Inorganica Chimica Acta, 28 (1978) 255–262
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Stabilities of Platinum(II) Chloro and Bromo Complexes and Kinetics for Anation of the Tetraaquaplatinum(II) Ion by Halides and Thiocyanate

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Received October 8, 1977

The anations of $Pt(H_2O)_4^{2+}$ *and* $PtX(H_2O)_3^+$ *(to* trans-$PtX_2(H_2O)_2$*) by* $X^- = Cl^-, Br^-, I^-$ *and* SCN^- *and the anation of* trans-$PtX_2(H_2O)_2$ *by* $X^- = Cl^-$, Br^- *and* I^- *have been studied at 25 °C and 1.00* M *perchlorate medium using both stopped-flow and conventional spectrophotometry. For large excess of* X^-, PtX_4^{2-} *is formed according to the mechanism in Figure 1. The results indicate an entering ligand order of* $Cl^- < Br^- < SCN^- < I^-$ *(1:8:50:350), a kinetic* trans-*effect order of* $H_2O < Cl^- < Br^- < I^- < SCN^-$ *(1:330:3300:~4 × 10⁴:~1 × 10⁵) and a kinetic* cis-*effect order of* $Br^- < Cl^- < H_2O < I^-$ *(0.3:0.4:1:~2). Acid hydrolysis rate constants for* $PtX_3H_2O^-$, trans-$PtX_2(H_2O)_2$ *and* $PtX(H_2O)_3^+$ *(X = Cl, Br) have also been determined. Bromide is about 3 times better as leaving ligand than chloride. The palladium chloro and bromo complexes react 2 × 10⁴ to 3 × 10⁶ times faster than the corresponding platinum complexes. Spectrophotometric equilibrium measurements performed as competition experiments with palladium give the stepwise stability constants* $K_1 = [PtX^+][Pt^{2+}]^{-1}[X^-]^{-1}$ *as (9 ± 2) × 10⁴* M^{-1} *(X = Cl) and (1.9 ± 0.4) × 10⁵* M^{-1} *(X = Br). These values combined with previous literature data enable a calculation of the over-all stability constants for the platinum(II) chloro and bromo complexes.* $\lg(\beta_n/M^{-n})$, *n = 1,2,3,4, are: 4.97 ± 0.11, 8.97 ± 0.20, 11.89 ± 0.35, and 13.99 ± 0.45 for the chloro complexes and 5.28 ± 0.09, 9.72 ± 0.18, 13.32 ± 0.35 and 16.11 ± 0.45 for the bromo complexes, at 25 °C and for a 0.50 to 1.00* M *perchloric acid medium.*

Introduction

The stepwise formation of square-planar chloro and bromo complexes of palladium(II) and platinum(II) has been described by the reaction model in Figure 1 [1, 2]. The palladium systems have been completely characterized starting from the tetraaqua complex $Pd(H_2O)_4^{2+}$ [2] whereas the experimental information for platinum systems [1] is more fragmentary, due to the non-availability of the corresponding tetraaquaplatinum(II) ion. The recent preparation [3] of $Pt(H_2O)_4^{2+}$ offers new possibilities for mechanistic and thermodynamic studies of several platinum(II) systems.

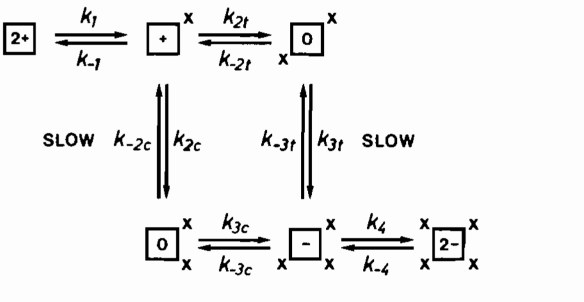

Figure 1. Reaction scheme [1b, 2b] for the stepwise anation of $Pt(H_2O)_4^{2+}$ by $X^- = Cl^-, Br^-, I^-$ and SCN^-.

The two consecutive processes (1) and (2)

$$Pt(H_2O)_4^{2+} + X^- \xrightarrow{k_1} PtX(H_2O)_3^+ + H_2O \qquad (1)$$

$$PtX(H_2O)_3^+ + X^- \xrightarrow{k_{2t}} trans\text{-}PtX_2(H_2O)_2 + H_2O \qquad (2)$$

have been followed by addition of excess entering ligand $X^- = Cl^-, Br^-, I^-, SCN^-$ to solutions of $Pt(H_2O)_4^{2+}$. The subsequent reactions of $PtX(H_2O)_3^+$ to *cis*-$PtX_2(H_2O)_2$ and of *trans*-$PtX_2(H_2O)_2$ to $PtX_3H_2O^-$ (*cf.* Figure 1) are slow and kinetically separated from reactions (1) and (2). Because of the large *trans*-effect of halides and thiocyanate compared to water, $k_1 \ll k_{2t}$. Therefore, the formation of *trans*-$PtX_2(H_2O)_2$ takes place with reaction (1) as the rate-determining step and with $PtX(H_2O)_3^+$ present in steady-state concentrations. Scheme (3) is therefore applicable.

$$\begin{tikzcd}
Pt(H_2O)_4^{2+} \arrow[r, "k_1"] & PtX(H_2O)_3^+ \arrow[r, "k_{2t}", "\text{fast}"'] \arrow[d, "+X^-\ \text{slow}"', "k_{2c}"] & trans\text{-}PtX_2(H_2O)_2 \arrow[d, "+X^-\ \text{slow}"', "k_{3t}"] \\
 & {} & {}
\end{tikzcd}$$

Reaction (2) can be observed as a rapid initial process when excess entering ligand is added to pre-equilibrated solutions containing $Pt(H_2O)_4^{2+}$ and $PtX(H_2O)_3^+$. In that time scale, reaction (1) will be negligibly slow. The over-all process

$$Pt(H_2O)_4^{2+} + 4X^- \rightarrow PtX_4^{2-} + 4H_2O \qquad (4)$$

takes place *via* the two parallel slow reactions described by k_{2c} and k_{3t} in Figure 1 with the observed first-order rate constant (5) for excess X^- [1b, 2c]:

$$k_{exp} = k_{3t}[X^-] + k_{2c}/K_{2t} \tag{5}$$

The stability constant K_{2t} is defined by (6)

$$K_{2t} = [trans\text{-}PtX_2(H_2O)_2]\,[PtX(H_2O)_3^+]^{-1}\,[X^-]^{-1} \tag{6}$$

Reaction (4) has been studied for X = Cl, Br, and I.

The stepwise stability constants K_4, K_3 and K_2 for the chloro complexes and K_4 and K_3 for the bromo complexes defined by eqn. (7) have been determined previously [1].

$$K_n = [PtX_n^{2-n}]\,[PtX_{n-1}^{3-n}]^{-1}\,[X^-]^{-1}; n = 1,2,3,4; \tag{7}$$

Starting from $Pt(H_2O)_4^{2+}$, the stability constants K_1 for $PtCl^+$ and $PtBr^+$ can be determined by competition experiments with the corresponding palladium complexes, which have a comparable stability [2a]. The four stability constants β_n for the chloride system can then be calculated from eqn. (8)

$$\beta_n = \prod_{n=1}^{4} K_n \tag{8}$$

The separately determined ratio between the overall stability constants for the bromo and chloro complexes, $\beta_{4Br}/\beta_{4Cl} = 133 \pm 15$ [5], enables a complete description of the bromide system also. The acid hydrolysis rate constants k_{-n} for the reverse reactions for X = Cl, Br can then be obtained from eqn. (9)

$$K_n = k_n/k_{-n} \tag{9}$$

Experimental

Solutions

Solutions of tetraaquaplatinum(II) and tetraaquapalladium(II) perchlorates in 1.00 *M* perchloric acid (Baker's *p.a.*) were prepared from K_2PtCl_4 (Johnson and Matthey) and palladium sponge (Johnson and Matthey, *Spec. pure*) as described previously [2a, 3]. The platinum(II) perchlorate solutions used in the kinetic experiments with hydrogen ion concentrations less than 0.5 *M* were mixed with sodium perchlorate immediately before use, in order to prevent polynuclear hydrolysis. Ligand solutions were prepared from 1.00 *M* stock solutions of perchloric acid (Baker's *p.a.*), sodium perchlorate (Baker's *p.a.*, recrystallized), hydrochloric acid (Merck's *p.a.*), hydrobromic acid (Merck's *p.a.*, freshly distilled), sodium iodide (Merck's *p.a.*) and sodium thiocyanate (Mallinckrodt's *p.a.*, recrystallized). The iodide stock solutions were neutral and were not mixed with acid until the start of the kinetic runs in order to eliminate oxidation of iodide. All solutions were flushed with nitrogen before experiments with iodide.

TABLE I. Equilibrium Measurements.

C_{Pd}/m*M*	C_{Pt}/m*M*	C_X/m*M*	*x*/m*M*	*K*
		X = Cl		
22.2	3.85	7.53	1.74 ± 0.20	2.3 ± 0.7
22.2	3.85	3.88	1.18 ± 0.06	3.2 ± 0.3
22.2	1.93	7.65	1.18 ± 0.12	3.8 ± 1.3
22.2	1.93	3.88	0.77 ± 0.04	4.0 ± 0.4
13.6	3.27	6.27	1.99 ± 0.19	3.4 ± 1.3
13.6	3.27	3.25	1.09 ± 0.07	2.7 ± 0.4
13.7	3.21	3.25	1.06 ± 0.05	2.6 ± 0.3
			Mean:	3.2 ± 0.7
		X = Br		
13.7	3.27	3.25	0.58 ± 0.12	0.9 ± 0.3
13.6	3.27	3.25	0.87 ± 0.20	1.7 ± 0.8
10.4	6.86	3.00	1.16 ± 0.22	1.0 ± 0.5
7.41	1.54	1.50	0.35 ± 0.07	1.6 ± 0.6
6.52	6.77	3.00	1.74 ± 0.12	1.4 ± 0.3
4.35	7.50	2.00	1.45 ± 0.04	1.7 ± 0.4
2.17	8.24	1.00	0.80 ± 0.03	1.1 ± 0.3
			Mean:	1.3 ± 0.3

Equilibrium Measurements

The solutions listed in Table I were mixed from platinum and palladium perchlorate and hydrochloric/hydrobromic acid. The ionic medium of 1.00 *M* perchloric acid is sufficient to suppress both mononuclear and polynuclear protolysis of the aqua species [2a, 3]. The small palladium concentrations used for X = Br were necessary in order to avoid precipitation of $PdBr_2(s)$ [2a]. The solutions were flushed with nitrogen and then equilibrated at 25.0 °C for 15 to 20 days (chloride) and 4 days (bromide). Their spectra were recorded between 450 and 270 nm.

Kinetic Measurements

All reactions were started by mixing a metal solution (M) containing platinum(II) perchlorate and sometimes extra ligand with an equal volume of a ligand solution (L). The kinetics were followed at (25.0 ± 0.1) °C using a large excess of ligand to obtain first-order kinetics and to suppress the reverse reactions. The pseudo-first-order rate constants were calculated directly from the transmittance *vs.* time curves or from ordinary logarithmic plots using least-squares programmes. A 1.00 *M* sodium perchlorate-perchloric acid medium was used. The hydrogen ion concentration varied between 0.010 *M* and 1.00 *M* which is sufficient to suppress mononuclear protolysis of $Pt(H_2O)_4^{2+}$ [3].

Table II and Figure 2 summarize the experiments for reaction (1). The rate constants for X = Cl were independent of pH for 0 ≤ pH ≤ 2. The slow subsequent changes due to reaction (4) and – for iodide

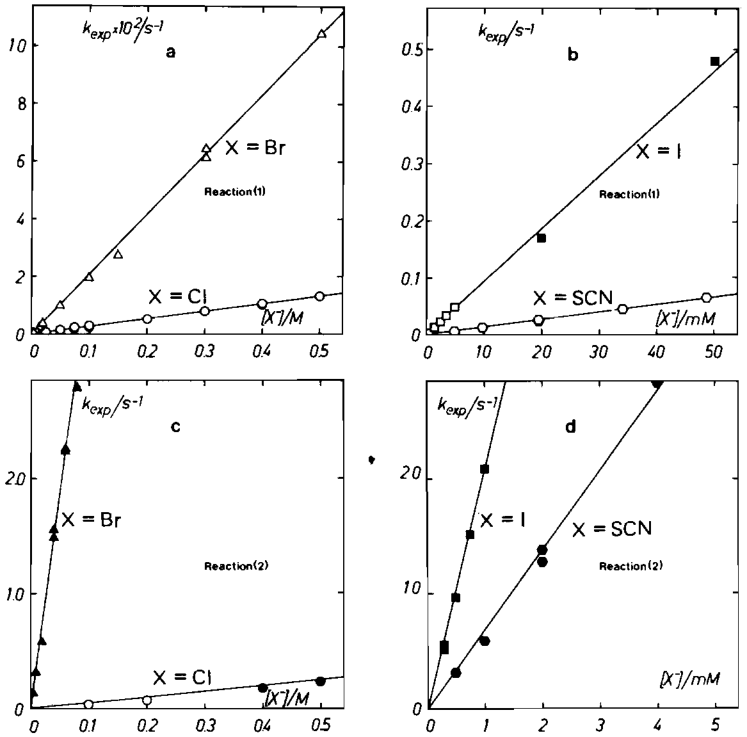

Figure 2. Observed rate constants for reactions (1) and (2) *vs.* concentration of entering ligand X = Cl^-, Br^-, I^-, and SCN^- at 25.0 °C and for a 1.00 *M* perchlorate medium. Filled symbols denote stopped-flow experiments.

TABLE II. Observed Rate Constants for Reaction (1) at 25 °C and 1.00 *M* Perchlorate Medium.

$[X^-]$/m*M*	C_{Pt}/m*M*	$10^3\ k_{exp}/s^{-1}$ [i]	$[X^-]$/m*M*	C_{Pt}/m*M*	$10^3\ k_{exp}/s^{-1}$ [i]
	X = Cl[a]			X = Br[f]	
25.00	0.82	0.76	5.00	0.41	1.04
50.0	0.82	1.51	10.00	0.41	1.64
75.0	4.5	1.97[b]	15.00	0.41	3.0
75.0	0.82	2.26	20.00	0.41	4.2
100.0	4.5	2.65[b]	50.0	0.41	10.5
100.0	0.82	2.97	100.0	0.41	20.2
100.0	0.41	2.86	150.0	0.41	28
200.0	0.82	5.4	302	0.46	62
300	0.82	8.1	302	0.23	65
400	0.82	10.6	501	0.46	105
400	0.83	10.5[c]			
400	0.83	10.7[d]			
500	0.82	13.3			
	X = SCN[e]			X = I[g]	
4.87	0.165	5.9	0.500	0.046	4.2
9.74	0.165	12.3	1.500	0.046	12.9
19.48	0.0823	26.8	2.50	0.046	23.6
19.48	0.165	23.7	2.50	0.103	24.2
34.1	0.165	45	3.50	0.046	34
48.7	0.165	65	5.00	0.050	49
			20.0	0.0057	171[h]
			50.0	0.0057	480[h]

[a] 291 nm, $[H^+]$ = 1.00 *M*, except when otherwise noted. [b] 355 nm. [c] $[H^+]$ = 0.100 *M*. [d] $[H^+]$ = 0.010 *M*. [e] 245 nm, $[H^+]$ = 1.0 *M*. [f] 250 nm, $[H^+]$ = 1.00 *M*. [g] 295 nm, $[H^+]$ = 0.50 *M*. [h] Stopped-flow experiment. [i] Standard deviation <5%.

TABLE III. Observed Rate Constants with Standard Deviations for Reaction (2) at 25 °C and for 1.00 *M* Perchlorate Medium. Stopped-flow experiments, except for 100 and 200 m*M* chloride.

$[X^-]/mM$	$10^5\ C_{Pt}/M$	$10^5\ [PtX(H_2O)_3^+]_0/M$	k_{exp}/s^{-1}
		$X = Cl^a$	
100	417	170	(4.26 ± 0.05) × 10^{-2}
200	417	170	(7.9 ± 0.1) × 10^{-2}
400	104	40	0.184 ± 0.003
500	104	40	0.236 ± 0.005
		$X = Br^b$	
5.00	5.0	2.0	0.155 ± 0.010
10.00	5.0	2.0	0.333 ± 0.015
20.0	5.0	2.0	0.60 ± 0.03
40.0	5.0	2.0	1.50 ± 0.10
40.0	2.5	1.0	1.57 ± 0.10
60.0	5.0	2.0	2.25 ± 0.15
60.0	2.5	1.0	2.27 ± 0.15
80.0	2.5	1.0	2.8 ± 0.2
		$X = I^c$	
0.25	2.0	0.5	5.6 ± 0.3
0.25	4.0	1.0	5.2 ± 0.1
0.50	4.0	1.0	9.7 ± 0.2
0.75	4.0	1.0	15.3 ± 0.3
1.00	4.0	1.0	20.9 ± 0.3
		$X = SCN^d$	
0.50	2.0	0.50	3.2 ± 0.1
1.00	2.0	0.50	5.9 ± 0.3
2.00	2.0	0.50	12.8 ± 0.6
2.00	4.0	1.0	13.8 ± 0.6
4.00	2.0	0.50	28.5 ± 1.0

[a] 291 nm, $[H^+] = 1.00\ M$. [b] 250 nm, $[H^+] = 1.00\ M$. [c] 300 nm, $[H^+] = 0.250\ M$. [d] 245 nm, $[H^+] = 0.250\ M$.

and thiocyanate – to side reactions, such as precipitation of $PtI_2(s)$, formation of I_3^-, and decomposition of thiocyanate in the acidic solutions, were easily eliminated by extrapolation.

Table III and Figure 2 summarize the experiments for reaction (2). The M-solutions were equilibrated $Pt(H_2O)_4^{2+}/PtX(H_2O)_3^+$ solutions with a mean ligand number $\bar{n}$ between 0.25 and 0.4 which were prepared

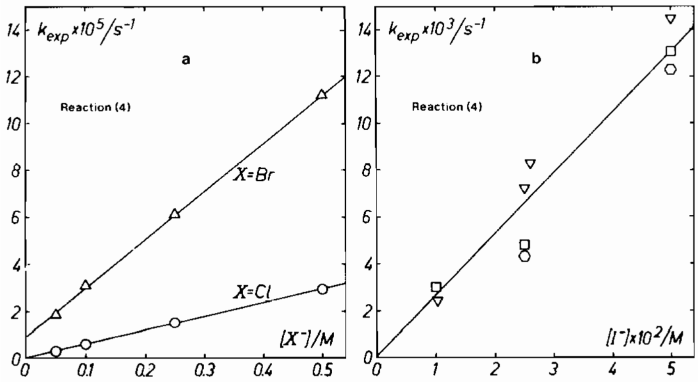

Figure 3. Observed rate constants for the over-all process (4) *vs.* concentration of entering ligand $X^- = Cl^-, Br^-$ and I^- at 25.0 °C and for a 1.00 *M* perchloric acid medium.

TABLE IV. Preparation of M-Solutions for Reaction (2).

X	C_{Pt}/m*M*	C_X/m*M*	$[H^+]$/*M*	$t_{1/2}$/min	Aging Time
Cl	4.17	1.67	1.00	144	24 h
Br	4.17	1.67	1.00	19	2 h
I	0.40	0.10	0.50	1.6	8 min
SCN	4.06	1.00	0.50	2.7	8 min

TABLE V. Observed Rate Constants for Reaction (4) at 25.0 °C and 1.00 *M* Perchlorate Medium.

X = Cl, Br[a]

$[X^-]$/m*M*	$10^5\ C_{Pt}/M$	$10^6\ k_{\mathrm{exp,\,Cl}}/s^{-1}$	$10^5\ k_{\mathrm{exp,\,Br}}/s^{-1}$
50.5	9.11	3.20	1.86
101	9.11	6.18	3.11
252	18.2	15.1	5.94
252	9.11	15.0	6.32
505	9.11	29.3	11.2

X = 1

$[I^-]$/m*M*	$10^4\ C_{Pt}/M$	$[H^+]$/*M*	$10^3\ k_{\mathrm{exp,\,I}}/s^{-1}$
10.0	1.75	0.50	3.0
10.3	4.12	1.00	2.4
25	1.78	0.050	4.3
25	1.75	0.50	4.8
25	4.12	1.00	7.2
26	1.65	1.00	8.3
50	1.78	0.050	12.3
50	1.75	0.50	13.1
50	4.12	1.00	14.5

[a] All experiments for X = Cl, Br had $[H^+]$ = 1.00 *M*.

according to Table IV. The two reactions (1) and (2) differ so much in rate (k_{2t}/k_1 is 17, 170, 1400 and 5000 for X = Cl, Br, I and SCN, respectively) that k_{2t} can be determined independently of the simultaneous, slow process (1). For X = Cl, the measurements were performed at the isosbestic point at 291 nm, where there is no change of absorbance for reaction (1). The subsequent reaction (4) is 10^4 to 10^7 times slower than (2) and the slow side reactions for X = I, SCN are also completely negligible in the time scale of reaction (2).

Table V and Figure 3 summarize the experiments on the slow process (4). The M-solutions were $Pt(H_2O)_4^{2+}$ solutions in 1.00 *M* perchloric acid – or in some cases for X = I freshly prepared $Pt(H_2O)_4^{2+}$ solutions in 0.100 *M* perchloric acid. The L-solutions had $[H^+]$ = 1.00 *M* for X = Cl, Br, whereas for X = I neutral sodium iodide or freshly prepared acidic sodium iodide solutions were used. The measurements were performed at the maxima for $PtCl_4^{2-}$ at 230 nm (7950 $cm^{-1}M^{-1}$), for $PtBr_4^{2-}$ at 268 nm (8500 cm^{-1} M^{-1}) and for PtI_4^{2-} at 390 nm (4100 cm^{-1} M^{-1}). At 390 nm, the molar absorptivity for I_3^- is comparatively small (5000 cm^{-1} M^{-1}, *cf.* Ref. 6, Fig. 1) which minimizes the absorbance change due to formation of I_3^- as much as possible. For X = Cl, Br there are no complications. The spectra of $PtCl_4^{2-}$ and $PtBr_4^{2-}$ appear quantitatively when a large excess of chloride or bromide is added to $Pt(H_2O)_4^{2+}$. For X = I the experimental accuracy is decreased by the slow precipitation of $PtI_2(s)$ and the formation of I_3^-. For X = SCN it is not possible to follow reaction (4) quantitatively using spectrophotometric detection, because of the simultaneous change of absorbance due to decomposition of thiocyanate in the acidic solutions which are necessary when $Pt(H_2O)_4^{2+}$ is the substrate complex.

Results and Discussion

Equilibrium Measurements

For the excess of palladium(II) perchlorate used in all experiments practically all halide reacts rapidly and quantatively to $PdX(H_2O)_3^+$ at the moment of mixing. The concentration of free halide in the solutions will be negligible and the subsequent slow equilibration can be described by the stoichiometric over-all process (10)

$$PdX(H_2O)_3^+ + Pt(H_2O)_4^{2+} \rightleftarrows PtX(H_2O)_3^+ + Pd(H_2O)_4^{2+} \qquad (10)$$

We define the equilibrium concentrations and molar absorptivities of the complexes as (11):

Complex	Equil. concn.	ϵ
$Pd(H_2O)_4^{2+}$	$C_{Pd} - C_X + x$	ϵ_{0Pd}
$Pt(H_2O)_4^{2+}$	$C_{Pt} - x$	ϵ_{0Pt}
$PdX(H_2O)_3^+$	$C_X - x$	ϵ_{1Pd}
$PtX(H_2O)_3^+$	x	ϵ_{1Pt}

(11)

The equilibrium concentration x can be calculated from the total concentrations and the previously determined [2a, 6] molar absorptivities using eqn. (12):

$$x = \frac{e_{eq} - (\epsilon_{0Pd}C_{Pd} + \epsilon_{0Pt}C_{Pt} + (\epsilon_{1Pd} - \epsilon_{0Pd})C_X)}{(\epsilon_{0Pd} + \epsilon_{1Pt}) - (\epsilon_{0Pt} + \epsilon_{1Pd})} \qquad (12)$$

The absorptivity e_{eq} for each solution was determined at seven different wavelengths (390, 400, ... 450 nm for X = Cl; 280, 290, 300, 310, 400, 420, 440 nm for X = Br). The mean values for x calculated from these determinations are given in Table I together with the equilibrium constant K for reaction (10) calculated from (13)

$$K = x(C_{Pd} - C_{Cl} + x)/(C_{Cl} - x)(C_{Pt} - x) \qquad (13)$$

Table VI summarizes all equilibrium constants. The stability constants K_1 for $PtCl^+$ and $PtBr^+$ were calculated from the relation (14)

$$K_{1Pt} = KK_{1Pd} \qquad (14)$$

using the K-values of Table I and the previously determined K_{1Pd}-values for $PdCl^+$ (2.98 ± 0.06) × 10^4 M^{-1} and $PdBr^+$ (1.47 ± 0.06) × 10^5 M^{-1} [2a]. The over-all stability constants β_n for the chloro complexes calculated from this K_1-value and the previously determined K_2, K_3 and K_4 agree satisfactorily with a previous estimation [1a].

The stepwise stability constant K_2 for the bromide system can be obtained as $\beta_4/(K_1K_3K_4)$ using the values in Table VI, where β_4 for the bromide system has been calculated from β_{4Cl} and the separately determined ratio β_{4Br}/β_{4Cl} = 133 ± 15 [5]. A refinement of the previous calculation of the *cis–trans* equilibrium constant for $PtBr_2(H_2O)_2$ using this value of K_2 gives 1.5 ± 0.3 instead of the previously reported 2.2 ± 0.2 [1e]. Figure 4 shows a graphical representation of the equilibrium distribution of platinum on the different chloro and bromo complexes, which summarizes these results.

Kinetics

The rate constants are contained in Table VII. The halide anation rate constants k_n have been

TABLE VI. Stepwise Stability Constants K_n Defined by Eqn. (7) and Overall Stability Constants β_n Defined by Eqn. (8) for Platinum(II) Chloro and Bromo Complexes at 25 °C. Estimated errors. Medium 0.50 or 1.00 *M* perchloric acid.

	X = Cl			X = Br		
	Constant	I/M	Ref.	Constant	I/M	Ref.
K_1/M^{-1}	(9.4 ± 2.3) × 10^4	1.0	This p.	(1.9 ± 0.4) × 10^5	1.0	This p.
K_2/M^{-1}	(1.0 ± 0.2) × 10^4	0.5	1a	(2.8 ± 1.4) × 10^4	0.5–1.0	This p.
K_3/M^{-1}	(8.3 ± 1.6) × 10^2	0.5	7	(4.0 ± 0.5) × 10^3	0.5	1d
K_4/M^{-1}	(1.25 ± 0.15) × 10^2	1.0	5	(6.2 ± 0.8) × 10^2	1.0	5
[*cis*-PtX_2]/[*trans*-PtX_2]	1.2 ± 0.1	0.5	1c	1.5 ± 0.3	0.5	This p.
K_{2c}/M^{-1}	(5.5 ± 1.5) × 10^3	0.5	1c	(1.7 ± 0.8) × 10^4	0.5–1.0	This p.
K_{2t}/M^{-1}	(4.5 ± 1.0) × 10^3	0.5	1c	(1.1 ± 0.5) × 10^4	0.5–1.0	This p.
K_{3c}/M^{-1}	(1.5 ± 0.3) × 10^3	0.5	1c	(6.7 ± 1.5) × 10^3	0.5–1.0	This p.
K_{3t}/M^{-1}	(1.8 ± 0.5) × 10^3	0.5	1c	(1.0 ± 0.2) × 10^4	0.5–1.0	This p.
$\lg(\beta_1/M^{-1})$	4.97 ± 0.11	1.0	This p.	5.28 ± 0.09	1.0	This p.
$\lg(\beta_2/M^{-2})$	8.97 ± 0.20	0.5–1.0	This p.	9.72 ± 0.18	0.5–1.0	This p.
$\lg(\beta_3/M^{-3})$	11.89 ± 0.35	0.5–1.0	This p.	13.32 ± 0.35	0.5–1.0	This p.
$\lg(\beta_4/M^{-4})$	13.99 ± 0.45	0.5–1.0	This p.	16.11 ± 0.45	0.5–1.0	This p.

TABLE VII. Rate Constants at 25.0 °C and 1.00 *M* Perchlorate Medium. Notation for rate constants in Figure 1. *n* is a statistical factor, equal to the number of equivalent leaving ligands, $Q = 5$ is a charge factor [2c, 8] and *q* is the ionic charge of the substrate complex. Values for palladium complexes from Ref. 2.

Reaction	X		k_{Pt}	k_{Pt}/n	$k_{Pt}/(nQ^q)$	k_{Pd}	k_{Pd}/k_{Pt}
A (1)	Cl	$k_1/s^{-1}\ M^{-1}$	$(2.66 \pm 0.04) \times 10^{-2}$	6.7×10^{-3}	2.7×10^{-4}	1.83×10^4	7×10^5
B (1)	Br		$(2.11 \pm 0.03) \times 10^{-1}$	5.3×10^{-2}	2.1×10^{-3}	9.2×10^4	4×10^5
C (1)	I		9.4 ± 0.2	2.4	$\sim 9.6 \times 10^{-2}$	–	–
D (1)	SCN		1.33 ± 0.02	0.32	$\sim 1.3 \times 10^{-2}$	–	–
E (2)	Cl	$k_{2t}/s^{-1}\ M^{-1}$	0.46 ± 0.03	0.46	9.2×10^{-2}	3.5×10^4	8×10^4
F (2)	Br		36.5 ± 0.8	37	7.4	6.9×10^5	2×10^4
G (2)	I		$(20.1 \pm 0.1) \times 10^3$	20×10^3	$\sim 4 \times 10^3$	–	–
H (2)	SCN		$(6.7 \pm 0.3) \times 10^3$	6.7×10^3	$\sim 1.3 \times 10^3$	–	–
I (4)	Cl	$k_{3t}/s^{-1}\ M^{-1}$	$(5.83 \pm 0.04) \times 10^{-5}$	2.9×10^{-5}	2.9×10^{-5}	21.7	4×10^5
J (4)	Br		$(2.09 \pm 0.07) \times 10^{-4}$	1.0×10^{-4}	1.0×10^{-4}	83	4×10^5
K (4)	I		0.26 ± 0.03	0.13	0.13	–	–
L - (1)	Cl	k_{-1}/s^{-1}	$(2.8 \pm 0.7) \times 10^{-7}$	2.8×10^{-7}	–	0.83	3×10^6
M -(1)	Br		$(1.1 \pm 0.3) \times 10^{-6}$	1.1×10^{-6}	–	0.83	8×10^5
N -(2)	Cl	k_{-2t}/s^{-1}	$(1.0 \pm 0.3) \times 10^{-4}$	5×10^{-5}	–	56	1×10^6
O -(2)	Br		$(3.3 \pm 1.5) \times 10^{-3}$	1.7×10^{-3}	–	260	2×10^5
P - (4)	Cl	k_{-3t}/s^{-1}	$(3.2 \pm 1.0) \times 10^{-8}$	3.2×10^{-8}	–	2.7×10^{-2}	8×10^5
R - (4)	Br		$(2.1 \pm 0.5) \times 10^{-8}$	2.1×10^{-8}	–	5.9×10^{-3}	3×10^5

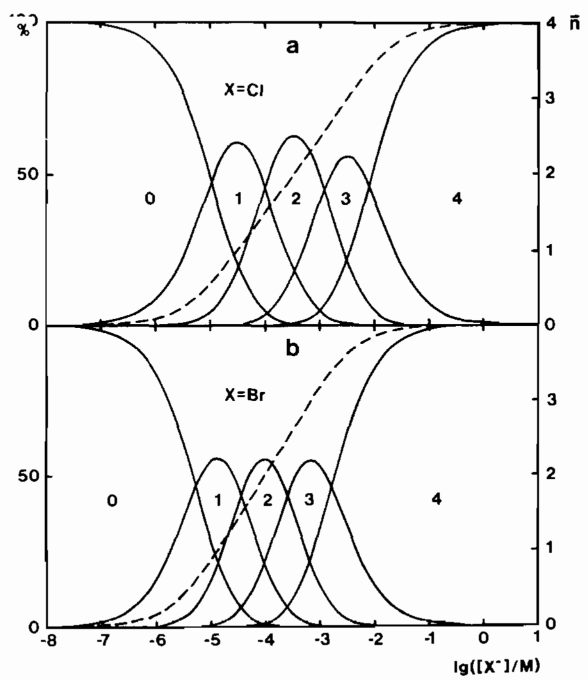

Figure 4. The mean ligand number $\bar{n}$ (dashed) and the distribution of platinum on the complexes $PtX_n(H_2O)_{4-n}^{2-n}$; $n = 0$, 1, 2, 3, 4 at 25 °C for a 0.5 to 1.0 *M* perchloric acid medium calculated from the stability constants β_n in Table VI.

obtained directly from the plots in Figures 2 and 3, and the acid hydrolysis rate constants k_{-n} have been calculated from eqn. (9) and the stability constants in Table VI. The values for k_{2t} (Cl), k_{3t} (Cl, Br), k_{-2t} (Cl) and k_{-3t} (Cl, Br) agree satisfactorily with previously reported values [1]. Approximate values of k_{2c} $\sim 1 \times 10^{-3}$ s^{-1} M^{-1} (Cl) and $\sim 9 \times 10^{-2}$ s^{-1} M^{-1} (Br) and of k_{-2c} $\sim 2 \times 10^{-7}$ s^{-1} (Cl) and $\sim 5 \times 10^{-6}$ s^{-1} (Br) can be obtained from the intercepts k_{2c}/K_{2t} of the lines in Figure 3 and the stability constants K_{2t} from Table VI.

Comparison of k_1 for reactions A, B, C and D shows that the entering ligand order for the substrate $Pt(H_2O)_4^{2+}$ is

$$Cl^- < Br^- < SCN^- < I^- \qquad (15)$$

$$1 \ : \ 8 \ : \ 50 \ : \ 350$$

The rate constants for the chloro and bromo complexes can be described in terms of the *cis*-effects (*C*), *trans*-effects (*T*) and ionic charge effects (*Q*) used previously for reactions of other platinum(II) chloro and bromo complexes [1c, e, 2c, 8]. For instance, the experimental value of k_1 for X = Cl in Table VII agrees with the previously calculated value of 3×10^{-2} s^{-1} M^{-1}. Table VII also contains values of k/n and $k/(nQ^q)$, where *n* is equal to the number of equivalent leaving ligands in the complex, Q is an ionic charge factor (approximately $Q = 5$, *cf.* Ref. 2c, 8) and q is the ionic charge of the complex. The relative *trans*-effect Cl^-/H_2O is obtained by comparison of $k/(nQ^q)$ for reactions E and A as $9.2 \times 10^{-2}/2.7 \times 10^{-4} = 340$ and the *trans*-effect Br^-/H_2O from reactions F and B as $7.4/2.1 \times 10^{-3} = 3500$. The *cis*-effect Cl^-/H_2O is obtained from I and A as $(2.9 \times 10^{-5}/2.7 \times 10^{-4})^{1/2} = 0.33$ and the *cis*-effect Br^-/H_2O from J and B as $(1.0 \times 10^{-4}/2.1 \times 10^{-3})^{1/2} = 0.22$, which all agree with previously reported values [1c, 1e, 2c, 8].

For the reactions of the iodo and thiocyanato complexes, comparisons between $k/(nQ^q)$ for reactions G, C and H, D indicate relative *trans*-effects $I^-/H_2O = 4 \times 10^3/9.6 \times 10^{-2} = 4 \times 10^4$ and $SCN^-/H_2O = 1.3 \times 10^{-3}/1.3 \times 10^{-2} = 1 \times 10$ [5]. Similarly, the *cis*-effect I^-/H_2O is obtained from K and C as $(0.13/9.6 \times 10^{-2})^{1/2} = 1.2$. These values must be regarded as tentative only, since the thermodynamic *trans*- and *cis*-influence of iodide and thiocyanate are not known (*cf.* Ref. 8). However, the thermodynamic influence is probably small compared to the kinetic *trans*-effect [8].

Alternatively, the relative *trans*-effects can be calculated by comparison of the quantities (k_{2t}/entering ligand effect from eqn. 15) as $Cl^-:Br^-:I^-:SCN^- = (0.46/1) : (37/8) : (20 \times 10^3/350) : (6.7 \times 10^3/50) = 1 : 10 : 130 : 300$, which gives the kinetic *trans*-effect order (16) relative to water:

$$T\begin{cases} H_2O < Cl^- < Br^- < I^- < SCN^- \\ 1 : 330 : 3300 : \sim 4 \times 10^4 : \sim 1 \times 10^5 \end{cases} \tag{16}$$

The relative *cis*-effects can be obtained similarly by comparison of the quantities (k_{3t}/entering ligand effect from eqn. 15)$^{1/2}$ as $Cl^-:Br^-:I^- = (5.7 \times 10^{-5}/1)^{1/2}:(2 \times 10^{-4}/8)^{1/2}:(0.26/350)^{1/2} = 1:0.7:4$, which gives the kinetic *cis*-effect order (17) relative to water:

$$C\begin{cases} Br^- < Cl^- < H_2O < I^- \\ 0.3 : 0.4 : 1 : \sim 2 \end{cases} \tag{17}$$

The constancy of C and T calculated by the two independent comparisons indicates that the entering ligand order (15) is approximately valid not only for $Pt(H_2O)_4^{2+}$ but also for $PtX(H_2O)_3^+$ and *trans*-$PtX_2(H_2O)_2$. Comparison of the rate constants k_{-1} for reactions L, M and k_{-2t} for reactions N, O shows that bromide is three to four times better as leaving ligand than chloride in the complexes *trans*-$PtX_2(H_2O)_2$ and $PtX(H_2O)_3^+$. There is no such difference for the corresponding palladium complexes (*cf.* Table VII). Nor is there any difference between chloride and bromide as leaving ligands for acid hydrolysis of the anionic platinum(II) complexes Pt_4^{2-} and $PtX_3H_2O^-$ (*cf.* Ref. 1c and e) or for acid hydrolysis and halide exchanges in the chloro–bromo complexes $PtCl_nBr_{4-n}^{2-}$; $n = 0, 1, 2, 3, 4$ (*cf.* Ref. 5).

It appears from Table VII that the palladium complexes react 2×10^4 to 3×10^6 times faster than the corresponding platinum complexes. If the differences in *trans*-effect between palladium and platinum are taken into account (*cf.* Ref. 2c) the difference is about 5×10^5 for all anation reactions and about 2×10^6 for all acid hydrolyses. This is also in accordance with previous findings [2c].

Acknowledgements

My thanks are due to Fil. mag. Ingegerd Lind for excellent experimental assistance and to the *Swedish Natural Science Research Council* for financial support.

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