

Bromide Anation Kinetics for Some Platinum(IV) Bromo Aqua Complexes

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Bromide anations of $PtBr_5H_2O^-$ in the presence of $PtBr_4^{2-}$ or bromine, of $trans-PtBr_4(H_2O)_2$ in the presence of $PtBr_4^{2-}$ and of $cis-PtBr_4(H_2O)_2$ in the presence of bromine have been studied in 0.50 M perchloric acid medium at 25 °C.

The rate law for the bromide anation of $PtBr_5H_2O^-$

$$\text{Rate} = \left(k' [Br^-]^2 + \frac{k'' [Br^-]}{1 + k''' [Br^-]} [PtBr_4^{2-}] \right) \times [PtBr_5H_2O^-]$$

indicates two parallel reaction paths. The term $k' [Br^-]^2$ corresponds to a bromide assisted mechanism. The second term in the rate expression can be accounted for by assuming that a dimeric intermediate is formed from the platinum(IV) substrate and hydrated $PtBr_4^{2-}$. The formation of the reaction product $PtBr_6^{2-}$ is preceded by a substitution of water by bromide in this dimer.

A bromide assisted mechanism can also describe the bromide anation kinetics for $cis-PtBr_4(H_2O)_2$ having the rate law

$$\text{Rate} = k' [Br^-]^2 [cis-PtBr_4(H_2O)_2]$$

The bromide anation of $trans-PtBr_4(H_2O)_2$ in the presence of $PtBr_4^{2-}$ occurs by the two-term rate law

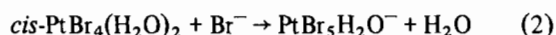
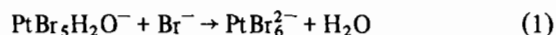
$$\text{Rate} = (k' + k'' [Br^-]) [PtBr_4^{2-}] [trans-PtBr_4(H_2O)_2]$$

indicating two parallel paths, k' corresponding to formation of $PtBr_5H_2O^-$ and k'' to formation of $PtBr_6^{2-}$.

*$trans-PtBr_4(H_2O)_2$ reacts so slowly with bromide in the absence of $PtBr_4^{2-}$ that no reaction can be observed. The large difference in bromide anation rates for $PtBr_5H_2O^-$ and $cis-PtBr_4(H_2O)_2$ compared to $trans-PtBr_4(H_2O)_2$ might indicate that halide assisted anations are possible only for complexes having a halide (or some other effective bridging group) in *trans*-position to the aqua ligand to be replaced.*

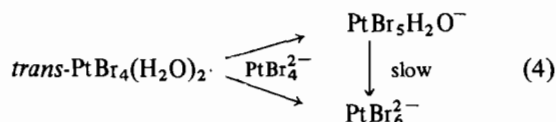
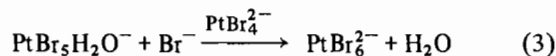
Introduction

We have previously described the bromide anation kinetics of $PtBr_5H_2O^-$ and (probably *cis*-) $PtBr_4(H_2O)_2$ in the absence of platinum(II) [1]:



The dominant terms in the observed rate laws were proportional to the squared concentration of bromide. They were interpreted as being due to bromide assisted reactions. Such paths, which have been found in other cases too [2–5], can be rather rapid. For instance the bromide anation of $Pt(CN)_4BrH_2O^-$ has a half-life in the millisecond region [2–5]. Chloride assisted reactions have also been observed [5]. The halide assisted reactions can be described by the path k_7, k_3, k_5 , in the reaction model Figure 1a (*cf.* also Ref. 5).

The present paper reports results for the bromide anation kinetics of $PtBr_5H_2O^-$ and *trans*- $PtBr_4(H_2O)_2$ in the presence of tetrabromoplatinate(II):



The observed rate law for reaction (3) is consistent with the reaction model in Figure 1b, which has been previously used for the chloride anations of $PtCl_5H_2O^-$ in the presence of $PtCl_4^{2-}$ [6] and of $Pt(CN)_4ClH_2O^-$ in the presence of $Pt(CN)_4^{2-}$ [7].

Reaction (4) is analogous to the previously described chloride anation of *trans*- $PtCl_4(H_2O)_2$ in the presence of tetrachloroplatinate(II) [6] and gives a mixture of $PtBr_5H_2O^-$ and $PtBr_6^{2-}$ as the immediate reaction products. The reaction model in Figure 1c accounts for these experimental results.

Extrapolation of the platinum(II)-dependent kinetics for reaction (3) to $[PtBr_4^{2-}] = 0$ should give the rate expression for the platinum(II)-independent

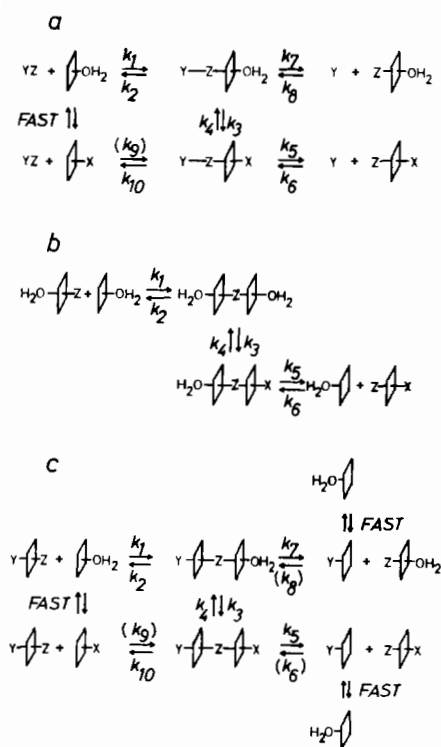


Figure 1. Suggested reaction models [5–7]. X, Y and Z denote halide. The four in-plane ligands of the platinum(IV) and platinum(II) complexes have been omitted.

reaction path (1) – dominated by the $[\text{Br}^-]^2$ term – determined in our earlier study [1]. The extrapolation gave an about 50% larger value for the third-order rate constant. It was observed, however, that addition of small concentrations ($10^{-5}M$ to $10^{-4}M$) of bromine to the platinum(IV) solutions used for the study of reaction (1) gave consistent results with the extrapolated values for reaction (3). We have therefore reinvestigated the rate laws for reaction (1) and (2) with small concentrations of bromine present. Possible reasons for the discrepancy – and similar discrepancies reported in the literature – will be discussed later in the paper.

Experimental

Chemicals

Potassium hexabromoplatinate(IV), K_2PtBr_6 , from Heraeus was the same as used previously [1]. Potassium tetrabromoplatinate(II), K_2PtBr_4 , from Degussa was used without further purification. A sample of K_2PtBr_4 prepared by reduction of potassium hexabromoplatinate(IV) with hydrazine sulfate (Merck's *p.a.*) under carbon dioxide according to Shagisultanova [8] gave identical results. The hydrobromic acid (Merck's *p.a.*) was distilled

immediately before preparing the solutions in order to remove dissolved bromine. Other chemicals were reagent grade.

Bromide Anation of $\text{PtBr}_5\text{H}_2\text{O}^-$

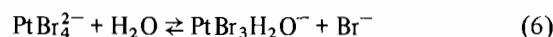
Solutions of $\text{PtBr}_5\text{H}_2\text{O}^-$ were prepared either by ageing solutions of potassium hexabromoplatinate(IV) ($1.6 \times 10^{-4}M$ or $0.75 \times 10^{-4}M$) in 0.5 M perchloric acid in UV light from a quartz lamp for about 2 h or by oxidation of solutions of tetrabromoplatinate(II) ($1.6 \times 10^{-4}M$ or $0.80 \times 10^{-4}M$) in 0.5 M perchloric acid with bromine in excess:



The excess bromine was then removed by flushing with nitrogen.

The kinetic runs were started by mixing equal volumes of these solutions and solutions containing hydrobromic acid and PtBr_4^{2-} or bromine. In some experiments the oxidation was performed at the start of the kinetic runs by mixing solutions of K_2PtBr_4 in hydrobromic acid with solutions of hydrobromic acid and bromine. Identical results were obtained by the two methods, which indicates that the oxidation is fast compared to the subsequent anation.

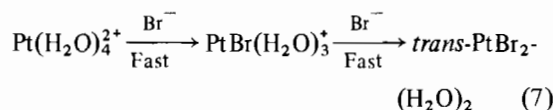
The equilibrium constant for the acid hydrolysis:



is $1.8 \times 10^{-3}M$ [9], so solutions of K_2PtBr_4 will contain negligible amounts of $\text{PtBr}_3\text{H}_2\text{O}^-$ for $[\text{Br}^-] \geq 50 \text{ mM}$.

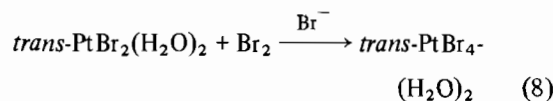
Bromide Anation of $\text{trans-PtBr}_4(\text{H}_2\text{O})_2$

Solutions of $\text{trans-PtBr}_4(\text{H}_2\text{O})_2$ ($6 \times 10^{-4}M$) were obtained from 1 M perchloric acid solutions of the tetra aqua complex $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ which was prepared according to Ref. 10. Addition of bromide to such solutions gave rapidly $\text{trans-PtBr}_2(\text{H}_2\text{O})_2$



The subsequent anations of $\text{PtBr}(\text{H}_2\text{O})_3^+$ to the *cis*-isomer and of $\text{trans-PtBr}_2(\text{H}_2\text{O})_2$ to $\text{PtBr}_3\text{H}_2\text{O}^-$ are slow [11].

Oxidation with bromine of $\text{trans-PtBr}_2(\text{H}_2\text{O})_2$ solutions containing 0.2 M hydrobromic acid then gave $\text{trans-PtBr}_4(\text{H}_2\text{O})_2$:

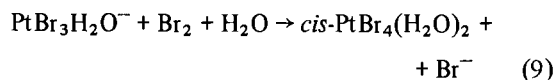


Solutions of $\text{trans-PtBr}_4(\text{H}_2\text{O})_2$ remained stable for several days in the presence of bromine, since the bromide anation of $\text{trans-PtBr}_4(\text{H}_2\text{O})_2$ in the absence of tetrabromoplatinate(II) is extremely slow (*vide infra*).

The kinetic runs were started by mixing solutions of *trans*-PtBr₄(H₂O)₂ diluted to about 1 × 10⁻⁴ M and solutions of K₂PtBr₄ and hydrobromic acid.

Bromide Anation of *cis*-PtBr₄(H₂O)₂

Solutions of *cis*-PtBr₄(H₂O)₂ were obtained by addition of bromine to solutions of PtBr₃H₂O⁻:



Stock solutions of PtBr₃H₂O⁻ were prepared by ageing solutions of K₂PtBr₄ (5 × 10⁻⁴ M) in 0.5 M perchloric acid for about 12 h at 25 °C [9].

The kinetic runs were started by mixing solutions of PtBr₃H₂O⁻ diluted to about 1 × 10⁻⁴ M and solutions containing bromine and hydrobromic acid.

Kinetic Procedure

A Zeiss Quartz PMQ II Spectrophotometer equipped with a Goertz compensation recorder and a thermostated cell holder was used. PtBr₆²⁻ was the final product in all reactions. The absorption maximum at 315 nm was used for all measurements. For the reactions studied in the presence of PtBr₄²⁻ the blank contained PtBr₄²⁻ and hydrobromic acid, in other cases water.

In all solutions the hydrogen ion concentration and ionic strength were 0.50 M with perchloric acid as the supporting electrolyte. Pseudo first-order conditions were obtained by having bromide and PtBr₄²⁻ in large excess. The concentrations of bromide were always large enough to suppress the reverse reactions [1].

The reacting solutions for the slow reactions were stored in bottles in closed water thermostats. The solutions for the fast runs were mixed directly in the spectrophotometer cell with thermostated syringes. These reactions were monitored using the recorder. The temperature was (25.0 ± 0.1) °C except when otherwise stated.

The anation of PtBr₅H₂O⁻ gave simple first-order plots with a reproducibility of the rate constants generally better than ±3%. The plots of ln(e_∞ - e) vs. t for the anation of *cis*- and *trans*-PtBr₄(H₂O)₂ indicated two consecutive reactions with the anation of PtBr₅H₂O⁻ as the slow step. Eqn. (10) describes these experiments (*cf.* Ref. 12):

$$e_\infty - e = \alpha e^{-k_a t} + \beta e^{-k_b t} \quad (10)$$

e denotes absorptivity and α and β are constants. The rate constant k_b for the slow anation of PtBr₅H₂O⁻ and the constant β were calculated for large values of t where the first term in eqn. (10) is negligible. The rate constant k_a for the fast step was then determined from linear plots of ln(e_∞ - e - βe^{-k_bt}) vs. t. The reproducibility in k_a was about ±7%.

TABLE I. Bromide Anation of PtBr₅H₂O⁻ in the Presence of PtBr₄²⁻ at 15, 25 and 35 °C. The concentration of platinum(IV) complex was 4 × 10⁻⁵ M or 8 × 10⁻⁵ M. The standard deviation in k_{exp} was about ±3%.

[Br ⁻] × 10 ³ /M	[PtBr ₄ ²⁻] × 10 ³ /M	k _{exp} × 10 ³ /s ⁻¹
25 °C		
25 ^a	0.94 ^a	2.25
50	0.30	1.70
50	0.48	2.37
50	0.96	4.5
100	0.15	1.78
100	0.31	2.92
100	0.75	6.2
100	0.80	5.7
100	1.51	12.0
150	0.15	3.04
150	0.30	4.5
150	0.32	4.9
150	0.75	8.7
150	1.51	16.6
200	0.15	4.4
200	0.31	6.3
200	0.75	11.1
200	0.80	12.3
200	1.51	22.1
200	1.61	21.1
250	0.15	6.2
250	0.30	8.4
250	0.75	15.4
250	1.51	25.7
15 °C		
100	0.30	1.52
100	0.75	3.5
200	0.30	3.4
200	0.75	7.2
35 °C		
100	0.15	3.7
100	0.30	5.7
100	0.75	10.4
200	0.15	11.2
200	0.30	13.6

^aAccording to the equilibrium constant for reaction (6), the amount of PtBr₃H₂O⁻ is about 7% of the total amount of Pt(II) for [Br⁻] = 25 mM. In the experiment using [Br⁻] = 25 mM, an equilibrated solution of K₂PtBr₄ in 25 mM hydrobromic acid was therefore mixed with a solution containing bromine and 25 mM hydrobromic acid. By this procedure [PtBr₄²⁻] was kept constant during the kinetic run.

Results

Bromide Anation of PtBr₅H₂O⁻

Table I reviews the experiments performed in the presence of tetrabromoplatinate(II). Figure 2 a shows plots of k_{exp} vs. the concentration of PtBr₄²⁻. The intercepts of these lines, k_{exp, extr}, correspond to the platinum(II)-independent reaction. Table II indi-

TABLE II. Bromide Anation of $\text{PtBr}_5\text{H}_2\text{O}^-$ in the Presence of Bromine at 25 °C. The concentration of platinum(IV) complex was about $5 \times 10^{-5} \text{ M}$ and that of bromine $2 \times 10^{-5} \text{ M}$ to $2 \times 10^{-4} \text{ M}$. The error in k_{exp} was about $\pm 3\%$. The mean value of $k_{\text{exp}}/[\text{Br}^-]^2$, calculated from the slope of the line $k_{\text{exp}}/[\text{Br}^-]$ vs. $[\text{Br}^-]$ was $(6.4 \pm 0.1) \times 10^{-2} \text{ s}^{-1} \text{ M}^{-2}$. The values of $k_{\text{exp,extr}}$ were obtained by extrapolation of the lines in Figure 2a to zero $[\text{PtBr}_4^{2-}]$.

$[\text{Br}^-] \times 10^3 / \text{M}$	$k_{\text{exp}} \times 10^4 / \text{s}^{-1}$	$k_{\text{exp}}/[\text{Br}^-]^2 \times 10^2 / \text{s}^{-1} \text{ M}^{-2}$	$k_{\text{exp,extr}} \times 10^4 / \text{s}^{-1}$
25	0.45	7.2	
50	1.74	7.0	4 ± 2
100	6.6	6.6	7 ± 1
150	14.0	6.2	15.7 ± 0.8
200	25.3	6.3	25.0 ± 0.5
250	41	6.6	40 ± 3
300	59	6.6	
400	103	6.4	

Weighted Mean: 6.4 ± 0.1

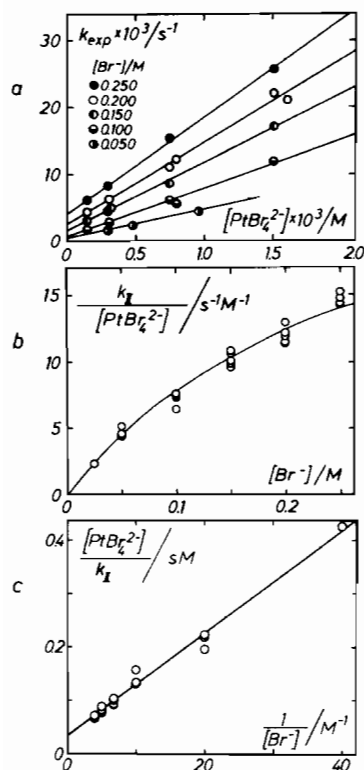


Figure 2. Bromide anation of $\text{PtBr}_5\text{H}_2\text{O}^-$. Experiments with PtBr_4^{2-} present. (a) The observed rate constant as a function of tetrabromoplatinate(II) concentration for different concentrations of bromide. (b) The rate constant k_{II} for the platinum(II)-dependent reaction divided by the concentration of tetrabromoplatinate(II) as a function of bromide concentration. (c) Linear plot according to eqn. (13).

icates a good agreement between $k_{\text{exp,extr}}$ and the rate constants determined separately from experiments without Pt(II) but with some bromine present in the solutions. It is also obvious from the results given in Table II that the platinum(II)-independent path is second-order in bromide

$$k_{\text{exp}} = k'[\text{Br}^-]^2 \quad (11)$$

with

$$k' = (6.4 \pm 0.1) \times 10^{-2} \text{ s}^{-1} \text{ M}^{-2}$$

In Figure 2 b the experimental rate constants k_{II} for the platinum(II)-dependent path divided by the concentration of tetrabromoplatinate(II) has been plotted as a function of bromide concentration. The curve indicates that k_{II} is given by

$$k_{\text{II}} = k_{\text{exp}} - k'[\text{Br}^-]^2 = \frac{k''}{1 + k'''[\text{Br}^-]} [\text{Br}^-] [\text{PtBr}_4^{2-}] \quad (12)$$

which can be transformed to the linear relation

$$\frac{[\text{PtBr}_4^{2-}]}{k_{\text{II}}} = \frac{k'''}{k''} + \frac{1}{k''} \times \frac{1}{[\text{Br}^-]} \quad (13)$$

shown in Figure 2 c. A least-squares calculation for the experiments at 25 °C gave $k'' = (105 \pm 5) \text{ s}^{-1} \text{ M}^{-2}$ and $k''' = (3.5 \pm 0.6) \text{ M}^{-1}$.

Experiments at 15 °C and 35 °C (cf. Table I) indicate that all three parameters k' , k'' and k''' increase with temperature. The activation parameters $\Delta H^\ddagger / \text{kcal mol}^{-1}$, $\Delta S^\ddagger / \text{cal mol}^{-1} \text{ K}^{-1}$ were 18 ± 1 , -2 ± 2 for k' and 13 ± 1 , -7 ± 4 for k'' . k''' was obtained approximately as 0.4 M^{-1} at 15 °C and 6 M^{-1} at 35 °C.

Bromide Anation of $\text{trans-PtBr}_4(\text{H}_2\text{O})_2$

Plots of k_a from Table III vs. the concentration of PtBr_4^{2-} for constant concentrations of bromide gave straight lines through the origin. Thus, the bromide anation in the absence of PtBr_4^{2-} is negligibly slow. The rate constant can be expressed as (cf. Figure 3):

$$k_a = (k' + k''[\text{Br}^-])[\text{PtBr}_4^{2-}] \quad (14)$$

with

$$k' = (3.5 \pm 0.9) \text{ s}^{-1} \text{ M}^{-1} \text{ and } k'' = (204 \pm 7) \text{ s}^{-1} \text{ M}^{-2}$$

TABLE III. Rate Constants with Standard Deviations for the Bromide Anation of *trans*-PtBr₄(H₂O)₂ in the Presence of PtBr₄²⁻ at 25 °C. The concentration of platinum(IV) complex was 6 × 10⁻⁵ to 8 × 10⁻⁵ M.

[Br ⁻] × 10 ³ /M	[PtBr ₄ ²⁻] × 10 ³ /M	k _a × 10 ² /s ⁻¹
50	1.02	1.4 ± 0.1
100	1.02	2.6 ± 0.2
150	1.02	3.5 ± 0.1
200	0.51	2.2 ± 0.1
200	0.77	3.2 ± 0.1
200	1.02	4.6 ± 0.1
250	1.02	6.0 ± 0.2

TABLE IV. Rate Constants with Standard Deviations for the Bromide Anation of *cis*-PtBr₄(H₂O)₂ in the Presence of Bromine at 25 °C. The concentration of platinum complex was about 5 × 10⁻⁴ M and that of bromine 5 × 10⁻⁵ M or 1 × 10⁻⁴ M.

[Br ⁻] × 10 ³ /M	k _a × 10 ² /s ⁻¹	k _a /[Br ⁻] ² /s ⁻¹ M ⁻²
50	0.24 ± 0.03	0.96
100	0.86 ± 0.05	0.86
150	2.20 ± 0.13	0.98
200	3.51 ± 0.06	0.88
250	5.6 ± 0.2	0.89

Weighted Mean: 0.89 ± 0.04.

Bromide Anation of *cis*-PtBr₄(H₂O)₂

The results are given in Table IV. The rate constant is

$$k_a = k' [\text{Br}^-]^2 \quad (15)$$

The parameter k' was obtained from the slope of the line $k_a/[\text{Br}^-]^2$ vs. $[\text{Br}^-]$ as $(0.89 \pm 0.04) \text{ s}^{-1} \text{ M}^{-2}$.

Discussion

Platinum(II)-dependent Kinetics for Reaction (3)

The rate constant for the platinum(II)-dependent bromide anation of PtBr₅H₂O⁻ – eqn. (12) – has the same form as those previously reported for the chloride anations of PtCl₅H₂O⁻ and *trans*-Pt(CN)₄ClH₂O⁻ in the presence of PtCl₄²⁻ and Pt(CN)₄²⁻ respectively [6, 7]. The value of the parameter $k''' = (3.5 \pm 0.6) \text{ M}^{-1}$ in the present case is too large to be identified with a stability constant for PtBr₅³⁻ (cf. the discussion in Ref. 6). Moreover, the experiments at 15 and 35 °C indicate that k''' increases with temperature, whereas a stability constant should be expected to decrease. Thus, reaction (3) is a further example of a platinum-

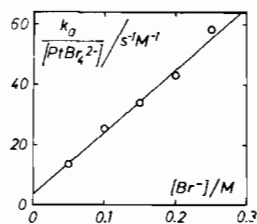


Figure 3. Bromide anation of *trans*-PtBr₄(H₂O)₂ in the presence of tetrabromoplatinate(II). The rate constant k_a calculated from eqn. (10) divided by the tetrabromoplatinate(II) concentration as a function of bromide concentration.

(IV) substitution which cannot be described by a mechanism [13] involving a complex formation between the entering ligand and the platinum(II) complex as the initial step. The model in Figure 1b gives a rate constant consistent with eqn. (12), viz.

$$k_{\text{II}} = \frac{k_1 k_3 k_5}{k_2 (k_4 + k_5)} \frac{[\text{Br}^-] [\text{PtBr}_4^{2-}]}{1 + \frac{k_3 k_5}{k_2 (k_4 + k_5)} [\text{Br}^-]} \quad (16)$$

if steady-state concentrations are assumed for the intermediates and if the reverse reaction is neglected.

Platinum(II)-independent Kinetics for Reactions (1) and (2)

The model in Figure 1a can be used to describe the experiments. Since the oxidation of a platinum(II) complex is fast in the presence of excess bromine or platinum(II) complex [5], the relation

$$\frac{d[\text{YZ}]}{dt} = -k_1 [\text{YZ}] [\text{Pt-OH}_2] - k_9 [\text{YZ}] [\text{Pt(II)-X}] + k_2 [\text{Y-Z-Pt(II)-OH}_2] + k_{10} [\text{Y-Z-Pt(II)-X}] = 0 \quad (17)$$

will be satisfied. With steady-state concentrations for the intermediates and assuming that the equilibrium Pt(II)-H₂O ⇌ Pt(II)-X is fast, the rate constant for the anation will be given by

$$k = \frac{k_3 k_5 k_8 [\text{Y}] [\text{X}]}{k_7 (k_4 + k_5 + k_{10}) + k_3 k_5 [\text{X}]} \quad (18)$$

Since a *trans*-halo-aqua complex is the primary reaction product in the oxidation of a platinum(II) complex with chlorine or bromine even in the presence of excess chloride or bromide, the condition $k_7 \gg k_3 [\text{X}]$ is valid. With $\text{Y} = \text{X} = \text{Br}$ eqn. (18) is then simplified to

$$k = \frac{k_3 k_5 k_8}{k_7 (k_4 + k_5 + k_{10})} [\text{Br}^-]^2 \quad (19)$$

which agrees with the experimental eqns. (11) and (15).

In our earlier study [1] of reactions (1) and (2) a first-order term in bromide was obtained as a rather small correction. This term disappeared and the rate constant for the second-order term increased when the experiments were performed in the presence of small concentrations of added bromine. Similarly, Mason (*cf.* Ref. 3, p. 1917) found a value of $4.1 \times 10^5 \text{ s}^{-1} \text{ M}^{-2}$ for the bromide anation rate constant of $\text{Pt}(\text{CN})_4\text{BrH}_2\text{O}^-$, whereas Skinner and Jones [2] reported a value for that constant of only $1.2 \times 10^5 \text{ s}^{-1} \text{ M}^{-2}$. Their experiments were performed under identical conditions, with the only exception that Mason's solutions contained some bromine from the synthesis.

We have also tried to measure independently the k_0 -term in the rate law for the chloride anation of $\text{PtCl}_5\text{H}_2\text{O}^-$ [6] in the absence of PtCl_4^{2-} , but these experiments gave a much smaller value than that obtained by extrapolation of the platinum(II)-dependent kinetics to zero tetrachloroplatinate(II) concentration. Moreover, the first-order plots in the absence of PtCl_4^{2-} were slightly curved. Similarly, the bromide anations of $\text{PtBr}_5\text{H}_2\text{O}^-$ and $\text{PtBr}_4(\text{H}_2\text{O})_2$ gave on the whole better first-order plots when bromine or PtBr_4^{2-} were present than in their absence. Curved first-order plots have previously been reported by Poë and Vaughan [14] for the reaction between *trans*-Pt(en)(tet)Cl₂ and bromide. Their experiments were also performed without addition of extra bromine or platinum(II).

These discrepancies cannot be explained by a formation of large amounts of Pt(II) complexes by a redox process with X^-/X_2 ($\text{X} = \text{Cl}, \text{Br}$). On the contrary, the redox equilibria are probably displaced towards Pt(IV). For instance, the equilibrium constant for reaction (5) can be calculated to be about 10^{12} from the redox potentials for $\text{PtBr}_4^{2-}/\text{PtBr}_6^{2-}$ [15] and for Br^-/Br_2 [16] and from the formation constant of PtBr_6^{2-} from $\text{PtBr}_5\text{H}_2\text{O}^-$ and bromide [1]. This means that the platinum(II) complexes in the model in Figure 1a are present only in very small concentrations, comparable to the steady-state concentrations of the intermediates.

However, if the assumption of a fast reaction between $\text{Pt}(\text{II})\text{-OH}_2$ and $\text{Pt}(\text{II})\text{-X}$ as marked in Figure 1a is not valid, the rate might depend on the concentrations of YZ and platinum(II) complex even if steady-state concentrations are assumed for $\text{Pt}(\text{II})\text{-H}_2\text{O}$ and $\text{Pt}(\text{II})\text{-X}$. This will cause deviations from first-order kinetics if the concentrations of halogen and platinum(II) complex are comparable in magnitude, which is probably valid for the experiments without added halogen or Pt(II).

If, on the other hand, the concentrations of halogen or platinum(II) are large enough to approximately satisfy the relations

$$k_1 [\text{YZ}] [\text{Pt}(\text{II})\text{-OH}_2] = k_2 [\text{Y-Z-Pt}(\text{II})\text{-OH}_2] \quad (20)$$

$$k_9 [\text{YZ}] [\text{Pt}(\text{II})\text{-X}] = k_{10} [\text{Y-Z-Pt}(\text{II})\text{-X}] \quad (21)$$

e.g. if the oxidations *via* k_1 and k_9 are fast compared to the reaction between $\text{Pt}(\text{II})\text{-OH}_2$ and $\text{Pt}(\text{II})\text{-X}$, the rate will be independent of the concentration of YZ and platinum(II) and strictly first-order plots will be obtained.

The different results obtained in the presence and in the absence of added platinum(II) complex or halogen might be explained in this manner, but of course another possible reason for the discrepancies observed might be for instance the presence of inhibitors, which are destroyed by addition of halogen or Pt(II).

Platinum(II)-dependent Kinetics for Reaction (4)

The bromide anation of *trans*-PtBr₄(H₂O)₂ in the presence of PtBr_4^{2-} gives PtBr_6^{2-} and $\text{PtBr}_5\text{H}_2\text{O}^-$ by the two parallel paths k_1, k_7 and k_1, k_3, k_5 in Figure 1c [17]. The interpretation is the same as for the previously described chloride anation of *trans*-PtCl₄(H₂O)₂ in the presence of PtCl_4^{2-} [6]. The model gives

$$k = k_1 \frac{k_7(k_4 + k_5 + k_{10}) + k_3 k_5 [\text{Br}^-]}{(k_2 + k_7)(k_4 + k_5 + k_{10}) + (k_5 + k_{10})k_3 [\text{Br}^-]} [\text{PtBr}_4^{2-}] \quad (22)$$

if steady-state concentrations are assumed for the bridged intermediates and if bromide and PtBr_4^{2-} are present in large enough excess to be considered constant. Eqn. (22) agrees with the experimental eqn. (14) if the bromide dependent term in the denominator is negligible.

Conclusions

There is a large difference in bromide anation rates between the three bromo aqua complexes in this study. Whereas $\text{PtBr}_5\text{H}_2\text{O}^-$ and *cis*-PtBr₄(H₂O)₂ react rapidly even in the absence of PtBr_4^{2-} with rate constants proportional to the squared concentration of bromide — eqn.s (11) and (15) — no reaction at all can be observed for the *trans*-isomer when PtBr_4^{2-} is absent — eqn. (14). This different reactivity might give some information about the intimate mechanism. Very likely the bromide Y is associated to a bromide ligand Z in *trans*-position to the replaced water molecule as depicted in Figure 1a (*cf.* also Ref. 1, p. 649). Water is a poor bridging ligand, *i.e.* $Z \neq \text{H}_2\text{O}$. For *cis*-PtBr₄(H₂O)₂ and $\text{PtBr}_5\text{H}_2\text{O}^-$ the aqua ligands are in *trans*-position to bromide ligands and can easily be replaced by bromide *via* a bromide assisted path. This possibility does not exist for *trans*-PtBr₄(H₂O)₂, having the two water molecules opposite to each other. Thus, halide assisted anations should only

be expected to occur for complexes having a halide (or some other effective bridging group) in *trans*-position to the aqua ligand to be replaced.

The substitutional inertness of the two aqua ligands in the *trans*-isomers of $\text{PtBr}_4(\text{H}_2\text{O})_2$ and $\text{PtCl}_4(\text{H}_2\text{O})_2$ [6] shows that water is not necessarily an easily replaceable ligand in these complexes. It is obvious that both the reaction mechanism and the rate of substitution are strongly dependent not only on the entering ligand, but also on the nature and geometrical arrangement of the ligands in the substrate complex. The situation resembles very much that for the square-planar systems. For instance the aqua ligands in *trans*- $\text{PtX}_2(\text{H}_2\text{O})_2$ [11, 18] and *trans*- $\text{PdX}_2(\text{H}_2\text{O})_2$ [19] (X = Cl, Br) are also replaced by halide very slowly compared to other reactions in these systems.

A further discussion of the effects on the kinetics of *cis*-, *trans*-, entering and bridging ligands and of assisting and reducing agents will be postponed to a subsequent paper, wherein complementary experimental results will also be published [20].

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Erratum

In our previous paper [1] on the platinum(IV)-bromo complexes there is a misprint on the first

line of Table II. The value for the stability constant $K_6 \times 10^{-3}/M^{-1}$ should be 1.9 ± 0.2 , not 1.09 ± 0.2 .

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