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Palladium(II) Halide Complexes. III. Acid Hydrolyses and Halide Anations of *cis*- and *trans*-Dichlorodiaquapalladium(II) and -Dibromodiaquapalladium(II)

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Chloride and bromide anations of $PdX(H_2O)_3^+$, cis-*$PdX_2(H_2O)_2$ and* trans-*$PdX_2(H_2O)_2$, acid hydrolyses of $PdX_3H_2O^-$,* cis-*$PdX_2(H_2O)_2$ and* trans-*$PdX_2(H_2O)_2$, X = Cl, Br, have been studied at different temperatures by means of a stopped-flow technique. Rate constants are given in Tables V and VII, activation parameters in Table VII. The palladium complexes react about 5×10^4 to 5×10^5 times faster than the analogous platinum(II) complexes. The activation enthalpies are 8 to 10 kcal mol^{-1} smaller for palladium. A simple model for description of the rates of acid hydrolyses and halide anations of palladium(II) and platinum(II) halide complexes by* cis-, trans-, *and ionic charge effects is introduced. For palladium, the relative* trans-*effect Cl/H_2O is about 50 and Br/H_2O about 500. The relative* cis-*effect H_2O/Cl is about 4 and H_2O/Br about 8. The* trans-*effects are 6 times smaller than for corresponding platinum complexes, the* cis-*effects somewhat greater.*

The equilibrium between cis-*$PdX_2(H_2O)_2$ and* trans-*$PdX_2(H_2O)_2$ has been studied. The* cis-*isomer is the dominant species at equilibrium, the equilibrium constant* cis/trans *being 2.1 ± 0.3 for X = Cl and 6.0 ± 0.8 for X = Br at 25°C. The ionic strength was 1.00* M *and the supporting electrolyte perchloric acid.*

Introduction

We have reported stability constants and spectra[1] for the chloro and bromo complexes of palladium(II) and kinetic results[2] for the first (n = 1) and fourth (n = 4) reactions in the sequence:

$$PdX_{n-1}(H_2O)_{5-n}^{3-n}+X^- \rightleftarrows PdX_n(H_2O)_{4-n}^{2-n}+H_2O$$

$$X = \text{Cl, Br}; \quad n = 1,2,3,4 \qquad (1)$$

A scheme for the stepwise reactions (1) and notation for rate constants was given in Ref. 2.

The present paper deals with kinetics and equilibria for the intermediate reactions (n = 2,3) of (1). The aim of these studies was to elucidate the *cis*- and *trans*-influence of the ligands H_2O, Cl, and Br in substitution reactions of palladium(II) complexes, and to compare these reactions with the previously studied reactions for platinum(II) chloro and bromo aqua complexes.[3]

For the palladium(II) complexes, as for the platinum(II) complexes, the experiments indicate a low *trans*-influence of water, compared to halide. Accordingly, the rate determining step for the conversion of $Pd(H_2O)_4^{2+}$ to PdX_4^{2-} by eq. (1) will be the two parallel processes (*cf*. ref. 2, Figure 1):

$$PdX(H_2O)_3^+ + X^- \xrightarrow{k_{2c}} cis\text{-}PdX_2(H_2O)_2 + H_2O \qquad (2)$$

$$trans\text{-}PdX_2(H_2O)_2 + X^- \xrightarrow{k_{3t}} PdX_3H_2O^- + H_2O \qquad (3)$$

In these reactions, aqua ligands in *trans*-position to other aqua ligands are displaced slowly by halide.

In comparison with (2) and (3), the halide anation

$$cis\text{-}PdX_2(H_2O)_2 + X^- \xrightarrow{k_{3c}} PdX_3H_2O^- + H_2O \qquad (4)$$

is fast. It can be followed by the stopped-flow method only for X = Cl at temperatures below 25°C. The halide anation of $PdX(H_2O)_3^+$ to *trans*-$PdX_2(H_2O)_2$ is too fast for this method to be used both for X = Cl and X = Br. It is feasible, however, to study its reverse, the acid hydrolysis of *trans*-$PdX_2(H_2O)_2$:

$$trans\text{-}PdX_2(H_2O)_2 + H_2O \xrightarrow{k_{-2t}} PdX(H_2O)_3^+ + X^- \qquad (5)$$

By adding excess halide ($[X^-]>50$ m*M*) to solutions containing mixtures of different complexes $PdX_n(H_2O)_{4-n}^{2-n}$, and recording the kinetic plots of the rate determining reaction, eqs. (2) and (3), the *fraction* of palladium, present at the start of the kinetic run as $Pd(H_2O)_4^{2+} + PdX(H_2O)_3^+ + trans\text{-}PdX_2(H_2O)_2$ can be calculated. From such experiments, and the stability constants of Ref. 1, the *cis*/*trans*-equilibrium constant defined by eq. (13) has been calculated.

Experimental Section

Chemicals. Stock solutions of palladium(II) per-

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[1] L.I. Elding, *Inorg. Chim. Acta*, *6*, 647 (1972).
[2] L.I. Elding, *Inorg. Chim. Acta*, *6*, 683 (1972).
[3] L.I. Elding *et al.* References cited in Ref. 2.

Table I. Halide anation of *trans*-$PdX_2(H_2O)_2$ and $PdX(H_2O)_3)^+$. The rate constant k_{exp} defined by eqn. (7) is given with its standard deviations. Measurements at 280 nm (chloride) and 330 or 275 nm (bromide).

Temperature		X=Cl			X=Br	
°C	C_{Cl}/M	$C_{Pd}\times10^6/M$	k_{exp}/s^{-1}	C_{Br}/M	$C_{Pd}\times10^6/M$	k_{exp}/s^{-1}
15	0.050	4.70	0.83±0.01	0.050	4.70	2.24±0.02
15	0.100	4.70	1.30±0.03	0.100	4.70	4.28±0.07
15	0.200	4.70	2.15±0.04	0.200	4.70	9.3 ±0.2
15	0.300	4.70	3.02±0.05	0.300	4.70	13.9 ±0.2
15	0.400	4.70	4.05±0.05	0.400	4.70	19.0 ±0.3
15	0.500	4.70	5.07±0.06	0.500	4.70	22.7 ±0.5
25	0.100	4.76	2.95±0.02	0.050	4.76	5.05±0.06
25	0.200	4.76	5.23±0.05	0.100	4.76	9.57±0.07
25	0.300	4.76	7.20±0.05	0.200	4.76	17.9 ±0.2
25	0.300	2.38	7.32±0.23	0.200	2.38	18.5 ±0.2
25	0.300	1.19	7.37±0.06	0.200	1.19	18.8 ±0.2
25	0.400	4.76	9.42±0.05	0.300	4.76	26.7 ±0.2
25	0.500	4.76	11.7±0.1	0.400	4.76	34.6 ±0.8
25				0.500	4.76	41.7 ±0.8
35	0.050	4.70	4.27±0.05	0.050	4.70	9.9 ±0.1
35	0.100	4.70	6.37±0.06	0.100	4.70	17.0 ±0.3
35	0.200	4.70	10.4±0.1	0.200	4.70	34.5 ±0.8
35	0.300	4.70	14.9±0.2	0.300	4.70	48.1 ±0.8
35	0.400	4.70	19.3±0.3	0.400	4.70	69 ±2
35	0.500	4.70	23.5±0.5	0.500	4.70	83 ±2

Table II. Chloride anation of *cis*-$PdCl_2(H_2O)_2$. The rate constant k_{exp} defined by eqn. (9) is given with its standard deviations. Measurements at 261 nm.

		k_{exp}/s^{-1}				
$C_{Cl}\times10^2/M$	$C_{Pd}\times10^5/M$	3.0 °C	8.0 °C	12.0°C	15.0°C	25.0°C
2.70	4.7, 9.4	39±2	55±4	63±1	86±5	162±10
3.95	4.7, 9.4	56±2	69±4	81±3	117±10	200±10
5.20	4.7, 9.4	71±6	91±11	115±4	153±10	—
7.70	4.7, 9.4	97±10	134±14	182±10	—	—
10.20	4.7, 9.4	138±10	170±20	—	—	—

chlorate in 1.00 *M* perchloric acid (Johnson and Matthey's *Specpure* palladium sponge), of hydrochloric acid (Merck's *p.a.*), of hydrobromic acid (Merck's *p. a.*) and of perchloric acid (Baker's *p.a.*) were prepared as described in Ref. 1.

Measurements. The Durrum-Gibson stopped-flow spectrophotometer and the kinetic procedure were the same as described in Ref. 2. The ionic strength was 1.00 *M* and the ionic medium perchloric acid in all experiments.[1,2]

Halide anation of $PdX(H_2O)_3^+$ *and trans*-$PdX(H_2O)_2$. Reactions (2) and (3) were started by mixing solutions of palladium(II) perchlorate with ligand solutions ($0.100\,M \leqslant [X^-] \leqslant 1.000\,M$). First order kinetics were attained and the reverse reactions suppressed for these large concentrations of halide (*cf.* Ref. 1, Figure 6). Table I gives concentrations, wave lengths, and rate constants for the experiments. For the choice of wave lengths, *vide* Ref. 1, Figures 7 and 8.

Chloride anation of cis-$PdCl_2(H_2O)_2$. Palladium(II) solutions with a mean ligand number of about 2.5 ($C_{Pd} = 18.8\times10^{-5}\,M$ or $9.4\times10^{-5}\,M$ and $C_{Cl} = 4.0\times10^{-3}\,M$; *cf.* Ref. 1, Figure 6) were mixed with ligand solutions ($0.050\,M \leqslant [Cl^-] \leqslant 0.200\,M$). For these concentrations of chloride, the reverse reaction was suppressed and first order kinetics obtained. The product of reaction was a mixture of $PdCl_3H_2O^-$ and $PdCl_4^{2-}$. All measurements were performed at 261 nm, where the molar absorptivities of $PdCl_3H_2O^-$ and $PdCl_4^{2-}$ are equal (ε = 4000 cm^{-1} M^{-1}; *cf.* Ref. 1, Figures 2, 7). At this wave length, the subsequent and slower chloride anation of $PdCl_3H_2O^-$ did not cause any change of absorbance.

The parallel chloride anation of *trans*-$PdCl_2(H_2O)_2$ is a slow reaction for these concentrations of chloride ($0.7\ s < t_{1/2} < 1.3\ s$ at 15°C; *cf.* Figure 2) and was therefore easily distinguished from the much faster chloride anation of *cis*-$PdCl_2(H_2O)_2$, having half-lives between 3.5 and 12 ms at 15°C. The reaction was too fast to be studied with precision at 25°C. Table II reviews the experiments.

Acid hydrolysis of trans-$PdX_2(H_2O)_2$. The rate of formation of $PdX(H_2O)_3^+$ from $Pd(H_2O)_4^{2+}$ was studied in Ref. 2 (Table I) using solutions with large concentrations of palladium and small concentrations of ligand. For these experimental conditions, the first complex exclusively is formed as the product of reaction. Larger concentrations of ligand ($1\times10^{-4}\,M < [Cl^-] < 5\times10^{-4}\,M$; $2\times10^{-5}\,M < [Br^-] < 1\times10^{-4}\,M$) correspond to equilibrium solutions containing 5 to 15 or 5 to 10% of the metal as *trans*-$PdX_2(H_2O)_2$ (*cf.* Ref. 1, Figure 6). Since the anation of $PdX(H_2O)_3^+$

Table III. Acid hydrolysis of *trans*-$PdX_2(H_2O)_2$. Each value of k_{-2t} represents the mean of several experiments. Measurements at 250 nm (chloride) and 260 nm (bromide).

X	$C_{Pd} \times 10^3/M$	$C_X \times 10^5/M$	k_{-2t}/s^{-1} 3.0 °C	9.0 °C	15.0 °C	25.0 °C	35.0 °C
Cl	10.0	10,20,50	—	—	—	53±5	—
	12.5	50	—	—	—	60±4	—
	15.0	10,20,50	—	—	27±1	57±7	115±5
	20.0	100	—	—	—	58±1	—
	25.0	20,50	—	—	28±3	58±3	122±9
		MEAN:	—	—	28±2	56±5	119±8
Br	15.0	2,5,10	69±5	113±7	145±7	—	—
	20.0	5,10	73±5	116±15	154±4	—	—
	25.0	5,10	78±6	108±4	154±8	—	—
		MEAN:	73±6	112±10	151±8	260±20*	—

* Extrapolated value.

to *trans*-$PdX_2(H_2O)_2$ is faster than the anation of $Pd(H_2O)_4{}^{2+}$ to $PdX(H_2O)_3{}^+$, small concentrations of *trans*-$PdX_2(H_2O)_2$ may be formed in the solution during the first period of the kinetic run, when the concentration of free ligand is still high. Local excess of ligand during the short period of mixing might also cause formation of *trans*-$PdX_2(H_2O)_2$. When the reaction proceeds, the concentration of free ligand will decrease and the formation of *trans*-$PdX_2(H_2O)_2$ will stop. Acid hydrolysis of *trans*-$PdX_2(H_2O)_2$ to $PdX(H_2O)_3{}^+$ will take place. For large concentrations of palladium (10 to 25 *mM*) the anations will be very fast compared to the acid hydrolysis. Figure 1 shows a representative record of a kinetic run. The first, rapid reaction corresponds to the anations, the subsequent, slow one corresponds to reaction (5). The latter reaction was studied by delaying the sweep of the oscilloscope for a suitable interval of time. Table III reviews these experiments.

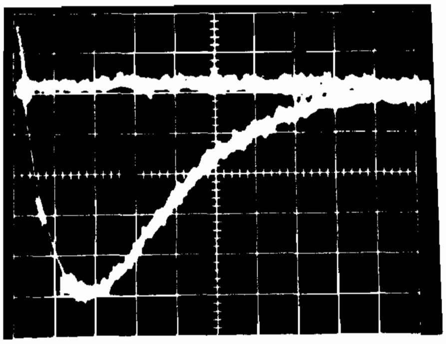

Figure 1. Stopped-flow record obtained by mixing 10 m*M* $Pd(ClO_4)_2$ with 4×10^{-4} *M* chloride. The first, rapid reaction is the formation of $PdCl(H_2O)_3{}^+$ and *trans*-$PdCl_2(H_2O)_2$, the subsequent, slow reaction is the acid hydrolysis of *trans* $PdCl_2(H_2O)_2$. Time scale: 10 ms/div., ordinate-axis scale: 10 mV/div. Wave length 250 nm, temperature 25°C, slit width 3 mm.

Experiments for calculation of equilibrium constants. Solutions with mean ligand numbers, $\bar{n}$, between 1 and 3 were thermostated at 25.0°C. Their concentrations are given in Table IV. They were mixed with equal volumes of 1.000 *M* hydrochloric or hydrobromic acid in the stopped-flow instrument. The kinetic plots for the rate determining process—reactions (2) and (3)—for the conversion of $Pd(H_2O)_4{}^{2+}$, $PdX(H_2O)_3{}^+$, and *trans*-$PdX_2(H_2O)_2$ to $PdX_3H_2O^-$ and $PdX_4{}^{2-}$ were recorded at 280 nm (chloride) or 335 nm (bromide). The display of the oscilloscope at zero time for these series gave $\Delta e_{\bar{n}>1}$, defined by eq. (10). The display for kinetic runs of solutions of palladium(II) perchlorate with $\bar{n} = 0$ and the same total concentration of palladium, C_{Pd}, which were mixed with 1.000 *M* acid also, gave $\Delta e_{\bar{n}=0}$, defined by eq. (11).

Calculations and Results

Halide anation of $PdX(H_2O)_3{}^+$ and trans-$PdX_2(H_2O)_2$. For excess halide, the rate of conversion of $Pd(H_2O)_4{}^{2+}$ to an equilibrium mixture of $PdX_3H_2O^-$ and $PdX_4{}^{2-}$ (*i.e.* $3.5 < \bar{n} < 4$ in the final solution) may be written (*cf.* Ref. 2, Figure 1):

$$\text{Rate} = k_{3t} \times [X^-] \times [\textit{trans}\text{-}PdX_2(H_2O)_2] + k_{2c} \times \times [X^-] \times [PdX(H_2O)_3{}^+] = (k_{3t} \times [X^-] + k_{2c}/K_{2t}) \times \times [\textit{trans}\text{-}PdX_2(H_2O)_2] \quad (6)$$

The stepwise stability constant K_{2t} is defined by eqn. (15).

Figure 2 shows the pseudo first order rate constant

$$k_{exp} = k_{3t} \times [X^-] + k_{2c}/K_{2t} \quad (7)$$

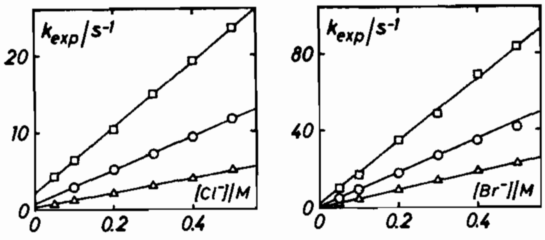

Figure 2. Halide anation of $PdX(H_2O)_3{}^+$ and *trans*-$PdX_2(H_2O)_2$. The observed rate constant k_{exp} of eqn. (7) *vs.* the concentration of halide at 35.0 (□), 25.0 (○) and 15.0°C (△).

Table IV. Equilibrium solutions used for determination of $K_{c/t}$. α_{exp} was obtained from kinetic plots according to eqn. (12). The mean of several experiments are given. The standard deviation of α_{exp} was 3 to 5%. $K_{c/t}$ was calculated from eqn. (14).*

$C_{Pd}\times10^4/M$	$C_X\times10^3/M$	α_{exp}	$K_{c/t}$
	X = Cl		
4.76	0.100	0.900	—*
4.76	0.200	0.825	2.1
4.76	0.400	0.705	1.8
4.76	0.600	0.622	1.7
9.45	0.100	0.932	—*
9.45	0.200	0.828	2.1
9.45	0.300	0.725	(3.4)*
9.45	0.400	0.687	2.3
9.45	0.600	0.622	1.7
9.45	1.000	0.492	1.9
9.45	2.000	0.365	1.5
9.45	4.00	0.219	1.7
9.45	6.00	0.138	2.2
9.45	10.00	0.089	2.0
9.45	20.00	0.040	2.0
18.80	0.600	0.591	2.5
18.80	0.800	0.538	2.1
18.80	1.000	0.466	2.4
18.80	2.000	0.308	2.5
18.80	3.00	0.222	2.7
18.80	4.00	0.190	2.3
94.0	6.00	0.146	2.1
94.0	8.00	0.108	2.2
94.0	10.00	0.090	2.1
94.0	20.00	0.041	2.0
94.0	30.00	0.024	2.0
		MEAN:	2.1±0.3
	X = Br		
0.952	0.0400	0.665	5.5
0.952	0.0600	0.569	4.5
0.952	0.1000	0.392	(9.0)
9.45	0.0200	0.881	—*
9.45	0.0400	0.715	—*
9.45	0.0600	0.610	6.3
9.45	0.1000	0.450	6.2
9.45	0.2000	0.277	5.6
9.45	0.400	0.156	5.4
9.45	0.600	0.103	5.9
9.45	1.000	0.061	5.9
9.45	2.000	0.030	5.5
94.0	0.600	0.137	7.4
94.0	1.000	0.070	7.4
94.0	2.000	0.030	6.5
94.0	4.00	0.0129	5.6
		MEAN:	6.0±0.8

* Calculation of $K_{c/t}$ involves the difference $\alpha_{exp}-(\alpha_0+\alpha_1)$. For high values of α_{exp}, this difference might be of the same magnitude as the experimental errors in α_{exp} and $(\alpha_0+\alpha_1)$, especially for X=Br.

as a function of [X$^-$]. The rate constant k_{3t} was obtained from the slope. Approximate values of the rate constant k_{2c} were calculated from the intercept and the stability constant K_{2t} determined separately. The rate constants are given in Table V.

Chloride anation of cis -PdCl₂(H₂O)₂. For excess chloride, the rate of disappearance of *cis*-$PdCl_2(H_2O)_2$ is simply

$$\mathrm{Rate}=k_{exp}\times[cis\text{-}PdCl_2(H_2O)_2] \tag{8}$$

Figure 3 shows the pseudo first order rate constant

$$k_{exp}=k_{3c}\times[Cl^-] \tag{9}$$

as a function of [Cl$^-$]. The values of k_{3c} are given in Table V.

Bromide anation of cis-*PdBr₂(H₂O)₂.* Experiments corresponding to those described for the chloride anation of *cis*-$PdCl_2(H_2O)_2$ were performed. The isosbestic wave length for the bromide complexes is 312 nm (*cf.* Ref. 1, Figures 3, 8). No reaction could be observed even at 3 °C for a bromide concentration [Br$^-$] $\geqslant 5\times10^{-3}$ *M*. This implies a rate constant $k_{exp} > 220$ s^{-1} at 3°C and an estimated $k_{exp} > 10^3$ s^{-1} at 25°C. Thus, $k_{3c} = k_{exp}/[Br^-]$ should be greater than about 2×10^5 s^{-1} M^{-1} for the bromide anation of *cis*-$PdBr_2(H_2O)_2$ (Table V).

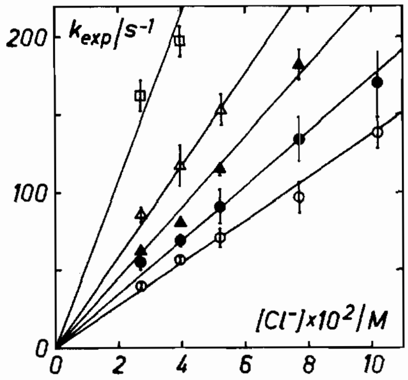

Figure 3. Chloride anation of *cis*-$PdCl_2(H_2O)_2$. The observed rate constant k_{exp} of eqn. (9) *vs.* the concentration of chloride at 25.0 (□), 15.0 (△), 12.0 (▲), 8.0 (●) and 3.0 °C (○).

Acid hydrolysis of trans-*PdX₂(H₂O)₂.* The first order rate constant k_{-2t} of reaction (5) was obtained directly from the final parts of the kinetic runs (Figure 1). It appears from Table III that the rate of reaction is independent of the concentration of halide, as expected for an acid hydrolysis. The obtained rate constants are given in Table V.

Equilibrium constants. For the solutions with $\bar{n} > 1$ the display of the kinetic curves at zero time may be expressed as

$$\Delta e_{\bar n>1}=\varepsilon''C_{Pd}-\varepsilon'C'-\varepsilon''(C_{Pd}-C')=C'(\varepsilon''-\varepsilon'), \tag{10}$$

where *e* denotes absorptivity, and *C'* is the concentration [$Pd(H_2O)_4^{2+}$] + [$PdX(H_2O)_3^+$] + [*trans*-$PdX_2(H_2O)_2$] at zero time. ε' and ε'' are the molar absorptivities for the equilibrium mixture of $Pd(H_2O)_4^{2+}$, $PdX(H_2O)_3^+$ and *trans*-$PdX_2(H_2O)_2$, and of *cis*-$PdX_2(H_2O)_2$, $PdX_3H_2O^-$ and PdX_4^{2-}, respectively.

For solutions with $\bar n = 0$ and the same total concentration of palladium, we have $C_{Pd} = C'$ and

$$\Delta e_{\bar n=0}=C_{Pd}(\varepsilon''-\varepsilon') \tag{11}$$

We define

$$\alpha_{exp}=\frac{\Delta e_{\bar n>1}}{\Delta e_{\bar n=0}}=\frac{C'}{C_{Pd}}=\alpha_0+\alpha_1+\alpha_{2t} \tag{12}$$

Table V. Rate constants with standard deviations. Review of experiments. Aqua ligands not shown. The temperature (t/°C) is given within parenthesis.

Process		Rate constant
$PdCl^+ + Cl^- \rightarrow$ *cis*-$PdCl_2$	$k_{2c}/K_{2t}/s^{-1}$ $k_{2c} \times 10^{-2}/s^{-1}M^{-1}$	0.32±0.04(15), 0.82±0.07(25), 2.04±0.16(35) 5.1 ±1.3 (25)
$PdBr^+ + Br^- \rightarrow$ *cis*-$PdBr_2$	$k_{2c}/K_{2t}/s^{-1}$ $k_{2c} \times 10^{-3}/s^{-1}M^{-1}$	0±1 (15), 1.5 ±1 (25). 2±1 (35) 4±3 (25)
trans-$PdCl_2 + Cl^- \rightarrow PdCl_3^-$	$k_{3t}/s^{-1}M^{-1}$	9.4 ±0.1 (15), 21.7 ±0.2 (25), 42.9 ±0.5 (35)
trans-$PdBr_2 + Br^- \rightarrow PdBr_3^-$	$k_{3t} \times 10^{-1}/s^{-1}M^{-1}$	4.6 ±0.2 (15), 8.3 ±0.4 (25), 16.2 ±0.8 (35)
cis-$PdCl_2 + Cl^- \rightarrow PdCl_3^-$	$k_{3c} \times 10^{-3}/s^{-1}M^{-1}$	1.37±0.05 (3), 1.73±0.05 (8), 2.27±0.10(12), 2.95±0.10(15), 5.4 ±0.6 (25)
cis-$PdBr_2 + Br^- \rightarrow PdBr_3^-$	$k_{3c} \times 10^{-5}/s^{-1}M^{-1}$	>2 (25)
trans-$PdCl_2 \rightarrow PdCl^+ + Cl^-$	$k_{-2t} \times 10^{-1}/s^{-1}$	2.8 ±0.2 (15), 5.6 ±0.5 (25), 11.9 ±0.8 (35)
trans-$PdBr_2 \rightarrow PdBr^+ + Br^-$	$k_{-2t} \times 10^{-1}/s^{-1}$	7.3 ±0.6 (3), 11.2 ±1.0 (9), 15.1 ±0.8 (15), 26±2 (25)

Table VI. Equilibrium constants at 25°C and I = 1.00 *M*. Defined by eqns. (13) and (15).

Constant	X = Cl	X = Br
$K_{c/t}$	2.1±0.3	6.0±0.8
$K_{2c} \times 10^{-2}/M^{-1}$	13±2	154±14
$K_{2t} \times 10^{-2}/M^{-1}$	6.2±1.0	26±4
$K_{3c} \times 10^{-2}/M^{-1}$	3.9±0.5	23.4±1.6
$K_{3t} \times 10^{-2}/M^{-1}$	8±2	140±30

Here, α_0, α_1 and α_{2t} denote the fractions of metal present as $Pd(H_2O)_4^{2+}$, $PdX(H_2O)_3^+$ and *trans*-$PdX_2(H_2O)_2$ respectively. The experimental quantity α_{exp} is given in Table IV. It has been plotted into the distribution diagrams of the two systems in Ref. 1, Figure 6. Introducing the equilibrium constant

$$K_{c/t} = [cis\text{-}PdX_2(H_2O)_2]/[trans\text{-}PdX_2(H_2O)_2] = \alpha_{2c}/\alpha_{2t} \quad (13)$$

and $\alpha_2 = \alpha_{2c} + \alpha_{2t}$ into eqn. (12) we arrive at

$$\frac{\alpha_{exp}}{\alpha_0+\alpha_1} = \frac{1}{1+K_{c/t}} \times \frac{\alpha_2}{\alpha_0+\alpha_1} + 1 \quad (14)$$

For the solutions used, α_0, α_1 and α_2 may be calculated from the stability constants of Ref. 1. $K_{c/t}$ was obtained from the linear plots of $\alpha_{exp}/(\alpha_0 + \alpha_1)$ *vs.* $\alpha_2/(\alpha_0 + \alpha_1)$ - *cf.* Figure 4 - or by direct insertion into eqn. (14) - *cf.* Table IV. The values obtained are given in Table VI. From $K_{c/t}$ and the stability constants K_2 and K_3 determined in Ref. 1, the following stepwise stability constants were also calculated (Table VI):

$$K_{2c} = \frac{[cis\text{-}PdX_2]}{[PdX^+][X^-]}; \qquad K_{2t} = \frac{[trans\text{-}PdX_2]}{[PdX^+][X^-]}$$

$$K_{3c} = \frac{[PdX_3^-]}{[cis\text{-}PdX_2]\cdot[X^-]}; \qquad K_{3t} = \frac{[PdX_3^-]}{[trans\text{-}PdX_2]\cdot[X^-]} \quad (15)$$

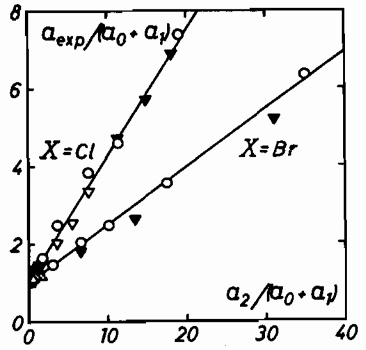

Figure 4. Plots of $\alpha_{exp}/(\alpha_0+\alpha_1)$ *vs.* $\alpha_2/(\alpha_0+\alpha_1)$ according to eqn. (14). $C_{Pd} \times 10^6/M$ was 0.952 (△), 4.76 (▲), 9.45 (○), 18.80 (▽), and 94.0 (▼).

Discussion

Table VII and Table V of Ref. 2 contain all rate constants for the chloride and bromide systems. The comparison with the kinetic parameters for the platinum(II) complexes, given in these tables, can be made regardless of the difference in ionic strength. When the ionic strength is changed from 0.50 *M* to 1.00 *M*, the acid hydrolysis rate constants remain the same within the experimental errors, and the halide anation rate constants for univalent complexes increase only about 15%.[4]

The experiments indicate that the palladium complexes react 5 × 10^4 to 5 × 10^5 times faster than the corresponding platinum complexes at 25 °C. The activation enthalpies are in general 8 to 10 kcal mol^{-1} smaller and the activation entropies some units more negative.

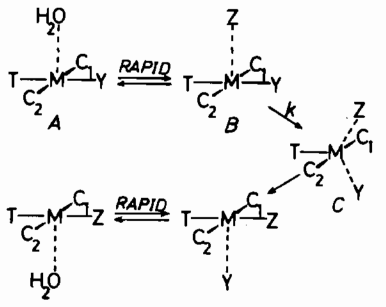

Figure 5. Model for a square planar substitution reaction.

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(4) L.I. Elding and A.B. Olsson, *Unpublished results.*
(5) L.I. Elding, *Unpublished results.*

Table VII. Rate constants, activation enthalpies and activation entropies at 25°C for substitution reactions of palladium(II) and platinum(II) complexes. Aqua ligands excluded. Standard state of water: unit mole fraction, of complexes and halide ligands: unit concentration (*M*). Values for platinum complexes from Ref. 3. Rate constants denoted by * have been calculated using the relation $K_n = k_n/k_{-n}$ and the equilibrium constants of Table VI. Ionic strength 1.00 *M* (Pd) and 0.50 *M*(Pt).

Process	M = Pd			M = Pt			
	k	$\Delta H^{\circ *}$ kcal mol^{-1}	$\Delta S^{\circ *}$ cal K^{-1}mol^{-1}	k	$\Delta H^{\circ *}$ kcal mol^{-1}	$\Delta S^{\circ *}$ cal K^{-1}mol^{-1}	k_{Pd}/k_{Pt}
$MCl^+ + Cl^- \rightarrow$ *cis*-MCl_2	$(5.1\pm1.3)\times10^2 s^{-1}M^{-1}$	—	—	$\sim2\times10^{-3}\ s^{-1}M^{-1}$	—	—	$\sim3\times10^5$
$MBr^+ + Br^- \rightarrow$ *cis*-MBr_2	$(4\pm3)\times10^3 s^{-1}M^{-1}$	—	—	—	—	—	—
$MCl^+ + Cl^- \rightarrow$ *trans*-MCl_2	$(3.5\pm0.9)\times10^4 s^{-1}M^{-1}$*	—	—	$\sim5\times10^{-1}\ s^{-1}M^{-1}$	—	—	$\sim7\times10^4$
$MBr^+ + Br^- \rightarrow$ *trans*-MBr_2	$(6.9\pm1.6)\times10^5 s^{-1}M^{-1}$*	—	—	—	—	—	—
trans-$MCl_2 + Cl^- \rightarrow MCl_3^-$	$21.7\pm0.2 s^{-1}M^{-1}$	13 ± 1	-9 ± 3	$4.6\times10^{-5}\ s^{-1}M^{-1}$	23 ± 1	-2 ± 3	5×10^5
trans-$MBr_2 + Br^- \rightarrow MBr_3^-$	$(8.3\pm0.4)\times10 s^{-1}M^{-1}$	11 ± 1	-14 ± 3	$1.8\times10^{-4}\ s^{-1}M^{-1}$	20 ± 1	-10 ± 3	5×10^5
cis-$MCl_2 + Cl^- \rightarrow MCl_3^-$	$(5.4\pm0.6)\times10^3 s^{-1}M^{-1}$	10 ± 1	-7 ± 3	$7.5\times10^{-2}\ s^{-1}M^{-1}$	18 ± 1	-4 ± 3	7×10^4
cis-$MBr_2 + Br^- \rightarrow MBr_3^-$	$>2\times10^5 s^{-1}M^{-1}$	—	—	$3.3\ s^{-1}M^{-1}$	14 ± 1	-9 ± 3	$>6\times10^4$
cis-$MCl_2 \rightarrow MCl^+ + Cl^-$	$(3.9\pm1.6)\times10^{-1} s^{-1}$*	—	—	$\sim3\times10^{-7}\ s^{-1}$	—	—	$\sim1\times10^6$
cis-$MBr_2 \rightarrow MBr^+ + Br^-$	$(2.5\pm2)\times10^{-1} s^{-1}$*	—	—	—	—	—	—
trans-$MCl_2 \rightarrow MCl^+ + Cl^-$	$(5.6\pm0.5)\times10 s^{-1}$	12 ± 1	-9 ± 3	$\sim1\times10^{-4}\ s^{-1}$	—	—	6×10^5
trans-$MBr_2 \rightarrow MBr^+ + Br^-$	$(2.6\pm0.2)\times10^2 s^{-1}$	9 ± 1	-17 ± 3	—	—	—	—
$MCl_3^- \rightarrow$ *trans*-$MCl_2 + Cl^-$	$(2.7\pm0.9)\times10^{-2} s^{-1}$*	—	—	$2.8\times10^{-8}\ s^{-1}$	24 ± 1	-12 ± 3	1×10^6
$MBr_3^- \rightarrow$ *trans*-$MBr_2 + Br^-$	$(5.9\pm1.5)\times10^{-3} s^{-1}$*	—	—	$1.4\times10^{-8}\ s^{-1}$	26 ± 1	-8 ± 3	4×10^5
$MCl_3^- \rightarrow$ *cis*-$MCl_2 + Cl^-$	$(1.4\pm0.3)\times10 s^{-1}$*	—	—	$6\times10^{-5}\ s^{-1}$	20 ± 1	-11 ± 3	2×10^5
$MBr_3^- \rightarrow$ *cis*-$MBr_2 + Br^-$	$>1\times10^2 s^{-1}$*	—	—	$6\times10^{-4}\ s^{-1}$	21 ± 1	-3 ± 3	$>1\times10^5$

Table VIII. *cis*- and *trans*-effects for reactions of palladium (II) and platinum(II) chloro and bromo aqua complexes at 25°C and ionic strength 1.00 *M* (Pd) and 0.50 *M* (Pt).

		Pd	Pt
trans-effect	Cl/H_2O	50	300
trans-effect	Br/H_2O	500	3000
cis-effect	H_2O/Cl	4	3
cis-effect	H_2O/Br	8	6

The acid hydrolysis rate constants of $PdCl(H_2O)_3^+$, $PdBr(H_2O)_3^+$, and, according to recent experiments, $PdI(H_2O)_3^+$, are the same within the experimental errors.[2,5] This is consistent with an associative mechanism. We might describe a general square planar substitution process by the model given in Figure 5, where Y denotes the leaving and Z the entering ligand (*cf.* Ref. 6 and Ref. 7, p. 16). There is a rapid pre-equilibrium between the solvated complex A and a five-coordinated complex B, containing the entering ligand weakly bonded in an axial position. The stability constant of this complex is

$$K = \frac{[B]}{[A][Z]} \tag{16}$$

The rate determining step involves an intramolecular rearrangement to an intermediate, C, having, for instance, a trigonal bipyramidal configuration. The rate of this process is

$$\text{Rate} = k\times[B] = kK\times[A][Z] \tag{17}$$

According to this description, the observed second order rate constant will be a product of the first order rate constant k and the stability constant K.

(*i*). *Acid hydrolyses.* The observed rate constant for Z = H_2O is k. It will depend on the nature of the metal and the leaving and entering ligands, and on the nature of the *trans*- and *cis*-ligands. When the incoming ligand is uncharged, as for Z = H_2O, k should be approximately independent of the ionic charge of the substrate complex, A. A relation of the type devised by D.S.Martin and coworkers[8,9,10] can be used to describe the rate constants for a series of complexes with the same metal and the same entering and leaving ligands. All six acid hydrolysis rate constants of the palladium(II) chloro aqua complexes can be calculated to within 25% by the eqn.

$$k/n = 0.6\times50^r\times(\frac{1}{4})^s, \tag{18}$$

and the acid hydrolysis rate constants for the bromo aqua complexes are given within a factor of 2 by

$$k/n = 0.6\times500^r\times(\frac{1}{8})^s \tag{19}$$

For this system, the experimental errors are somewhat greater than for the chloride system. In eqns. (18) and (19), n = 1, 2 or 4 denotes the number of equivalent halide ligands in the complex, r = 0 or 1 is the number of halide ligands *trans* to the replaced ligand, and s = 0, 1 or 2 is the number of halide ligands *cis* to it. These relations indicate the relative *trans*- and *cis*-effects given in Table VIII together with previosly calculated values for platinum(II) complexes[11,12] The relative *trans*-effect is about 6 times smaller for Pd than for Pt, whereas the *cis*-effect is a little greater.

The equation was first devised to describe the acid hydrolyses of the chloroammine platinum(II) com-

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(6) D.S. Martin, *Inorg. Chim. Acta Revs.*, *1*, 87 (1967).

(7) L.I. Elding, Substitution Reactions and Stabilities of Chloro Aqua and Bromo Aqua Platinum(II) Complexes, Diss., Lund 1970.

(8) M.A. Tucker, C.B. Colvin, and D.S. Martin, *Inorg. Chem.*, 3, 1373 (1964).

(9) D.S. Martin, *Coord. Chem. Revs.*, *1*, 79 (1966).

(10) C.B. Colvin, R.G. Gunther, L.D. Hunter, J.A. McLean, M.A. Tucker and D.S. Martin, *Inorg. Chim. Acta*, *2*, 487 (1968).

(11) L.I. Elding, *Acta Chem. Scand. 24*, 1527 (1970).

(12) L.I. Elding, *Acta Chem. Scand. 24*, 2557 (1970).

plexes, for which the rate constants varies only by a factor of 16, and where the relative *cis*- and *trans*-effects are of similar magnitude.[8] For the platinum(II) and palladium(II) chloro and bromo aqua systems, the relative *cis*- and *trans*-effects are much greater and the *trans*-effect is predominant. The acid hydrolysis rate constants for the platinum(II) chloro aqua complexes, for instance, vary by a factor of 3×10^4. It is satisfying that the equation can describe such a wide variation of rates.

The first factor of eqns. (18) and (19) is the same for the chloro and bromo complexes. This implies that there is no observable effect of the leaving halide ligand on the rates of these hydrolyses. This fact is also evident from the similar rates of acid hydrolysis of $PdX(H_2O)_3^+$. The hydrolysis rate constants of *cis*-$PdX_2(H_2O)_2$ differ by a factor of about 2, which is equal to the difference in *cis*-effect between Cl/H_2O and Br/H_2O, and the rate constants for the acid hydrolyses of $PdX_3H_2O^-$ to the *trans*-isomer differ by a factor of 4, which is also in accordance with a negligible effect of the leaving ligand, if the difference in *cis*-effects is considered.

(*ii*). *Halide anations.* The observed second order rate constant is kK. As for acid hydrolyses, k will depend on the nature of the metal, the entering and leaving ligands, and the *cis*- and *trans*-ligands. In addition, for charged entering ligands Z, k might depend on the ionic charge of the substrate complex, A. The equilibrium constant K will also be a function of the ionic charge of A. Thus, for a series of complexes with the same metal and the same entering and leaving ligands, the observed rate constant kK will depend on the nature of the *cis*- and *trans*-ligands, and on the ionic charge of the substrate complex. If we postulate that the relative *cis*- and *trans*-effects for a given pair of ligands are the same for anations and for acid hydrolyses, we can describe the halide anation rate constants for the various systems by the relation

$$k/m = \text{const} \times T^r \times C^s \times Q^q, \qquad (20)$$

where m is the number of equivalent aqua ligands in the complex, r and s have the same meaning as for eqns. (18) and (19), q is the ionic charge of the substrate complex with its sign, and T and C are the relative *trans*– and *cis*-effects. The charge factor, Q, contains the charge dependence of both k and K. For halide as entering ligand, the stability constants K will increase in the order $K_{MX_4^{2-}} < K_{MX_3^-} < \ldots < K_{M^{2+}}$. Q contains the quotient between adjacent constants as a factor.

The following relations describe the obtained anation rate constants:

$$\begin{aligned}
k/m &= 200 \times 50^r \times (\tfrac{1}{4})^s \times 5^q && \text{(Pd-Cl)}\\
k/m &= 1000 \times 500^r \times (\tfrac{1}{8})^s \times 5^q && \text{(Pd-Br)}\\
k/m &= 3 \times 10^{-4} \times 300^r \times (\tfrac{1}{3})^s \times 5^q && \text{(Pt-Cl)}\\
k/m &= 4 \times 10^{-3} \times 3000^r \times (\tfrac{1}{6})^s \times 5^q && \text{(Pt-Br)}
\end{aligned} \qquad (21)$$

The six constants for the palladium chloride system are given within 40%, and the six constants for the bromide system within a factor of 3. The five rate constants for the platinum chloro complexes and the three constants for the bromo complexes are described within 40%.

The charge factor is equal for these similar systems. A quotient between adjacent stability constants K of about 5 seems probable. The first factor in eqns. (21) is 5 times greater for the palladium bromide than for the palladium chloride system. This implies that bromide is about 5 times more efficient than chloride as entering ligand in these complexes (*cf.* for instance the halide anation rate constants of $Pd(H_2O)_4^{2+}$, which differ by a factor of 5). The same order of efficiency is valid for the platinum systems.

The simple electrostatic model outlined for the substitution processes describes the observed rate constants of both chloride systems fairly well, if we suppose that the relative *cis*- and *trans*-effects are the same for water and halide as entering ligands.

Examples are known, however, where *cis*- and *trans*-effects may depend on the nature of the entering ligand, also.[13] This possibility, in addition to the somewhat greater experimental uncertainty, may be the reason for the less accurate description of the palladium bromide system.

Activation energies and ionic strength effects will be different for the various reactions compared. Therefore, the parameters used to describe the rate constants, *i.e. cis*-, *trans*-, and charge-effects, will be functions of temperature and ionic strength. This dependence, however, will not necessarily invalidate comparisons, as claimed by Coe *et al.*[14]

The unique position of water in the *trans*-effect series should be emphasized. Its *trans*-effect is 50 (Pd) or 500 (Pt) times smaller than the *trans*-effect of chloride, which itself is considered to be a weak *trans*-director. Consequently, aqua ligands *trans* to other aqua ligands are replaced very slowly - *e.g.* reactions (2) and (3). The usual statement that water is an excellent leaving ligand, which can be rapidly replaced by other groups, is not valid in this case.

Note added in proof. A preliminary report on these studies was given at the XVth ICCC-conference in Moscow, 1973.[15] Syrkin *et al.*[16] recently published rate constants and activation parameters for the equilibrium.

$$PdX_4^{2-} + H_2O \rightleftharpoons PdX_3H_2O^- + X^-$$

determined by the temperature-jump technique. Their results agree within 30% with those published simultaneously by me in Ref. 2. Recently, Pearson and Hynes[17] published some kinetic results for the chloro system. Some of their rate constants (k_1 and k_{3t}) agree within

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(13) L. Cattalini, *Progr. Inorg. Chem.*, *13*, 263 (1969).

(14) J.S. Coe, M.D. Hussain, and A.A. Malik, *Inorg. Chim. Acta, 2,* 65 (1968).

(15 Proc. XVth. Int. Conf. Coord. Chem., Moscow 1973, p. 409.

(16) M.N. Vargaftik, V.A. Igoshin and Y.K. Syrkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 6, 1426 (1972).

(17) R.G. Pearson and M.G. Hynes, Transactions of the Royal Institute of Technology, Stockholm, Sweden, No. 285, 460 (1972).

a factor of two with our results, whereas their value of 210 $s^{-1}M^{-1}$ for the rate constant k_{3c} is probably much too small. When adding excess bromide to solutions of palladium perchlorate, they found a reaction with an observed rate constant $85\times[Br^-]$. The value of 85 $s^{-1}M^{-1}$ is in excellent agreement with our rate constant defined by eqn. (7), equal to $84.5+0.5$ $s^{-1}M^{-1}$ (*cf.* Table V).

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