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Stabilities, Solubility, and Kinetics and Mechanism for Formation and Hydrolysis of some Palladium(II) and Platinum(II) Iodo Complexes in Aqueous Solution

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Abstract

Complex formation between Pd(II), Pt(II) and iodide has been studied at 25 °C for an aqueous 1.00 M perchloric acid medium. Measurements of the solubility of $PdI_2(s)$ in aqueous mercury(II) perchlorate and of AgI(s) and $PdI_2(s)$ in aqueous solutions of $Pd^{2+}(aq)$ and $Ag^+(aq)$ gave the solubility product of $PdI_2(s)$ as $K_{s0} = (7 \pm 3) \times 10^{-32}$ M^3, which is much smaller than previous literature values.

The stability constants $\beta_1 = [MI(H_2O)_3^+]/([M(H_2O)_4^{2+}][I^-])$ for the two systems were obtained as the ratio between rate constants for the forward and reverse reactions of (i).

$$M^{2+}(aq) + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MI^+(aq) + H_2O \qquad \text{(i)}$$

The following values of k_1 (s^{-1} M^{-1}), k_{-1} (s^{-1}) and β_1 (M^{-1}) were obtained at 25 °C: $(1.14 \pm 0.11) \times 10^6$, (0.92 ± 0.18), $(12 \pm 4) \times 10^5$ for M = Pd, and (7.7 ± 0.4), $(8.0 \pm 0.7) \times 10^{-5}$, $(9.6 \pm 1.3) \times 10^4$ for M = Pt. Combination with previous literature data gives the following values of $\log(\beta_1\ (M^{-1}))$ to $\log(\beta_4\ (M^{-4}))$: 6.08, ~22, 25.8 and 28.3 for M = Pd, and 4.98, ~25, ~28, and ~30 for M = Pt. The present results show that the large overall stability constants β_4 observed for the M^{2+}–I^- systems are most likely due to a very large stability of the second complex $MI_2(H_2O)_2$, which is probably a *cis*-isomer. A distinct plateau in the formation curve for mean ligand number 2 is obtained both for M = Pd and Pt. The other iodo complexes are not especially stable compared to those of chloride and bromide.

$\Delta H^{\neq}$ (kJ mol^{-1}) and $\Delta S^{\neq}$ (JK^{-1} mol^{-1}) for the forward reaction of (i), M = Pd, are (17.3 ± 1.7) and (-71 ± 5), and for the reverse reaction of (i) M = Pd, (45 ± 3) and (-95 ± 6), respectively. The kinetics are compatible with associative activation (I_a). The contribution from bond-breaking in the formation of the transition state seems to be less important for Pd than for Pt.

Introduction

Both stabilities [1–7] and mechanisms for formation and aquation [7, 8] of square-planar chloro and bromo complexes of palladium(II) and platinum(II) have been comprehensively studied. Much less is known about the corresponding iodo complexes. Investigation of those systems is difficult due to low solubility of PdI_2 [9–11] and PtI_2, easy formation of dinuclear iodide-bridged complexes [12], and very high overall stabilities [6, 13]. Since experiments must be performed in acidic ionic media to prevent hydrolysis of the aqua complexes involved, there might be disturbing redox reactions with I_3^-/I^-, unless air is excluded.

Stability data for the palladium(II) iodo complexes is scarce and in part very discordant [12–17], solubility products of PdI_2 scatter several orders of magnitude [9–11], and there are no studies of the kinetics except for a report on the PdI_4^{2-}–$Pd_2I_6^{2-}$ reaction [12]. As to platinum(II), the overall stability constant for PtI_4^{2-} [9] and the stepwise formation constants for $PtI_3H_2O^-$ and PtI_4^{2-} [18] have been determined. The kinetics for formation of $PtI(H_2O)_3^+$ and *trans*-$PtI_2(H_2O)_2$ from $Pt(H_2O)_4^{2+}$ have also been studied [7].

The present investigation was undertaken in an attempt to obtain a better understanding of the complex formation between iodide and those two metals. We have studied the kinetics for the reversible reaction (M = Pd, Pt)

$$M(H_2O)_4^{2+} + I^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MI(H_2O)_3^+ + H_2O \qquad (1)$$

which gives the rate constants for both forward and back reactions. By use of eqn. (2), those experiments also give the stability constant β_1 defined by eqn. (3).

$$\beta_1 = k_1/k_{-1} \qquad (2)$$

$$\beta_n = [MI_n(H_2O)_{4-n}^{2-n}]/([M(H_2O)_4^{2+}][I^-]^n); \qquad (3)$$

$n = 1,2,3,4$

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We have also measured the solubility of $PdI_2(s)$ in mercury(II) perchlorate solutions, according to eqn. (4):

$$Pd(I)_2(s) + 2Hg^{2+} \rightleftharpoons Pd^{2+} + 2HgI^{+} \qquad (4)$$

Such experiments give the solubility product K_{s0} defined by eqn. (5) and approximate values for the stability constants β_3 and β_4 of the palladium(II) iodide system.

$$K_{s0} = [Pd^{2+}][I^-]^2 \qquad (5)$$

Further check of the solubility product of PdI_2 is given by a study of the solubility of AgI(s) and $PdI_2(s)$ in aqueous perchlorate solutions containing $Pd^{2+}(aq)$ and $Ag^+(aq)$.

An attempt to determine the solubility of $PtI_2(s)$ in mercury(II) perchlorate solutions was unsuccessful. The solubilities calculated were not reproducible, probably due to formation of solid phases containing both platinum and mercury.

The present results, although fragmentary due to the experimental limitations, can be combined with previous literature data [1, 6, 12, 18] to give a relatively good, but still in part only qualitative, picture of the complex formation in those systems.

Experimental

Solutions

Stock solutions (*ca.* 5 mM) of tetraaquapalladium(II) perchlorate and tetraaquaplatinum(II) perchlorate in 1.00 M perchloric acid (Baker's p.a.) were prepared from palladium sponge (Johnson and Matthey, Spec. pure), and K_2PtCl_4 (Johnson and Matthey) and silver perchlorate (G. F. Smith) as described previously [1, 19]. Electrolysis of silver from the platinum(II) perchlorate solutions [19] took about one week and was interrupted when the concentration of silver was smaller than 0.5 μM, which was checked by atomic absorption. C_{Ag}/C_{Pt} was $<10^{-4}$ in these solutions. Iodide solutions were prepared from sodium iodide (Merck Suprapur) dissolved in neutral 1.00 M sodium perchlorate (Baker's p.a., recrystallized once). All solutions were flushed with nitrogen to remove dissolved oxygen. Water was doubly distilled from quartz.

Kinetics

For both reactions, it was necessary to use extremely low concentrations of reactants to prevent precipitation of $MI_2(s)$. Special precautions were necessary to avoid air oxidation of iodide.

The reaction between the tetraaquapalladium(II) and iodide was monitored at 250 nm and three temperatures, by use of a Durrum–Gibson stopped-flow spectrophotometer [8]. Iodide in excess of the palladium complex gave pseudo first-order kinetics. The heat of mixing of the palladium(II) solution (with 1.00 M $HClO_4$) and the iodide solution (with 1.00 M $NaClO_4$) was negligible. Fig. 1 reviews those experiments.

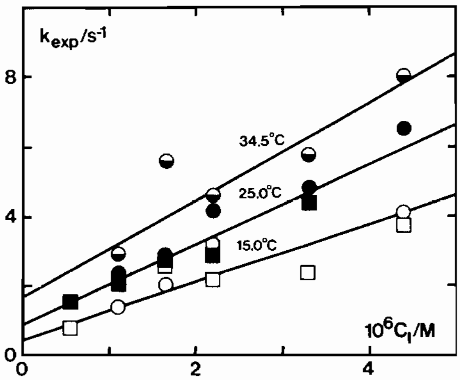

Fig. 1. Observed rate constants for reaction (1), M = Pd, *vs.* excess iodide for a 1.00 M perchlorate medium at 15.0 °C (□, ○), 25.0 °C (■, ●) and 34.5 °C (◒). The total concentration of palladium was 1.24×10^{-7} M (■, □) and 2.48×10^{-7} M (○, ◒, ●). Values of intercepts and slopes in Table II.

Attempts to study the reaction by use of excess palladium(II) instead of excess iodide were difficult to reproduce, probably because of rapid precipitation of $PdI_2(s)$. Precipitation was slower for excess iodide, since the *trans*-$PdI_2(H_2O)_2$ which is formed rapidly under the experimental conditions used probably polymerizes much slower than $PdI(H_2O)_3^+$ and *cis*-$PdI_2(H_2O)_2$, which are predominant in the solutions when excess palladium is used (due to the *trans*-effect of iodide).

The reaction between the platinum complex and iodide was monitored at 225 nm, where iodide has an absorbance maximum with $\epsilon = 13\,500$ cm^{-1} M^{-1} [20]. Pseudo first-order kinetics were obtained for excess platinum. A Zeiss PMQ II spectrophotometer with a cell compartment for 20 cm long cylindrical cells, a logarithmic converter and a chart recorder was used.

The reaction is slow and had to be followed for up to 20 h. To avoid precipitation of $PtI_2(s)$, iodide concentrations less than about 1 μM had to be used. To remove trace amounts of oxidizing impurities, all glassware was carefully rinsed in aqua regia. The titration vessel shown schematically in Fig. 2 and described in more detail elsewhere [21, 22] was used in order to avoid air oxidation and to accomplish a constant temperature (25.0 ± 0.1 °C). It was continuously flushed with nitrogen and was connected with a 20 cm cylindrical cell (Hellma 120-QS) via glass tubings at B and C.

Before measurement, a known volume (≥100 ml) of ionic medium (0.50 M $NaClO_4$ + 0.50 M $HClO_4$) was added to A (capacity 150 ml). The magnetic stirrer was started. After removal of all gas bubbles in the cell and the glass tubings [21],

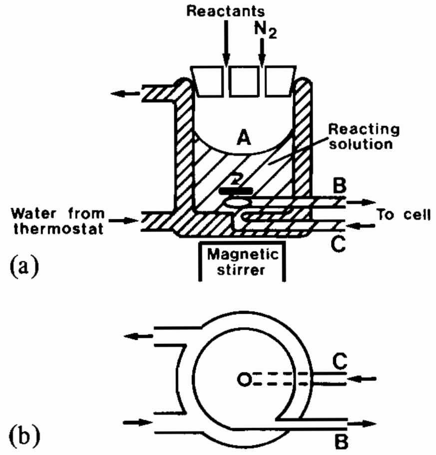

Fig. 2. Cross-section of circulating pump. (a) From the side. (b) From the top. Further details in refs. 21, 22.

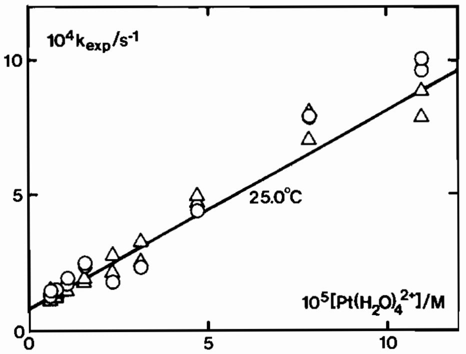

Fig. 3. Observed rate constants for reaction (1), M = Pt, *vs.* excess $Pt(H_2O)_4^{2+}$ at 25.0 °C, 1.00 M perchlorate medium. The total concentration of iodide was 3.3×10^{-7} M (△) and 6.6×10^{-7} M (○). Kinetics were followed by use of a 20 cm flow cell connected to the circulating pump of Fig. 2. Values of intercept and slope in Table II.

the chart recorder was started and a small volume (say 200 μl) of an iodide solution ($C_I = 4.3 \times 10^{-4}$ M, $C_{NaClO_4} = 1.00$ M) was added. The full deflection was recorded within 3 min. Reactions with half-lives of 6 min or more could be monitored. 15 min later an appropriate volume (1 to 30 ml) of tetraaquaplatinum(II) (0.2 or 2.0 mM in 0.50 M $HClO_4$ + 0.50 M $NaClO_4$) was added to give a final volume of 130 ml in all experiments, and the kinetics were recorded. Figure 3 reviews those experiments.

The spectrum of iodide between 260 and 205 nm was checked under the same conditions as used for the kinetics. Even after 15 h the spectrum had changed less than 5 percent, which shows that oxidation of iodide in the acidic solutions was negligible in the apparatus used.

TABLE I. Solubility Measurements According to Reaction (4) at 25 °C. 1.00 M Perchloric Acid Medium

C_{Hg} (mM)	$[HgI^+]$ (mM)[a]	C_{Pd} (mM)[b]	$10^6 K$ (M)[c]
100.0	4.2	2.1	4.0 ± 1.5
50.0	1.6	1.0	1.1 ± 0.3
24.0	1.6	0.7	3.6 ± 1.5
10.0	0.9	0.42	4.1 ± 1.5
5.00	0.57	0.26	4.3 ± 1.5
		Mean =	4 ± 2

[a] From UV spectra. [b] From atomic absorption. [c] Defined by eqn. (8), errors (± 3σ) calculated from the errors in the analyses.

Solubility Measurements

Solid $PdI_2(s)$ prepared as described previously [12] was transferred to five 50 ml Erlenmeyer flasks. 40 ml of aqueous solutions containing various concentrations of mercury(II) perchlorate prepared from HgO (Riedel-de Haen, p.a.) and 1.00 M perchloric acid (Baker's p.a.) was added. The solutions were flushed with nitrogen for 20 min. The flasks were stoppered, wrapped in a foil and placed in a shaking thermostat at 25.0 °C. Spectra of the equilibrated solutions between 250 and 350 nm were recorded after 5 and 12 days. They were practically constant within this interval of time and were compatible with the formation of HgI^+ and $Pd(H_2O)_4^{2+}$, other complexes being negligible. The concentration of HgI^+ was calculated from the 12 days' spectra at 280 nm, where the molar absorptivity of HgI^+ is 1770 cm^{-1} M^{-1} * and those of Hg^{2+} (0.47 cm^{-1} M^{-1}*) and Pd^{2+} (1.10 cm^{-1} M^{-1} [1]) are negligible. The total palladium concentrations of the solutions were measured separately by atomic absorption. In agreement with the stoichiometric relation (4), $C_{Pd} = (0.5 \pm 0.1) \times [HgI^+]$. The concentration of free iodide in those experiments varied in the interval $5 \times 10^{-15} < [I^-] < 2 \times 10^{-14}$ M, as calculated from $[I^-] = ([HgI^+]/[Hg^{2+}]) \times K_1^{-1}$, with the stability constant $K_1 = 10^{12.87}$ M^{-1} [23]. Table I summarizes the experiments.

In another series of experiments, aged precipitates of AgI(s) and $PdI_2(s)$ (*ca.* 100 mg of each) were added to aqueous solutions of $Pd^{2+}(aq)$ and $Ag^+(aq)$ in a 1.00 M N_2-flushed perchloric acid medium. After shaking for *ca.* 1 week at 25.0 °C under nitrogen, the total concentrations of palladium and silver in the supernatant were analyzed by atomic absorption. The following values of 10^3 C_{Pd}/M, 10^3 C_{Ag}/M, and $[I^-]$/M were obtained: 0.200, 0.043, 2.9×10^{-12}; 0.450, 0.061, 2.0×10^{-12}; 2.56, 0.25, 4.9×10^{-13}; 4.72, 12.9, 9.8×10^{-15}; and 9.93, 33.9,

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*Spectra (250 to 300 nm) of Hg^{2+} and HgI^+ were separately determined, the latter by use of a solution with $C_{Hg} = 6.15$ mM and a mean ligand number ≤ 0.25, where $[I^-]$ and HgI_2] can be neglected [23]. The spectrum of HgI^+ has a maximum at 275 nm with $\epsilon = 1850 \pm 20$ cm^{-1} M^{-1}.

3.6×10^{-15}. Values of $[I^-]$ were calculated as $K_{s0,\,AgI}/[Ag^+]$, assuming that $C_{Ag} = [Ag^+]$ and $K_{s0,\,AgI} = 1.26 \times 10^{-16}$ **

Results

Kinetics

For the reversible reaction (1) the rate can be written

$$\text{Rate} = (k_{-1} + k_1[I^-]) \times [M(H_2O)_4{}^{2+}] \quad (6)$$

for excess iodide and

$$\text{Rate} = (k_{-1} + k_1[Pt(H_2O)_4{}^{2+}])[I^-] \quad (7)$$

for excess tetraaquaplatinum(II). In both cases, the observed pseudo first-order rate constant is a linear function of the concentration of excess reactant, as shown by Figs. 1 and 3. The values of k_{-1} and k_1 ($\pm 3\sigma$) given in Table II were obtained from a least-squares calculation of the intercepts and slopes of those plots. k_1 for $Pt(H_2O)_4{}^{2+}$ agrees satisfactorily with the value obtained previously [7] using excess iodide, *cf.* Table II.

Equilibria

The values of β_1 for $PdI(H_2O)_3{}^+$ and $PtI(H_2O)_3{}^+$ obtained from the kinetics according to eqn. (2) are given in Table II. The equilibrium constant K for reaction (4) can be expressed as in eqn. (8):

$$K = [Pd^{2+}][HgI^+]^2/(C_{Hg} - [HgI^+])^2 = K_{s0}\beta_{1Hg}{}^2 \quad (8)$$

where β_{1Hg} is the stability constant for HgI^+ and K_{s0} is the solubility product of PdI_2 according to eqn. (5).

From the values of K given in Table I and $\beta_{1Hg} = 10^{12.87}$ M^{-1} from [23], we get the solubility product $K_{s0} = (7 \pm 3) \times 10^{-32}$ M^3. Combination with previously determined values [12] of

$$K_{s4} = K_{s0}\beta_4 = (1.24 \pm 0.02) \times 10^{-3}\ M^{-1} \quad (9)$$

$$K_4 = \beta_4/\beta_3 = (3.6 \pm 0.6) \times 10^2\ M^{-1} \quad (10)$$

gives the stability constants

$$\beta_4 = (2 \pm 1) \times 10^{28}\ M^{-4}$$

$$\beta_3 = (6 \pm 4) \times 10^{25}\ M^{-3}$$

for $PdI_4{}^{2-}$ and $PdI_3(H_2O)^-$, respectively.

In the solubility experiments with AgI(s) and PdI_2(s), the product $C_{Pd}[I^-]^2$ approaches the solubility product of eqn. (5) when the concentration of free iodide approaches zero, independent of which palladium–iodide or mixed palladium–silver–iodide complexes are formed at higher concentrations. The series of measurements gives $C_{Pd}[I^-]^2$ from 1.7×10^{-27} M^3 for 2.9×10^{-12} M iodide to *ca.* 1.3×10^{-31} M^3 for 3.6×10^{-15} M iodide. Thus, those experiments indicate $K_{s0} < 1.3 \times 10^{-31}$ M^3 for the solubility product of palladium iodide, which compares well with the value of $(7 \pm 3) \times 10^{-32}$ M^3, obtained from reaction (4).

Discussion

The Solubility Product of PdI_2

The present value of $K_{s0} = (7 \pm 3) \times 10^{-32}$ M^3 at 25.0 °C and 1.00 M ionic strength is several orders of magnitude smaller than those reported previously [9–11], which range from 5.59×10^{-13} M^3 for a 0.4 M ionic medium [11] to 2.5×10^{-23} M^3 for pure water [9]. According to our findings, however, super-saturated solutions of PdI_2 are very easily formed. The solutions used here had to be equilibrated for five to twelve days before analysis. Shorter equilibration times gave higher and irreproducible solubilities.

We also observed that freshly prepared PdI_2-precipitates gave too high solubilities. Before use in the present experiments, the precipitates were

TABLE II. Rate Constants ($\pm 3\sigma$) from Figs. 1 and 3 and Stability Constants with Estimated Maximum Errors from eqn. (2) for Reaction (1). 1.00 M Perchlorate Medium

M	t (°C)	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})	10^{-5} β_1 (M^{-1})
Pd	15.0	$(8.3 \pm 1.3) \times 10^5$	0.47 ± 0.22	18 ± 12
	25.0	$(1.14 \pm 0.11) \times 10^6$	0.92 ± 0.18	12 ± 4
	34.5	$(1.4 \pm 0.4) \times 10^6$	1.7 ± 0.8	8 ± 6
Pt	25.0	7.7 ± 0.4	$(8.0 \pm 0.7) \times 10^{-5}$	0.96 ± 0.13
	25.0	9.4 ± 0.2[a]		

[a] Determined from experiments with excess iodide (1–50 mM) [7].

**$K_{s0,\,AgI}$ for 1.00 M $HClO_4$ and 25.0 °C was determined separately by potentiometric titrations with a silver ion selective electrode (Orion 94-16A) and a Ag/AgCl reference [24]. $K_{s0,\,AgI}$ was calculated according to [25] but with the activity coefficients included in the solubility product, cf. [25], eqn. (4). Iterative least-squares calculations gave $pK_{s0,\,AgI}$ = 15.91; 15.89; and 15.90.

TABLE III. Stability Constants β_1 with Estimated Maximum Errors for Halide Complexes $M(H_2O)_3L^+$ at 25 °C. 1.00 M Perchloric Acid Medium

L	$10^{-4}\,\beta_{1Pt}$	$10^{-4}\,\beta_{1Pd}$	Reference
Cl^-	9.4 ± 2.3	2.98 ± 0.06	1, 7
Br^-	19 ± 4	14.7 ± 0.6	1, 7
I^-	9.6 ± 1.3	120 ± 40	This paper

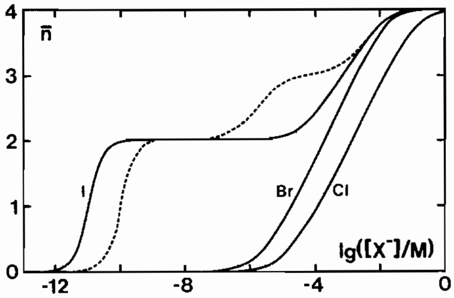

Fig. 4. Tentative complex formation curves for the palladium(II) iodide system. The full-drawn curve calculated from the stability constants of Table IV. The dashed curve is obtained if β_2 is changed to 10^{20} M^{-2}, *cf.* text. For comparison, curves for the bromide and chloride systems from ref. 1 have also been included.

refluxed at ambient temperature for 2 to 3 days with a 0.1 M sodium iodide solution (oxygen absent) [12]. X-ray powder diffractograms indicated a reproducible crystalline structure of the palladium iodide obtained in this manner [12, 26, 27]. Finally, the qualitative agreement between the experiments with mercury(II) and silver(I) speak in favour of the present low value.

Stabilities

Table III compares the values of β_1 for the three halide systems of Pd(II) and Pt(II). Palladium shows the expected b-metal increase in stability $Cl^- < Br^- < I^-$, whereas the stabilities of the three platinum complexes are approximately equal within a factor of two, the bromide complex being a little more stable than the other two. Corain and Poë [18] similarly found that $PtBr_4^{2-}$ is a little more stable than both $PtCl_4^{2-}$ and PtI_4^{2-}.

Table IV gives the known values of β_1, β_3 and β_4 for the palladium(II) iodide complexes. β_2 is not directly measurable because of the extremely low solubility of PdI_2. Only a qualitative estimation can be made here. The product $K_2K_3 = \beta_3/\beta_1$ is as large as $10^{19.7}$ for the iodide system, compared to $10^{7.5}$ for the bromide and $10^{5.7}$ for the chloride systems. This indicates that either $PdI_3H_2O^-$ or $PdI_2(H_2O)_2$ or both these complexes are much more stable than the corresponding bromo and chloro complexes. An extremely large stability of $PdI_3H_2O^-$ is not very probable, however. The other unsymmetric complex with a *trans*-H_2O–I^--axis $PdI(H_2O)_3^+$ is only about ten times more stable than $PdBr(H_2O)_3^+$. A stability constant K_3 for $PdI_3H_2O^-$ of about 10^4 M^{-1} therefore seems reasonable. That gives a value of β_2 of about 10^{22} M^{-2} which corresponds to the full-drawn formation curve of Fig. 4. If $PdI_3H_2O^-$ is more stable (say K_3 about 10^6 M^{-1}) which is less probable, the dashed formation curve of Fig. 4 is obtained. Under all circumstances, it is very likely that there is a distinct stop in the formation curve of the palladium iodide system for a mean ligand number $\bar{n} = 2$, indicating a very large stability of the $PdI_2(H_2O)_2$ complex. The existence of such stops in the formation curves of the square-planar systems has been discussed previously [28] and has been demonstrated for a palladium(II) phosphine system [29].

Noteworthy, the stability trend for PdX_4^{2-}, $\beta_4(PdX_4^{2-})/\beta_4(PdCl_4^{2-}) \approx 1:10^3:10^{17}$ for X = Cl, Br, I as indicated by the β_4-values, is similar to that for square-planar d^8 AuX_4^-, which is $1:10^7:10^{22}$. Those later ratios are given by the known standard potentials [30] for the process $AuX_4^- + 3e^- \rightarrow Au + 4X^-$ and agree with those estimated by Skibsted and Bjerrum from Edward plots [31].

TABLE IV. Stability Constants at 25 °C for Halide Complexes of Pd(II) and Pt(II)

	Pd(II)			Pt(II)		
	Cl[a]	Br[a]	I	Cl[b]	Br[b]	I
log β_1 (M^{-1})	4.47	5.17	6.08[c]	4.97	5.28	4.98
log β_2 (M^{-2})	7.76	9.42	~22[e]	8.97	9.72	~25[h]
log β_3 (M^{-3})	10.17	12.72	25.8[d]	11.89	13.32	~28[g]
log β_4 (M^{-4})	11.54	14.94	28.3[d]	13.99	16.11	~30[f]
Medium		1.00 M $HClO_4$		0.5–1.0 M $HClO_4$	0.5–1.0 M $HClO_4$	Variable

[a] Ref. 1. [b] Ref. 7. [c] This work, kinetics of reaction (1); eqn. (2). [d] This work, solubility measurements combined with K_4 = (360 ± 60) M^{-1} and K_{s4} = (1.24 ± 0.02) × 10^{-3} M^{-1} from ref. 12. [e] Estimated, *cf.* text. [f] Ref. 6. [g] $\beta_3 = \beta_4/K_4$ with K_4 = 50 M^{-1} from ref. 18. [h] $\beta_2 = \beta_3/K_3$ with K_3 = 3 × 10^3 M^{-1} from ref. 18.

The equlibrium constants for the *cis*/*trans*-equilibria of $PdX_2(H_2O)_2$, X = Cl, Br, are 2.1 ± 0.3 and 6.0 ± 0.8, respectively [8]. It is reasonable to expect that this trend continues to the iodide system. Thus, *cis*-$PdI_2(H_2O)_2$ is probably the predominant second complex at thermodynamic equilibrium. This is compatible with the very easy formation of precipitates of PdI_2, since the *cis*-isomer, due to the large *trans*-effect of iodide, has two very reactive aqua ligands. Those are easily involved in polymerization (and precipitation) reactions, forming doubly iodide-bridged complexes. The situation for the platinum system should be similar although the polymerization rates are slower in this case.

The present stability constants for the palladium(II) iodide system differ largely from those reported by Victori *et al.* [17] who report a value of $\log(\beta_4 (M^{-4}))$ of only 14.94 for 20 °C and a 1.00 M perchlorate medium (calculated from spectrophotometry and interpolation). The main reason for this very large discrepancy is probably that those authors neglected the existence of polynuclear complexes in their solutions. Such species are easily formed in large concentrations in solutions of palladium and iodide (contrary to those of chloride and bromide, treated by those authors with identical assumptions) and they have very large molar absorptivities, *cf.* ref. 12.

Srivastava and Newman [32] determined stability constants for mixed halide complex systems of palladium(II). Table V contains the ratios between the overall stability constants β_4 obtained from their experiments together with those calculated from the present work. In view of the large difference in ionic media and strength, the agreement between the Cl–Br systems is satisfactory, whereas the discrepancies for the constants involving iodide complexes are large. We also feel that in this case the neglect of di- or polymeric iodo bridged species, such as $Pd_2I_2Cl_4^{2-}$, might have influenced the interpretation and calculations in ref. 32 strongly.

In the case of platinum(II) the estimation [6] of $\beta_4 \approx 10^{30}$ M^{-4} and the values of Corain and Poë [18] for $K_4 = 50$ M^{-1} and $K_3 \approx 3 \times 10^3$ M^{-1} together with our present β_1-value (differences in ionic media being neglected) gives the stability constants of Table IV. Those also correspond to a formation curve with a long plateau for $\bar{n} = 2$, Fig. 5. This general shape of the formation function is not changed, even if the β_4-value of Grinberg and Gelfman [6] might be wrong by some orders of magnitude (the values of β_4 for the chloro and bromo systems given in ref. 6 are probably between two and four orders of magnitude too large, *cf.* ref 7).

The iodo complexes both of palladium(II) and platinum(II) have generally been considered (based on β_4-estimations) to be much more stable than those of chloride and bromide. The present results show that the large values of the overall stability constants β_4 for the iodo systems compared to those for the chloro and bromo systems, are most likely due to a very large stability of the second complex $MI_2(H_2O)_2$, which is probably a *cis*-isomer. The other iodo complexes are not especially stable compared to those of chloride and bromide.

TABLE V. Logarithmic Ratios between Overall Stability Constants for Palladium(II) Halide Complexes at 25 °C

	Reference 30	This work and reference 7
$\log(\beta_{4I}/\beta_{4Cl})$	12.15 ± 0.35	16.8 ± 0.4
$\log(\beta_{4I}/\beta_{4Br})$	8.25 ± 0.20	13.4 ± 0.4
$\log(\beta_{4Br}/\beta_{4Cl})$	4.14 ± 0.10	3.4 ± 0.17[a]
Ionic strength (M)	4.5	1.00

[a] Reference 7.

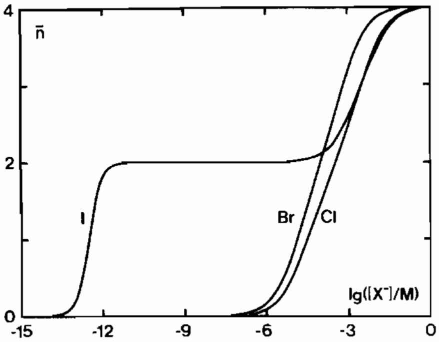

Fig. 5. Qualitative formation curve for the platinum(II) iodide system calculated from the stability constants of Table IV. Varying ionic media, curves for bromide and chloride systems from ref. 7.

Kinetics and Mechanism

Rate constants for formation and hydrolysis of $MX(H_2O)_3^+$; M = Pd, Pt; X = Cl, Br, I; are given in Table VI, and activation parameters for M = Pd in Table VII. For both tetraaqua ions, the order of entering ligand efficiency is $Cl^- < Br^- < I^-$. $Pt(H_2O)_4^{2+}$ has a somewhat better discriminating ability between those entering ligands than $Pd(H_2O)_4^{2+}$ (1:8:300 compared to 1:5:60).

The nature of the leaving ligand influences the rates of hydrolysis of $PtX(H_2O)_3^+$ ($Cl^- < Br^- < I^-$ = 1:4:290), whereas the rate of hydrolysis of $PdX(H_2O)_3^+$ is practically independent of which halide is the leaving ligand at 25 °C. An inspection of the activation parameters of Table VII, however, reveals that this apparent constancy of k_{-1} for the acid hydrolysis of $PdX^+(aq)$ is due to a close balance between the $\Delta H^{\neq}$ and $T\Delta S^{\neq}$ contributions to the free energy of activation.

TABLE VI. Rate Constants for Halide Complexes at 25 °C. 1.00 M Perchloric Acid Medium

Reaction	X	Rate constant	k_{Pt}	k_{Pd}	k_{Pd}/k_{Pt}	Reference
$M(H_2O)_4^{2+} + X^- \rightarrow$	Cl	k_1 ($M^{-1} s^{-1}$)	2.66×10^{-2}	1.83×10^4	7×10^5	1, 7
	Br		2.11×10^{-1}	9.2×10^4	4×10^5	1, 7
	I		7.7	1.14×10^6	1.4×10^5	This paper
$M(H_2O)_3X^+ + H_2O \rightarrow$	Cl	k_{-1} (s^{-1})	2.8×10^{-7}	0.83	3×10^6	1, 7
	Br		1.1×10^{-6}	0.83	8×10^5	1, 7
	I		8.0×10^{-5}	0.92	1.2×10^4	This paper

TABLE VII. Rate Constants and Activation Parameters with Estimated Maximum Errors at 25 °C for the Reaction $Pd^{2+} + X^- \rightleftharpoons PdX^+$. Aqua Ligands Excluded

Reaction	Rate constant	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ ($JK^{-1} mol^{-1}$)	Reference
	$10^4 k_1$ ($M^{-1} s^{-1}$)			
$Pd^{2+} + Cl^- \rightarrow PdCl^+$	1.83	41 ± 4	−25 ± 12	1
$Pd^{2+} + Br^- \rightarrow PdBr^+$	9.2	41.7 ± 1.1	−10 ± 4	1
$Pd^{2+} + I^- \rightarrow PdI^+$	114	17.3 ± 1.7	−71 ± 5	This work
	k_{-1} (s^{-1})			
$PdCl^+ \rightarrow Pd^{2+} + Cl^-$	0.83	58 ± 8	−51 ± 24[a]	1
$PdBr^+ \rightarrow Pd^{2+} + Br^-$	0.83	50 ± 3	−81 ± 9[a]	1
$PdI^+ \rightarrow Pd^{2+} + I^-$	0.92	45 ± 3	−95 ± 6[a]	This work

[a] Calculated for first-order rate constants.

Those results are in qualitative agreement with previous studies, for instance refs. 1 and 7, and are compatible with an associative activation (I_a), in which formation of the transition state involves bond formation between the incoming ligand and the complex. Bond breaking seems to be much less important in the case of palladium than of platinum. The negative entropies of activation are also in accordance with this interpretation.

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Note Added in Proof

A recent determination [33] of the equilibrium constant for the dimerization $2PtI_4^{2-} \rightleftarrows Pt_2I_6^{2-} + 2I^-$ gives 9 ± 3 M to be compared with 20 ± 2 M for the corresponding palladium complex reaction [12].