In the case of reaction (2) it may be written:



The equilibria between $PtBr_5H_2O^-$ and $PtBr_6^{2-}$ and the associated species $PtBr_5H_2O \ldots Br^{2-}$ and $PtBr_6 \ldots Br^{3-}$, respectively, are established instantaneously. If the association constant is K_a, the concentration of $PtBr_5H_2O \ldots Br^{2-}$ will be $K_a[PtBr_5H_2O^-][Br^-]$ and the reaction rate may be expressed as

$$-\frac{d[PtBr_5H_2O^-]}{dt} = (k_6'[Br^-] + kK_a[Br^-]^2)[PtBr_5H_2O^-]$$

which is in accordance with the experimentally deduced equations (4) and (6), if $kK_a = k_6''$ and $[PtBr_5H_2O^-] \gg [PtBr_5H_2O \ldots Br^{2-}]$. This rate expression is similar to that found by Skinner and Jones[34] for the bromide anation of $Pt(CN)_4BrH_2O^-$. A mechanism, involving an outer sphere complex, has also been proposed to explain a second order term, obtained in the rate expressions for reactions of five-coordinate platinum(II) complexes.[44]

Skinner and Jones[34] postulate dissociative mechanisms for the slow reactions involved in their reaction scheme. No conclusions concerning the intimate mechanisms of the slow reactions in the present case can be drawn from our kinetic measurements. For instance, an outer sphere complex might also be involved in the reaction path described by the term containing $[Br^-]$ in the rate expressions, *e.g.* by the following mechanism:

$$PtBr_5H_2O^- + Br^- \xrightleftharpoons{\text{fast}} PtBr_5H_2O \ldots Br^{2-}$$

$$PtBr_5H_2O \ldots Br^{2-} \rightarrow \text{products}$$

The observed second order rate constant k_6' for this path would then be a product of a first order rate constant and a stability constant of the outher sphere complex. This alternative seems appealing if association of bromide in the outer sphere causes a general labilisation of the complex.

Such a labilisation could be connected with a formal partial reduction of platinum(IV). For instance, if the outer sphere bromide is associated to the bromide ligand *trans* to the replaced water molecule, a certain transfer of negative charge to the central atom will occur, causing an increased reactivity of the remote water molecule and being equivalent to a partial reduction of platinum(IV). A complete reduction to platinum(II) and a simultaneous release of a bromine molecule as has been discussed extensively by Poë and Vaughan[43] does not seem to be necessary to describe our experiments. The two-term rate equation with one term containing $[Br^-]$ and the other $[Br^-]^2$ does not seem to speak in favour of Poë's model in our case.

The $PtBr_4(H_2O)_2$ formed in the successive acid hydrolyses of $PtBr_6^{2-}$ can be either the *cis*- or the *trans*-complex or a mixture of these two species. Both fresh and aged solutions containing $PtBr_4(H_2O)_2$ as the dominating species gave the same spectra and there was no indication of a slow reaction which might convert one of the isomers into the other. Since the two isomers should be expected to have different spectra and also different rates of bromide anation this might indicate that one of the isomers is present in much greater concentration than the other in the start solutions. It seems reasonable that this should be the *cis*-isomer since, statistically, the *cis*-isomer would be formed more frequently than the *trans*-isomer. Also, the *trans*-effect of bromide is greater than that of water which should favour kinetically the formation of *cis*–$PtBr_4(H_2O)_2$ in the second hydrolysis step.

The bromide anation of $PtBr_4(H_2O)_2$ follows the same experimental rate law as the anation of $PtBr_5H_2O^-$. If the assumption that the $PtBr_4(H_2O)_2$ is mainly the *cis*-isomer is correct, it should be a water ligand *trans* to a bromide that is replaced in this case, too.

Preliminary experiments on the chloride anations of $PtCl_4(H_2O)_2$ and $PtCl_5H_2O^-$ have been made. Because of the slow rates and sensitivity to illumination of these reactions, these experiments are difficult to reproduce, however.

Acknowledgements. We are indebted to Professor Ido Leden for kind interest and valuable discussions, to Mrs. Gunilla Larsson for experimental assistance, and to *The Swedish Natural Science Research Council* for financial support.

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