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Palladium(II) Halide Complexes. II. Acid Hydrolyses and Halide Anations of Palladium(II) Chloro and Bromo Aqua Complexes

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The rate constants for the chloride and bromide anations of $Pd(H_2O)_4^{2+}$, the chloride anation of $PdCl_3H_2O^-$, the bromide anation of $PdBr_3H_2O^-$ and the acid hydrolysis of $Pd(H_2O)_3^+$, $PdBr(H_2O)_3^+$, $PdCl_4^{2-}$, and $PdBr_4^{2-}$ have been determined at 15, 25 and 35 °C using a stopped-flow technique. The ionic strength was 1.00 M and the supporting electrolyte perchloric acid. The obtained rate constants are given in Table IV and the activation enthalpies and entropies in Table V. A comparison with the corresponding reactions for platinum(II) complexes indicates that the acid hydrolyses are 1×10^5 to 2×10^5 times faster and the halide anations 4×10^4 to 6×10^4 times faster for palladium. The increased rates of reaction are due to a decrease in activation enthalpies. The reactions are typically square planar substitutions with respect to entering and leaving groups. The mechanism appears to be associative in nature.

Introduction

We have previously investigated the kinetics and equilibria of the stepwise acid hydrolyses and halide anations of the platinum(II) chloro aqua and bromo aqua complexes $PtX_n(H_2O)_{4-n}^{2-n}$, X = Cl, Br, n = 1, 2,3,4.[1-9] These studies indicated large *trans*-effects of chloride and bromide relative to water. No studies on the analogous square planar palladium(II) chloro aqua and bromo aqua complexes have been found in the literature. Palladium(II) complexes are generally considered to react about 10^5 times faster than the corresponding platinum(II) species,[10] but the magnitudes of *cis*- and *trans*-effects for reactions of palladium(II) complexes are unknown.

In the present and subsequent papers,[11] kinetic studies on halide anations and acid hydrolyses of the complexes $PdX_n(H_2O)_{4-n}^{2-n}$, X = Cl, Br, n = 0,1,2,3,4, will be described. These reactions may be followed using a stopped-flow technique. The experiments indicate that there is a large difference in *trans*-effect between water and halide ligands for these reactions, as was observed for the corresponding platinum(II) complexes. Thus, *cis*- and *trans*-isomers of $PdX_2(H_2O)_2$ may be distinguished by their widely different rates of halide anation.[11] The reaction model, introduced previously[5,7] to describe the stepwise reactions of the platinum(II) complexes, may therefore be used for the palladium(II) systems, too. Figure 1 gives the reaction scheme and the notations for the rate constants that will be used in the present and subsequent papers.

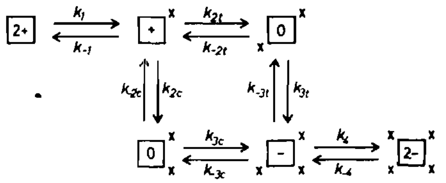

Figure 1. Reaction scheme (*cf*. Ref. 5). The aqua ligands have been omitted. X denotes chloride or bromide. The acid hydrolyses are first order with respect to complex, the halide anations first order with respect to both complex and halide.

The stability constants necessary for the planning and interpretation of the kinetic experiments have been determined previously.[12] The absorption spectra of the chloro and bromo aqua complexes have also been calculated.[12]

Pure solutions of palladium(II) perchlorate were prepared by a previously described method.[12] These solutions were used to study the first complex formation step and its reverse

$$Pd(H_2O)_4^{2+} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} PdX(H_2O)_3^+ + H_2O \qquad (1)$$

For the platinum(II) systems, the corresponding reaction has not been investigated, since the ion $Pt(H_2O)_4^{2+}$ is unknown.

The present paper describes kinetic studies on reaction (1) and on the fourth complex formation step (2):

$$PdX_3H_2O^- + X^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} PdX_4^{2-} + H_2O \qquad (2)$$

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The rate constants k_n and k_{-n}, $n = 1,4$, of these reactions have been obtained from kinetic experiments with excess halide using a previously described method.[2,3] The rate constant k_1 has also been determined from experiments with excess palladium. Subsequently, kinetic and equilibrium studies on *cis*- and *trans*-$PdX_2(H_2O)_2$ will be reported.[11]

Experimental Section

Chemicals. Stock solutions of palladium(II) perchlorate 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 previously.[12]

Apparatus. A modified Durrum-Gibson stopped-flow spectrophotometer equipped with a Tektronix storage oscilloscope type RM 564 was used. The transmittance *vs.* time curves were recorded on Polaroid 3000 Type 107 film using a Tektronix oscilloscope camera, type C-27. The dead time of the stopped-flow instrument was about 2 ms. The drive syringes, the valve block, and the cuvette block were thermostated by water at the chosen temperature ±0.1°C. The cuvette was also exposed to a stream of dry air at the relevant temperature ±0.3°C.

Kinetic procedure. For each kinetic run, two solutions were mixed. Solution I was made twice the concentration of palladium appropriate for the kinetic run. In the studies on reaction (2), this solution also contained ligand (as hydrochloric or hydrobromic acid) in order to get an appropriate mean ligand number of about 3.5 at the start of the kinetic run. Solution II contained twice the concentraion of ligand needed for the kinetic run. It was mixed from hydrochloric or hydrobromic acid and perchloric acid.

All solutions had an ionic strength of 1.00 *M* with perchloric acid as supporting electrolyte. The acid concentration of 1.00 *M* is sufficient to suppress the protolysis of the aqua complexes.[12,13,14]

The solutions were boiled at decreased pressure and room temperature for 1 to 2 min in order to remove dissolved air, and then added to the drive syringes of the stopped-flow apparatus and thermostated at 15, 25, or 35°C.

All experiments were arranged to give a change from a low to a higher mean ligand number, $\bar{n}$. First-order kinetics were always attained by having either the metal or the ligand in large enough excess. The experimental rate constants were calculated by a least squares programme and a computer from the transmittance *vs.* time curves using a simple integrated first-order rate expression.

Halide anation of $Pd(H_2O)_4^{2+}$, *excess metal.* The results of these experiments are shown in Table I and Figures 2 and 3. The concentrations given in the table refer to the kinetic runs, *i.e.* the concentrations after mixing. For the chloride system, the measurements were performed near the minimum of absorbance of $Pd(H_2O)_4^{2+}$ at 280 nm (Ref. 12, Figure 7). For the bromide system, the concentrations of palladium and bromide had to be chosen about 10 times smaller than for the chloride system, in order to get suitable half-lives and to prevent precipitation of $PdBr_2$. These experiments were performed at 234 nm, where the molar absorptivities are large enough to give measurable changes (Ref. 12, Figure 8).

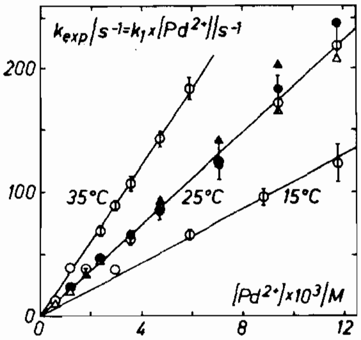

Figure 2. Chloride anation of $Pd(H_2O)_4^{2+}$. Experiments with palladium in excess. $C_{Cl} \times 10^5/M$ was: 2.50 (△), 5.00 (○), 10.00 (●) and 20.00 (▲).

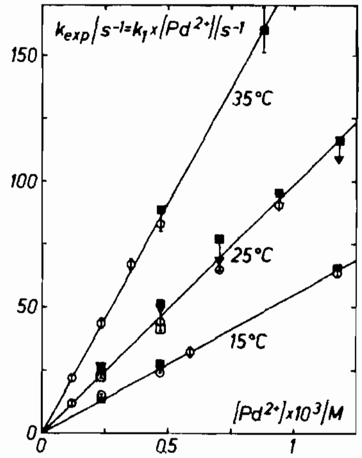

Figure 3. Bromide anation of $Pd(H_2O)_4^{2+}$. Experiments with palladium in excess. $C_{Br} \times 10^6/M$ was: 1.25 (□), 2.50 (○), 5.00 (▼) and 10.00 (■).

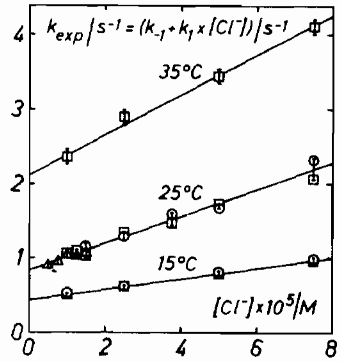

Figure 4. Chloride anation of $Pd(H_2O)_4^{2+}$. Experiments with chloride in excess. $C_{Pd} \times 10^6/M$ was: 2.35 (△), 4.73 (○) and 5.50 (□).

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Table I. Halide anation of $Pd(H_2O)_4^{2+}$. Experiments with palladium in excess. The rate constant k_{exp} defined by eqn. (3) is given with its standard deviations. Measurements at 274 nm (chloride) and 234 nm (bromide).

Temperature	Entering ligand: chloride			Entering ligand: bromide		
°C	$C_{Pd}\times10^3/M$	$C_{Cl}\times10^4/M$	k_{exp}/s^{-1}	$C_{Pd}\times10^3/M$	$C_{Br}\times10^5/M$	k_{exp}/s^{-1}
15	2.94	0.5	38±3	0.235	0.25, 1.0	15±1
15	5.87	0.5	66±3	0.470	0.25, 1.0	26±2
15	8.81	0.5	96±7	0.588	0.25	32±2
15	11.75	0.5	123±15	1.175	0.25, 1.0	64±2
25	0.59	0.25,0.5	11±2	0.118	0.25	12±1
25	1.18	0.25,0.5,1.0	22±2	0.235	0.13,0.25,0.5,1.0	24±2
25	1.79	0.25,0.5	36±4	0.470	0.13,0.25,0.5,1.0	47±5
25	2.36	0.25,0.5, 1.0	47±4	0.705	0.25,0.5,1.0	70±6
25	3.52	0.5,1.0	64±6	0.940	0.25,0.5,1.0	92±3
25	4.70	0.25,0.5.1.0.2.0	87±9	1.175	0.5,1.0	112±5
25	7.05	0.25,0.5.1.0.2.0	125±15			
25	9.40	0.25,0.5.1.0.2.0	179±15			
25	11.75	0.25,0.5,1.0	224±15			
35	1.18	0.5	39±2	0.118	0.25	22±1
35	2.35	0.5	69±4	0.235	0.25	44±2
35	2.94	0.5	89±4	0.353	0.25	67±2
35	3.53	0.5	107±6	0.470	0.25, 1.0	85±5
35	4.70	0.5	143±10	0.880	1.0	160±10
35	5.87	0.5	184±10			

Table II. Halide anation of $Pd(H_2O)_4^{2+}$. Experiments with halide in excess. The rate constant k_{exp} defined by eqn. (4) is given with its standard deviations. Measurements at 217±5 nm (chloride) and 227±3 nm (bromide).

Temperature	Entering ligand: chloride			Entering ligand: bromide		
°C	$C_{Cl}\times10^5/M$	$C_{Pd}\times10^6/M$	k_{exp}/s^{-1}	$C_{Br}\times10^6/M$	$C_{Pd}\times10^7/M$	k_{exp}/s^{-1}
15	1.00	4.7,5.6	0.48±0.02	2.50	2.4,4.7	0.61±0.06
15	2.50	4.7,5.6	0.61±0.02	5.00	2.4,4.7	0.75±0.05
15	5.00	4.7,5.6	0.79±0.03	10.00	4.7,9.4	0.97±0.06
15	7.50	4.7,5.6	0.96±0.04	15.00	4.7,9.4	1.22±0.07
25	0.50	2.4	0.90±0.02	1.50	2.4	0.91±0.02
25	0.75	2.4	0.95±0.05	2.50	2.4	1.08±0.03
25	1.00	2.4,4.7	1.04±0.03	3.75	2.4,4.7	1.17±0.10
25	1.25	2.4,4.7	1.06±0.05	5.00	2.4,4.7	1.27±0.09
25	1.50	2.4,4.7,5.5	1.10±0.09	7.50	2.4,4.7,9.4	1.45±0.12
25	2.50	4.8,5.5	1.29±0.07	10.00	2.4,4.7,9.4	1.77±0.08
25	3.75	4.8,5.5	1.52±0.09	12.50	2.4,4.7,9.4	1.95±0.10
25	5.00	4.8,5.5	1.69±0.04	15.00	2.4,4.7,9.4	2.09±0.16
25	7.50	4.8,5.5	2.19±0.15			
35	1.00	4.7	2.4 ±0.1	2.50	2.4,4.7	2.5 ±0.1
35	2.50	4.7	2.9 ±0.1	5.00	2.4,4.7	3.0 ±0.2
35	5.00	4.7	3.4 ±0.1	10.00	4.7,9.4	3.6 ±0.2
35	7.50	4.7	4.1 ±0.1	15.00	4.7,9.4	4.6 ±0.4

It appears from the previously determined values of β_1[12] that only $Pd(H_2O)_4^{2+}$ and $PdX(H_2O)_3^+$ were present at equilibrium at the concentrations used. Thus, the subsequent reaction to $PdX_2(H_2O)_2$ did not disturb these measurements. The reverse of reaction (1) could also be neglected.

Halide anation of $Pd(H_2O)_4^{2+}$, excess ligand. Table II and Figures 4 and 5 review these experiments. The concentrations given in the table refer to the kinetic runs after mixing of solutions I and II. Wave lengths about 217 nm (chloride) and 227 nm (bromide) were used. The equilibrium measurements[12] indicate that the fraction of palladium present as $PdX_2(H_2O)_2$ at equilibrium was only about 10% (chloride) and about 15% (bromide) in the solutions containing the highest concentrations of ligand ($[Cl^-] = 7.5\times10^{-5}\,M$; $[Br^-] = 1.50\times10^{-5}\,M$), and much less in the other solutions. Therefore, the subsequent reaction to $PdX_2(H_2O)_2$ was neglected in the regions of ligand concentration used.

Halide anation of $PdX_3H_2O^-$ and acid hydrolysis of PdX_4^{2-}. First order kinetics for reaction (2) was obtained by having ligand in excess. Table III and Figures 6 and 7 review these experiments. The concentrations used for the start solutions (I) are given in the figure captions, and the concentrations of the mixed solutions used for the kinetic runs in the table.

The equilibrium measurements (Ref. 12, Figure 6) indicate that the mean ligand number of the start solutions was 3.50 for the chloride system ($[Cl^-] = 5\times10^{-2}\,M$), corresponding to only about 3% of the palladium present as $PdCl_2(H_2O)_2$ at zero time. For the bromide system, the start mean ligand numbers were 3.62, 3.40, and 3.05 for $[Br^-] = 1\times10^{-2}\,M$, $5\times10^{-3}\,M$, and $2\times10^{-3}\,M$, respectively. In these

Table III. Halide anation of $PdX_3H_2O^-$. Experiments with halide in excess. The rate constant k_{exp} defined by eqn. (5) is given with its standard deviations. Measurements at 280 nm (chloride) and 330 nm (bromide).

Temperature	X=Cl			X=Br		
°C	$C_{Cl}\times10^3/M$	$C_{Pd}\times10^5/M$	k_{exp}/s^{-1}	$C_{Br}\times10^3/M$	$C_{Pd}\times10^5/M$	k_{exp}/s^{-1}
15	75	0.47,2.4	13±1	7.5	4.7,9.4	23±1
15	125	0.47,2.4	17±2	12.5	4.7,9.4	33±1
15	175	0.47,2.4	22±2	17.5	4.7,9.4	41±1
15	275	0.47,2.4	32±2	22.5	4.7,9.4	51±1
15	375	0.47,2.4	42±2	32.5	4.7,9.4	70±2
15	525	0.47,2.4	56±5	42.5	4.7,9.4	85±2
15				52.5	4.7,9.4	102±8
25	75	0.47,2.4,9.4	22±2	5.0	2.4	33±3
25	125	0.47,2.4,9.4	32±3	7.5	9.4	40±2
25	175	0.47,2.4,9.4	40±3	10.0	2.4,4.7	49±4
25	275	0.47,2.4,9.4	58±4	12.5	9.4	59±3
25	375	0.47,2.4,9.4	75±9	15.0	4.7,9.4	68±4
25	525	0.47,2.4,9.4	104±7	17.5	9.4	78±4
25				20.0	2.4,4.7,9.4	79±5
25				22.5	9.4	86±5
25				30.0	2.4,4.7,9.4	111±13
25				40.0	2.4,4.7,9.4	140±20
25				50.0	4.7,9.4	200±20
35	75	0.47,2.4	46±4	7.5	4.7, 14.1	69±8
35	125	0.47,2.4	58±4	12.5	4.7, 14.1	101±5
35	175	0.47,2.4	78±6	15.0	14.1	103±11
35	275	0.47,2.4	110±12	17.5	4.7, 14.1	122±12
35	375	0.47,2.4	138±14	20.0	14.1	126±7
35				22.5	4.7, 14.1	146±14
35				25.0	14.1	146±19
35				27.5	14.1	157±7
35				30.0	14.1	186±20
35				32.5	4.7, 14.1	187±20
35				35.0	14.1	191±9

solutions, about 1,5 and 15% of the palladium was present as $PdBr_2(H_2O)_2$. Except for the single solution having 15% $PdBr_2(H_2O)_2$, the halide anation of $PdX_2(H_2O)_2$ was therefore negligible for all these kinetic runs. These measurements were performed at the charge-transfer bands of PdX_4^{2-} at 280 nm (chloride) and 330 nm (bromide) - *cf.* Ref. 12, Figures 2 and 3.

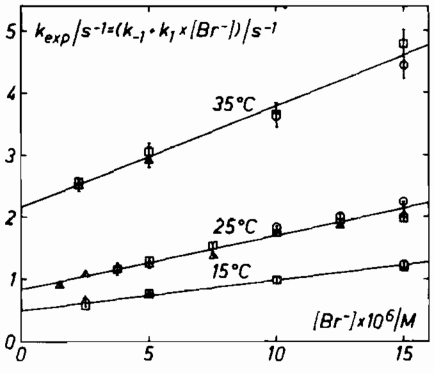

Figure 5. Bromide anation of $Pd(H_2O)_4^{2+}$. Experiments with bromide in excess. $C_{Pd}\times10^7/M$ was: 2.35 (△), 4.70 (□) and 9.40 (○).

Results and Discussion

The Figures give the experimental pseudo first-order rate constants *vs.* the concentrations of the excess reagent at 15, 25 and 35 °C. For the experiments with excess palladium, the observed rate constant is

$$k_{exp} = k_1 \times [Pd(H_2O)_4^{2+}] \tag{3}$$

Thus, the rate constant k_1 was obtained from the slopes of the straight lines given in Figures 2 and 3.

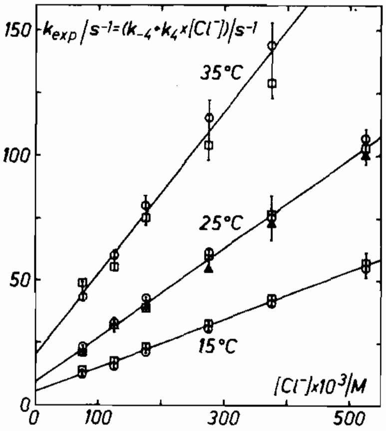

Figure 6. Chloride anation of $PdCl_3H_2O^-$. Experiments with chloride in excess. The palladium start solutions (I) had the following concentrations: $C_{Pd} = 47.0\times10^{-6}\,M$, and $C_{Cl} = 50\times10^{-3}\,M$ (○); $C_{Pd} = 18.8\times10^{-6}\,M$ and $C_{Cl} = 50\times10^{-3}\,M$ (△); $C_{Pd} = 9.40\times10^{-6}\,M$ and $C_{Cl} = 50\times10^{-3}\,M$ (□).

For the experiments with excess ligand, the pseudo first-order rate constant may be expressed (*cf.* Ref.

Table IV. Rate constants with their standard deviations. Aqua ligands excluded. The equilibrium constants K_1 and K_4 used for the calculation of k_1 and k_4 from eqn. (6), have been determined previously at 25°C.[12] The values of k_{-1} and k_{-4} at 15 and 35°C were calculated using $\Delta H°$-values from Ref. 15 and 16.

Process	Method			Rate constant	
			15 °C	25 °C	35 °C
$Pd^{2+} + Cl^- \rightarrow PdCl^+$	Pd excess	$k_1 \times 10^{-4}/s^{-1}M^{-1}$	1.04±0.04	1.85±0.03	3.1±0.1
	Cl excess		0.73±0.03	1.80±0.04	2.7±0.2
	Mean value		*0.9 ±0.2*	*1.83±0.07*	*2.9±0.3*
$Pd^{2+} + Br^- \rightarrow PdBr^+$	Pd excess	$k_1 \times 10^{-4}/s^{-1}M^{-1}$	5.3 ±0.1	9.6 ±0.1	18.1±0.2
	Br excess		4.9 ±0.2	8.8 ±0.4	16 ±1
	Mean value		*5.1 ±0.3*	*9.2 ±0.5*	*17 ±1*
$PdCl_3^- + Cl^- \rightarrow PdCl_4^{2-}$	Cl excess	$k_4 \times 10^{-2}/s^{-1}M^{-1}$	0.96±0.02	1.80±0.03	3.15±0.10
$PdBr_3^- + Br^- \rightarrow PdBr_4^{2-}$	Br excess	$k_4 \times 10^{-3}/s^{-1}M^{-1}$	1.76±0.03	3.0 ±0.2	4.5 ±0.2
$PdCl^+ \rightarrow Pd^{2+} + Cl^-$	Cl excess	k_{-1}/s^{-1}	0.42±0.02	0.83±0.03	2.1 ±0.1
	Calculation	$(k_1/K_1)/s^{-1}$	0.26±0.07	0.62±0.06	1.2 ±0.2
$PdBr^+ \rightarrow Pd^{2+} + Br^-$	Br excess	k_{-1}/s^{-1}	0.48±0.02	0.83±0.03	2.1 ±0.1
	Calculation	$(k_1/K_1)/s^{-1}$	0.26±0.04	0.63±0.06	1.5 ±0.2
$PdCl_4^{2-} \rightarrow PdCl_3^- + Cl^-$	Cl excess	k_{-4}/s^{-1}	5.5 ±0.4	8.9 ±0.8	21±2
	Calculation	$(k_4/K_4)/s^{-1}$	3.3 ±0.3	7.6 ±0.7	16±2
$PdBr_4^{2-} \rightarrow PdBr_3^- + Br^-$	Br excess	k_{-4}/s^{-1}	10±1	19±2	37±4
	Calculation	$(k_4/K_4)/s^{-1}$	9±1	18±2	35±4

Table V. 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 the platinum complexes from Ref. 3, 5 and 7.

Process	M = Pd			M = Pt			
	k	$\Delta H°^*$/kcal mol^{-1}	$\Delta S°^*$/calK^{-1}mol^{-1}	k	$\Delta H°^*$/kcal mol^{-1}	$\Delta S°^*$/calK^{-1}mol^{-1}	k_{Pd}/k_{Pt}
$M^{2+} + Cl^- \rightarrow MCl^+$	1.83×10^4 $s^{-1}M^{-1}$	10±2	— 6±6	—	—	—	—
$M^{2+} + Br^- \rightarrow MBr^+$	9.2×10^4 $s^{-1}M^{-1}$	10±1	— 3±3	—	—	—	—
$MCl_3^- + Cl^- \rightarrow MCl_4^{2-}$	1.80×10^2 $s^{-1}M^{-1}$	10±1	—15±3	2.8×10^{-3} $s^{-1}M^{-1}$	18±1	—11±3	6×10^4
$MBr_3^- + Br^- \rightarrow MBr_4^{2-}$	3.0×10^3 $s^{-1}M^{-1}$	8±1	—17±3	8.3×10^{-2} $s^{-1}M^{-1}$	14±1	—15±3	4×10^4
$MCl^+ \rightarrow M^{2+} + Cl^-$	0.83 s^{-1}	14±2	—13±6	—	—	—	—
$MBr^+ \rightarrow M^{2+} + Br^-$	0.83 s^{-1}	14±2	—13±6	—	—	—	—
$MCl_4^{2-} \rightarrow MCl_3^- + Cl^-$	8.9 s^{-1}	12±2	—13±6	3.6×10^{-5} s^{-1}	22±1	—6±3	2×10^5
$MBr_4^{2-} \rightarrow MBr_3^- + Br^-$	19 s^{-1}	11±1	—15±3	1.9×10^{-4} s^{-1}	21±1	—6±3	1×10^5

2, 3) according to eqns. (4) and (5):

$$k_{exp} = k_{-1} + k_1 \times [X^-] \qquad (4)$$

$$k_{exp} = k_{-4} + k_4 \times [X^-] \qquad (5)$$

The rate constants for both the forward and the reverse reactions (1) and (2) could be obtained from the slopes and intercepts of the plots given in Figures 4, 5, 6 and 7.

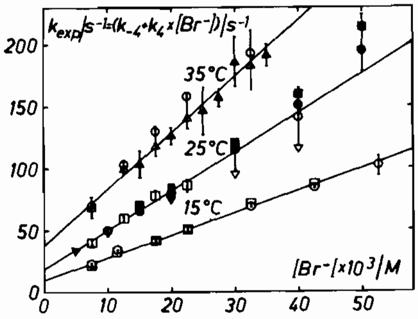

Figure 7. Bromide anation of $PdBr_3H_2O^-$. Experiments with bromide in excess. The palladium start solutions (I) had the following concentrations: $C_{Pd} = 4.70 \times 10^{-5}\ M$ and $C_{Br} = 2 \times 10^{-3}\ M$ (▼); $C_{Pd} = 4.70 \times 10^{-5}\ M$ and $C_{Br} = 5 \times 10^{-3}\ M$ (▽); $C_{Pd} = 9.40 \times 10^{-5}\ M$ and $C_{Br} = 5 \times 10^{-3}\ M$ (○); $C_{Pd} = 9.40 \times 10^{-5}\ M$ and $C_{Br} = 10 \times 10^{-3}\ M$ (●); $C_{Pd} = 18.8 \times 10^{-5}\ M$ and $C_{Br} = 5 \times 10^{-3}\ M$ (□); $C_{Pd} = 18.8 \times 10^{-5}\ M$ and $C_{Br} = 10 \times 10^{-3}\ M$ (■); $C_{Pd} = 28.2 \times 10^{-5}\ M$ and $C_{Br} = 5 \times 10^{-3}\ M$ (△); $C_{Pd} = 28.2 \times 10^{-5}\ M$ and $C_{Br} = 10 \times 10^{-3}\ M$ (▲).

The experiments indicate that the acid hydrolyses are first order with respect to complex and the anations first order with respect to both complex and halide. Table IV gives the rate constants obtained. The rate constants k_1 determined by the two independent methods agree within the limit of three standard deviations.

The acid hydrolysis rate constants k_{-1} and k_{-4} were obtained as intercepts of straight lines. They may also be calculated from the rate constants k_1 and k_4 and the stepwise stability constants K_1 and K_4 determined previously at 25 °C,[12] using the relation

$$K_n = k_n / k_{-n} \qquad (6)$$

From values of the enthalphy changes for the forward reactions (1) and (2):

$\Delta H_1° = -3.0$ kcal/mol (chloride)[15]
$\Delta H_1° = -5.1$ kcal/mol (bromide)[15]
$\Delta H_4° = -3.4$ kcal/mol (chloride)[15]
$\Delta H_4° = -4.3$ kcal/mol (bromide)[16],

k_{-1} and k_{-4} may also be calculated at 15 and 35 °C. It appears from Table IV that these calculated rate constants agree with the experimental values within the limit of three standard deviations. In some cases, the calculated k_{-1} at 15 and 35°C differs somewhat more from the experimentally determined constants, but this might be due to errors in the $\Delta H°$-values used.

It may therefore be concluded that the results of these kinetic experiments are consistent with the previous equilibrium measurements.[12]

The temperature dependence of the rate constants gives the activation enthalpies and entropies of Table V. A comparison with the corresponding platinum(II) complexes is also given in this table. The anation reactions of the palladium complexes are 4×10^4 to 6×10^4 times faster than those of the platinum complexes. The acid hydrolyses are 1×10^5 to 2×10^5 times faster for palladium. The increased rate of reaction is mainly due to a large decrease of the activation enthalpies compared to platinum.

The activation entropies are negative, indicating an associative reaction mechanism. They are relatively small for the two halide anations of $Pd(H_2O)_4^{2+}$. For these reactions, the loss in entropy due to the association of two reactants to a transition state, is partly cancelled out by a release of solvent water due to the reduced ionic charge of the activated complex. The activation entropies are more negative for the palladium complexes than for the platinum complexes, which might also be due to differences in solvation.

The bromide anation of $Pd(H_2O)_4^{2+}$ is about 5 times faster than the chloride anation. This is the same order of efficiency of these entering ligands as has been observed for platinum(II) complexes.[17]

The acid hydrolyses of $PdCl(H_2O)_3^+$ and $PdBr(H_2O)_3^+$ have the same rate constants and activation parameters. This is a strong indication that the formation of the transition state involves primarily bond formation between the incoming water and the complex, whereas the bond breaking between the complex and the leaving halide should be much less important.

To conclude, the reactions studied appear to be typically square planar substitutions, analogous to the reactions of the corresponding platinum(II) complexes. Subsequently, rate constants and activation parameters for the intermediate reactions of the model given in Figure 1 will be reported.[11] That will make possible a discussion of the *cis*- and *trans*-effects in these complexes.

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