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The Stepwise Dissociation of the Tetrachloroplatinate(II) Ion in Aqueous Solution

VI. Rates of Formation and Equilibria of the Chloro Aqua Complexes of Platinum(II)

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Equilibrated solutions of K_2PtCl_4 contain measurable concentrations of the species $PtCl_n(H_2O)_{4-n}^{2-n}$; $n=1, 2, 3, 4$. At equilibrium, 55 % of the neutral complex $PtCl_2(H_2O)_2$ is present as the *cis*-isomer, 45 % as the *trans*-isomer. The equilibrium constants of the system are given in Table 2 for 15, 25, 35, and 60°C.

The above mentioned species are formed by consecutive acid hydrolysis reactions, starting from $PtCl_4^{2-}$. These have been studied; the rate constants are given in Table 5 for 15, 25, and 35°C. Ionic strength 0.500 M; medium $HClO_4$.

The reaction model previously [1, Fig. 1] used to describe the chloride anations of the chloro aqua complexes of platinum(II) includes two geometrical isomers of the neutral species $PtCl_2(H_2O)_2$. The equilibrium constant, $K_{c/t}$, is defined as

$$K_{c/t} = [cis\text{-}PtCl_2(H_2O)_2]\cdot[trans\text{-}PtCl_2(H_2O)_2]^{-1} \quad (1)$$

The total concentration of *trans*-$PtCl_2$* and $PtCl^+$ present in the equilibrated solution may be calculated from measurements of the rate of chloride anation of *trans*-$PtCl_2$ studied earlier.[1] The concentrations of $PtCl_2$ (*i.e.* the sum of the concentrations of the *cis*- and *trans*-complexes), and $PtCl^+$ may be obtained from the equilibrium constants determined previously.[2] Thus, the concentrations of *cis*- and *trans*-$PtCl_2$ may be calculated and $K_{c/t}$ obtained.

The rates of formation of *trans*-$PtCl_2$ and $PtCl^+$ and of $PtCl_3^-$ and *cis*-$PtCl_2$ by the consecutive acid hydrolysis reactions, starting from $PtCl_4^{2-}$, have also been studied. These reactions, too, may be described by the reaction model used earlier.[1, Fig. 1]

* In the text to follow, the water ligands will be omitted.

THE EQUILIBRIUM *cis-/trans*-$PtCl_2(H_2O)_2$

Experimental

Chemicals and apparatus were the same as in Refs. 3 and 4.

Measurements. Solutions of K_2PtCl_4 ($5\times10^{-5}-5\times10^{-3}$ M; Table 1) containing $HClO_4$ (0.500 M) were aged at 25.0, 35.0, or 60.0°C. The time required to reach equilibrium was about 70 days at 25°C, about 25 days at 35°C and less than 3 days at 60°C. The equilibrated solutions were mixed with stock solutions containing HCl and $HClO_4$ and having the ionic strength 0.500 M. The concentration of chloride of the resulting solution became 0.250 M. The slow increase of absorbance at 230 nm due to the chloride anation of *trans*-$PtCl_2$ was followed at 25.00 or 35.00°C as described in Ref. 1. Fig. 1 shows some examples of such experiments. The solutions equilibrated at 60°C were rapidly chilled [3,p.1332] to 25°C before starting these kinetic runs. At equilibrium, the solutions will contain [5,Fig.5] 95 % of the platinum as $PtCl_4^{2-}$ and 5.0 % as $PtCl_3^-$.

Table 1. The equilibrium *cis/trans*-$PtCl_2(H_2O)_2$. C_{Pt} is the total concentration of platinum of the equilibrated solutions in M. α_1 and α_2 were calculated from the equilibrium constants, K_4, K_3 and K_2, given in Table 2.

Temperature °C	$C_{Pt}\times10^3$	α_1	α_2	α_{exp} Eqn.(7)	$K_{c/t}$ Eqn.(9)	$K_{c/t}$ Mean
	2.505	0.010	0.274	0.130	1.28	
	1.002	0.030	0.441	0.221	1.31	
	0.750	0.043	0.494	0.257	1.31	
	0.501	0.067	0.561	0.316	1.25	
25.0	0.401	0.085	0.592	0.340	1.32	1.2 ± 0.1
	0.301	0.112	0.621	0.379	1.33	
	0.2005	0.163	0.642	0.452	1.22	
	0.1002	0.284	0.616	0.583	1.06	
	0.0750	0.341	0.584	0.612	1.15	
	0.0501	0.433	0.520	0.674	1.16	
	2.019	0.015	0.332	0.167	1.18	
	1.009	0.035	0.461	0.250	1.14	
35.0	0.807	0.045	0.505	0.279	1.16	1.2 ± 0.1
	0.505	0.076	0.577	0.338	1.20	
	0.2523	0.149	0.639	0.451	1.12	
	5.00	0.007	0.225	0.105	1.30	
	2.500	0.017	0.341	0.168	1.26	
	1.004	0.051	0.509	0.279	1.23	
	0.753	0.070	0.555	0.322	1.20	
	0.500	0.107	0.606	0.384	1.19	
60.0	0.400	0.133	0.624	0.421	1.17	1.2 ± 0.1
	0.300	0.172	0.635	0.467	1.31	
	0.2000	0.238	0.627	0.539	1.08	
	0.1000	0.381	0.554	0.631	1.22	
	0.0700	0.464	0.493	0.698	1.11	
	0.0500	0.546	0.427	0.735	1.26	

Calculations and results

α_1, α_t, and α_c denote the mole fractions of platinum, present in the initial, equilibrated solution as $PtCl^+$, *trans*-$PtCl_2$ and *cis*-$PtCl_2$. We define

$$\alpha_2 = \alpha_t + \alpha_c \quad (2)$$

The values of α_1 and α_2 given in Table 1 were obtained from the equilibrium constants K_n, $n = 2,3,4$, determined previously [2] and given in Table 2.

When chloride is added in excess to these equilibrated solutions, the main part of $PtCl^+$ reacts almost instantly with chloride, forming *trans*-$PtCl_2$ (Ref. 1, p. 1351). The equilibria between *cis*-$PtCl_2$, $PtCl_3^-$ and $PtCl_4^{2-}$ are also established quite quickly. The absorptivity of the solution when these rapid reactions are complete, but no *trans*-$PtCl_2$ has reacted with chloride, is

$$e_0 = \varepsilon_t ([I] + [t]) + \varepsilon_{eq} (C_{Pt} - [I] - [t]) \quad (3)$$

Here, [I] and [t] stand for the initial concentrations of $PtCl^+$ and *trans*-$PtCl_2$ before the rapid chloride anation of $PtCl^+$ has occurred and C_{Pt} denotes the total concentration of platinum. ε_t and ε_{eq} are the molar absorptivities of *trans*-$PtCl_2$ and of the equilibrium mixture of $PtCl_3^-$ and $PtCl_4^{2-}$, formed by the reaction.

At equilibrium, when the slow chloride anation of *trans*-$PtCl_2$ is complete, the solution contains $PtCl_3^-$ and $PtCl_4^{2-}$ exclusively (only 0.1 % of the platinum is left as $PtCl_2$), and its absorptivity will be

$$e_\infty = \varepsilon_{eq} C_{Pt} \quad (4)$$

The fraction of platinum, present as $PtCl^+$ and *trans*-$PtCl_2$ in the original solution may be obtained from eqns. (3) and (4) as

$$\alpha_1 + \alpha_t = C \alpha_{exp} \quad (5)$$

where

$$C = \varepsilon_{eq} (\varepsilon_{eq} - \varepsilon_t)^{-1} \quad (6)$$

and

$$\alpha_{exp} = (e_\infty - e_0) e_\infty^{-1} \quad (7)$$

By extrapolation of the logarithmic plots of the kinetic runs to zero time (Fig. 1) the quantity $(e_\infty - e_0)$ is obtained and α_{exp} may be calculated from eqn. (7). The values obtained are given in Table 1. Eqns. (1) – (5) give

$$\alpha_2 \alpha_1^{-1} = \alpha_{exp} \alpha_1^{-1} C(1 + K_{c/t}) - (1 + K_{c/t}) \quad (8)$$

In Fig. 2, plots of $\alpha_2 \alpha_1^{-1}$ *vs.* $\alpha_{exp} \alpha_1^{-1}$ for the measurements at the three temperatures are given. The graphs coincide, having identical intercepts and slopes. Thus the equilibrium constant, $K_{c/t} = 1.2 \pm 0.1$, obtained from the intercept, does not vary within the interval of temperature studied. At equilibrium, about 55 % of the neutral complex is present as *cis*-$PtCl_2$ and about 45 % as *trans*-$PtCl_2$.

The constant C of eqn. (6), obtained from the slope of the straight line (8), is 1.0 ± 0.1. Thus, ε_t is negligible compared to ε_{eq} in the numerator of eqn. (6). Since ε_{eq} is 7720 $cm^{-1} M^{-1}$ (Ref. 2, p. 1338), ε_t will be less than, say,

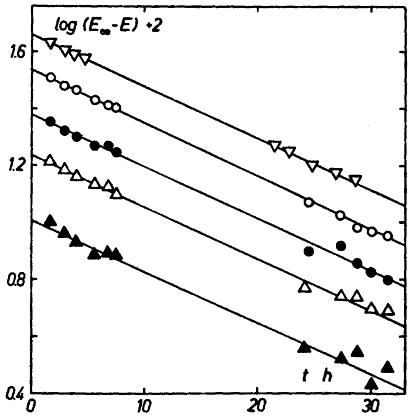

Fig. 1. log $(E_\infty - E)$ *vs.* t for kinetic runs used to determine the amount of *trans*-$PtCl_2 + PtCl^+$ present in equilibrated solutions of K_2PtCl_4 (C_{Pt} M). These solutions were mixed with stock solutions of HCl and $HClO_4$, so that the concentration of chloride became 0.250 M and the concentration of platinum 1.002×10^{-4} M (○, ●, △, ▲) or 5.01×10^{-5} M (▽). The absorbance of these solutions, E, was measured as a function of time in 1.000 or 2.000 cm cells, respectively. The experiments shown have the following values of $C_{Pt} \times 10^3$ M, $E_\infty - E_0$, E_∞ and α_{exp}: 0.1002, 0.456, 0.782, 0.583 (▽); 0.2005, 0.349, 0.772, 0.452 (○); 0.501, 0.243, 0.775, 0.314 (●); 1.002, 0.173, 0.785, 0.221 (△); 2.505, 0.102, 0.783, 0.130 (▲).

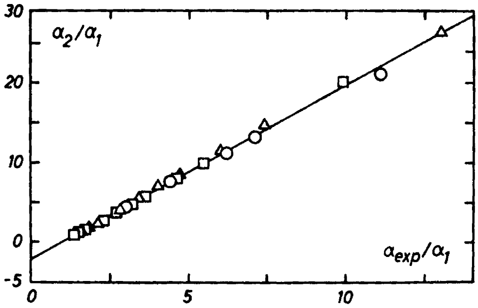

Fig. 2. $\alpha_2\alpha_1^{-1}$ as a function of $\alpha_{exp}\ \alpha_1^{-1}$ according to eqn. (8) for measurements at 25 (△), 35 (○), and 60°C (□).

800 $cm^{-1}M^{-1}$. Attempts to calculate ε_t from the molar absorptivities of equilibrated solutions fail, since ε_t is obtained as a small difference between almost equal, large numbers.*

Since C is equal to unity within the experimental errors, eqn. (8) reduces to

$$K_{c/t} = \alpha_2\,(\alpha_{exp} - \alpha_1)^{-1} - 1 \tag{9}$$

The constants calculated from this approximate relation are also given in Table 1.

The constant $K_{c/t}$, obtained in this manner, and the equilibrium constants K_3 and K_2 determined previously,[2] were used to calculate the constants K_{3c}, K_{3t}, K_{2c}, and K_{2t}, defined in Ref. 1, Fig. 1. The values calculated are given in Table 2.

* From the values of $\varepsilon_2 = 700$ (Ref. 2, Table 2), $\varepsilon_c = 1100$ (*vide infra*), and $K_{c/t} = 1.2$, a value of $\varepsilon_t = 210$ may be calculated. This agrees with the value of $C = 1.0$ obtained here.

Table 2. Equilibrium constants. Notation in Ref. 1, Fig. 1. $K_{c/t}$ is defined by eqn. (1). All values, except for $K_{c/t}$, are given in M.

Constant	15°C	25°C	35°C	60°C	Ref.
K_4 $\times 10^2$	1.1 ± 0.1^a	1.26 ± 0.09	1.5 ± 0.1^a	2.06 ± 0.15	2
K_3 $\times 10^3$	1.2 ± 0.1^a	1.4 ± 0.1	1.5 ± 0.1^a	2.00 ± 0.15	2
$K_{c/t}$	1.2 ± 0.1^a	1.2 ± 0.1	1.2 ± 0.1	1.2 ± 0.1	This paper
K_{3c} $\times 10^4$	7 ± 2	8 ± 2	8 ± 2	11 ± 3	» »
K_{3t} $\times 10^4$	5 ± 1	6 ± 2	7 ± 2	9 ± 2	» »
K_2 $\times 10^4$	—	1.0 ± 0.1	1.1 ± 0.1^a	1.6 ± 0.1	2
K_{2c} $\times 10^4$	—	1.8 ± 0.5	2.0 ± 0.5	2.9 ± 0.7	This paper
K_{2t} $\times 10^4$	—	2.2 ± 0.5	2.4 ± 0.6	3.5 ± 0.9	» »

[a] Values obtained by inter- or extrapolation.

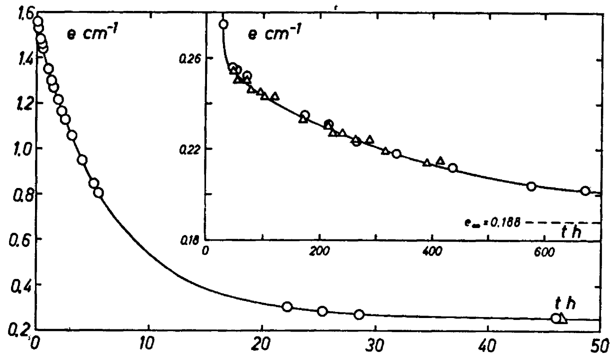

Fig. 3. The absorptivity at 230 nm as a function of time at 25°C for two aging solutions of K_2PtCl_4 (each 2.00×10^{-4} M) containing $HClO_4$ (0.500 M). The fast change, lasting for about 30 h, is due to the formation of $PtCl_3^-$ and *cis*-$PtCl_2$. The subsequent, slow decrease is caused by the formation of *trans*-$PtCl_2$ and $PtCl^+$.

FORMATION OF *trans*-$PtCl_2(H_2O)_2$ AND $PtCl(H_2O)_3^+$

The chloride anation of *trans*-$PtCl_2$ and $PtCl^+$ was studied previously.[1] The reverse, slow formation of these complexes in aging solutions of K_2PtCl_4 may be studied using the decrease of absorbance at 230 nm, lasting for about 60 days (Fig. 3). The formation of these species may also be followed by taking samples of the aging solution and analysing these to find the total concentration of *trans*-$PtCl_2$ and $PtCl^+$, as described in the previous section.

Experimental

Chemicals and apparatus were the same as in Refs. 3 and 4.

Measurements. (i). The decrease of absorbance of aging solutions of K_2PtCl_4, containing 0.500 M $HClO_4$ (Table 3), was followed in 1, 2, or 5 cm cells for about 30 days at 25.0°C and for about 10 days at 35.0°C. Fig. 3 shows a typical plot. The equilibrium values, E_∞, were measured after about 60 and 30 days, respectively. They remained constant for several months.

(ii). Solutions (Table 3) were aged at 25.0°C. Samples were taken during a period of about 600 h. These were mixed with stock solutions containing HCl and $HClO_4$ (ionic strength 0.500 M), so the concentration of chloride of the resulting solution became 0.250 M. The slow increase of absorbance at 230 nm due to the chloride anation of the equilibrium mixture of *trans*-$PtCl_2$ and $PtCl^+$ was followed. Fig. 4 shows examples of such experiments. The mole fraction of platinum present as *trans*-$PtCl_2$ and $PtCl^+$, α_{exp}, was calculated as a function of time from eqn. (7).

Table 3. Formation of *trans*-$PtCl_2$ and $PtCl^+$ in aging solutions of K_2PtCl_4. Concentrations are in mM, k_{exp} in s^{-1} and k_{2c-} in $s^{-1}M^{-1}$. The concentration of free chloride varied between b_0 and b_∞ during the course of reaction. α_c' and α_3' are defined by eqns. (13) and (14), k_{2c-} was calculated from eqn. (16).

C_{Pt}	C_{Cl}	b_0	b_∞	α_{c0}'	$\alpha_{c\infty}'$	α_{30}'	$\alpha_{3\infty}'$	$k_{exp}\times 10^7$	$k_{2c-}\times 10^3$
					25°C				
1.000	4.00	1.31	1.45	0.34	0.31	0.60	0.61	7.3[b]	2.7
0.750	3.34	1.32	1.43	0.34	0.31	0.60	0.61	6.8[b]	2.4
0.500	2.68	1.35	1.41	0.34	0.31	0.60	0.61	6.6[b]	2.4
0.2000	1.88	1.35	1.37	0.34	0.31	0.60	0.61	5.5[b]	1.9
0.500	2.00	0.73	0.84	0.49	0.46	0.48	0.51	6.4[b]	2.3
0.500	2.00	0.73	0.84	0.49	0.46	0.48	0.51	7.5[a]	2.8
0.2000	0.800	0.34	0.39	0.68	0.60	0.31	0.32	7.0[b]	2.7
0.2000	0.800	0.34	0.39	0.68	0.60	0.31	0.32	7.4[a]	2.8
0.1000	0.400	0.18	0.22	0.80	0.77	0.20	0.22	7.7[b]	3.1
0.1000	0.400	0.18	0.22	0.80	0.77	0.20	0.22	7.3[a]	2.9
								Mean	2.6 ± 0.6
					35°C				
0.557	2.223	0.82	0.93	0.49	0.46	0.48	0.51	24[a]	7.6
0.2230	0.891	0.37	0.44	0.68	0.65	0.31	0.34	23[a]	7.6
0.1110	0.446	0.20	0.24	0.80	0.77	0.19	0.22	23[a]	8.0
								Mean	7.7 ± 1

[a] Calculated from plots of eqn. (17).
[b] Calculated from plots of eqn. (18).

Calculations and results

During the first 25 h of aging, an equilibrium between $PtCl_4^{2-}$, $PtCl_3^-$ and *cis*-$PtCl_2$ is established. This equilibrium mixture is reacting to *trans*-$PtCl_2$ and $PtCl^+$ which are also in a rapid equilibrium with each other (*vide* Fig. 8).

Using the previous [1, Fig. 1] notation, the rate of formation of the latter two species may be written

$$\frac{dx}{dt} = k_{2c}\,[cis\text{-}PtCl_2] + k_{3t}\,[PtCl_3^-] - k_{2c-}\,b\,[PtCl^+] - k_{3t-}\,b\,[trans\text{-}PtCl_2] \qquad (10)$$

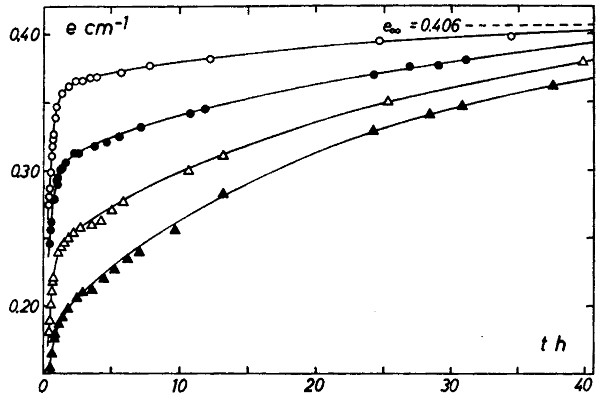

Fig. 4. Change of absorptivity with time at 230 nm and 25°C, due to the chloride anation of *trans*-$PtCl_2$ and $PtCl^+$. Samples of an aging solution of K_2PtCl_4 (10^{-4} M) in $HClO_4$ (0.500 M) were mixed with equal volumes of HCl (0.5 M). The age of the platinum solution was: ○36, ●180, △550, and ▲2000 h (equilibrium reached).

where

$$x = [PtCl^+] + [trans\text{-}PtCl_2] \tag{11}$$

If the concentration of free chloride, b M, is a constant – which is an approximation – the following equations will be valid:

$$[PtCl^+]\, b\, [trans\text{-}PtCl_2]^{-1} = K_{2t} \tag{12}$$

$$[cis\text{-}PtCl_2] = \alpha_c' \,(C_{Pt} - x) \tag{13}$$

$$[PtCl_3^-] = \alpha_3' \,(C_{Pt} - x) \tag{14}$$

Here, α_c' and α_3' denote the mole fractions of platinum present as *cis*-$PtCl_2$ and $PtCl_3^-$ in the initial equilibrium mixture. C_{Pt} is the total concentration of platinum. Eqns. (10) – (14) give

$$dx/dt = k_{exp}\,(x_\infty - x) \tag{15}$$

Introducing $k_{2c} = k_{2c-}\,K_{2c}$ and $k_{3t} = k_{3t-}\,K_{3t}$, k_{exp} may be written

$$k_{exp} = k_{2c-}\,(K_{2c}\alpha_c' + b\,K_{2t}\,(b + K_{2t})^{-1}) + k_{3t-}\,(K_{3t}\,\alpha_3' + b^2\,(b + K_{2t})^{-1}) \tag{16}$$

Integrating eqn. (15) and substituting concentrations by absorptivities or, alternatively, by the fraction α_{exp}, defined by eqn. (7), we arrive at

$$\ln(e - e_\infty) = -k_{exp}\,t + const. \tag{17}$$

or

$$\ln(\alpha_{exp\infty} - \alpha_{exp}) = -k_{exp}\,t + const. \tag{18}$$

Figs. 5 and 6 give examples of logarithmic plots used to determine k_{exp} according to eqns. (17) and (18). The uncertainty of k_{exp} obtained from the slopes was about 10 %. The values are given in Table 3. The two methods give accordant results within the experimental accuracy.

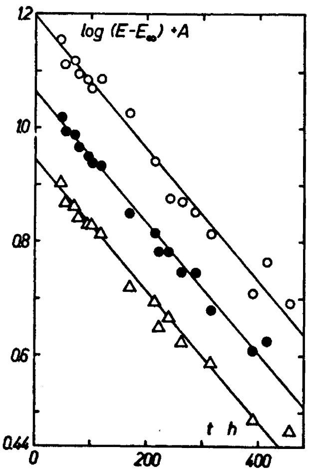

Fig. 5. Plots of log $(E-E_{\infty})$ *vs.* t for the formation of *trans*-$PtCl_2$ and $PtCl^+$ at 25°C, 230 nm. The concentration of platinum was 0.501 (○), 0.2005 (●), and 0.1003 (△) mM. The term A added to the ordinates was 2.00 (○), 1.90 (●), and 1.64 (△).

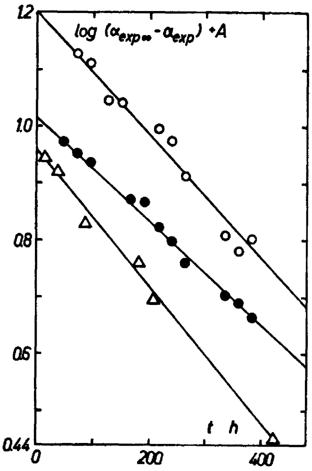

Fig. 6. Plots of log $(\alpha_{\exp\infty}-\alpha_{\exp})$ *vs.* t for the formation of *trans*-$PtCl_2$ and $PtCl^+$ at 25°C. The concentration of platinum was 1.002 (○), 0.501 (●) and 0.1056 (△) mM. The term A added to the ordinates was 1.90 (○), 1.60 (●), and 1.25 (△).

The rate constant k_{2c-} given in Table 3 was calculated from eqn. (16), using the values of the equilibrium constants of Table 2 and of the rate constant k_{3t-} determined previously.[1]

Deducing eqn. (15), the concentration of chloride, b, and the fractions α_c' and α_3' were assumed to be constant. Adding extra chloride in excess to platinum in order to keep b constant would have stopped the reaction. All free chloride present originated from the dissociation of the complexes and varied between the value b_0, the concentration before the start of the slow reaction, and b_{∞}, the concentration at the final equilibrium. These values, and the corresponding values of α_c' and α_3', were calculated from the equilibrium constants of Table 2, and are given in Table 3. The variation of b does not exceed 20 %, so the approximation used will be fairly good. The mean of the b's given in Table 3 was used for the calculation of k_{2c-} from eqn. (16).

The values of $k_{\exp}$ given in Table 3 correspond to half-lives for the formation of *trans*-$PtCl_2$ and $PtCl^+$ of about 270 h at 25°C and 80 h at 35°C. Since the rate constants k_{3t} and k_{3t-} (Table 5 and Ref. 1) correspond to half-lives of 2700 h at 25°C and 700 h at 35°C, and at $b=10^{-3}$(M), the direct formation of *trans*-$PtCl_2$ by acid hydrolysis of $PtCl_3^-$ has only minor importance. The major path for the formation of this complex in aging solutions is the reaction *via* the species *cis*-$PtCl_2$ and $PtCl^+$.

The rate constant k_{2c-} obtained from eqn. (16) should agree with the approximate values obtained in the previous paper [1, Table 5] from measurements of the reverse chloride anation. These were $(1\pm1)\times10^{-3}$ s^{-1} at 25°C and $(3\pm2)\times10^{-3}$ s^{-1} at 35°C. The present values, $(2.6\pm0.6)\pm10^{-3}$ s^{-1} and $(7.7\pm1)\times10^{-3}$ s^{-1} are somewhat higher. However, in view of the great experimental uncertainties, the agreement is obviously good enough not to invalidate the reaction model proposed.

FORMATION OF $PtCl_3(H_2O)^-$ AND *cis*-$PtCl_2(H_2O)_2$

The initial, fast change of absorbance of aging solutions, complete within about one day (Fig. 3), is due to the formation of $PtCl_3^-$ and *cis*-$PtCl_2$. The further reaction to *trans*-$PtCl_2$ and $PtCl^+$ is much slower and may be neglected during the first 25 h (*vide* Fig. 8). The following equations are valid for the rate of disappearance of $PtCl_4^{2-}$ and of formation of *cis*-$PtCl_2$ (notation in Ref. 1, Fig. 1):

$$dy/dt = k_4 (C_{Pt} - y) - k_{4-} (y^2 - z^2) \tag{19}$$

$$dz/dt = k_{3c} (y - z) - k_{3c-} z (y + z) \tag{20}$$

C_{Pt} denotes the total concentration of platinum, $(y-z)$ and z are the concentrations of $PtCl_3^-$ and *cis*-$PtCl_2$ at time t.

Table 4. Determination by curve fitting of the rate constant k_4 s^{-1} at 25°C from kinetic runs at 315 or 230 nm. The concentration of platinum was C_{Pt} M.

λ	$C_{Pt}\times10^4$	$k_4\times10^5$
	106.9	3.6
315	53.6	3.6
	32.9	3.6
	11.2	3.9
	4.8	4.1
	1.95	4.3
230	1.00	4.7
	0.49	6.1
	0.21	6.4

The change of absorbance with time for some aging solutions ($2\times10^{-5}<C_{Pt}<5\times10^{-4}$(M); Table 4) containing no extra chloride were recorded at 230 nm. C_{Pt} and the values of the rate constants determined previously were introduced into eqns. (19) and (20). The concentrations of the complexes were calculated as a function of time using the Runge-Kutta method [8] and a high-speed computer. The left part of Fig. 8 gives the result of such a calculation. The change of absorptivity of the complex solution with time was then calculated from the molar absorptivities of the complexes. ε_4 and ε_3 have been previously [3,p.2562] determined to be 8020 and 2060 cm^{-1} M^{-1}, respectively, ε_c was chosen as 1100 cm^{-1} M^{-1} (*vide infra*). Three such curves are shown in Fig. 7.

The over-all change of absorptivity with time at 230 nm during the first 10 h is due almost exclusively to the disappearance of the complex $PtCl_4^{2-}$, which has the greatest molar absorptivity. The shape of this part of the curve is therefore determined by the rate constant k_4 and the molar absorptivity ε_4 (ε_3 has only minor influence, and the reverse reaction, described by k_{4-}, may be neglected). Since ε_4 is known with good precision (better than 1 %), k_4 can be determined from this part of the curve by variation until the best fit between the calculated curve and the experimental points is obtained (*vide* Fig. 7). The values of k_4 determined by such curve-fitting for solutions having different C_{Pt} are given in Table 4, which also includes some analogous experiments performed at 315 nm, using more concentrated solutions.

It appears from the table that the value of k_4 increases when C_{Pt} and the concentration of free chloride ions decreases. The value of k_4 obtained earlier [1,3] from measurements with chloride ions in excess, was 3.6×10^{-5} s^{-1}, which agrees with the value obtained here for the most concentrated solutions. In these previous measurements, the concentration of chloride was never smaller than 5×10^{-3} M, whereas C_{Pt} varied between 10^{-2} and 5×10^{-5}, *i.e.* within the same limits as here.

The increasing rate of acid hydrolysis of $PtCl_4^{2-}$ observed here for very low values of the concentrations of *both* complex and chloride may possibly be due to some additional mechanism of reaction. A catalyzed reaction path seems most probable. A disappearance of $PtCl_4^{2-}$ by disproportionation to Pt(0) and Pt(IV) is favoured by low concentrations of chloride (Ginstrup and Leden [9]), but no detectable amounts of Pt(IV) could be found in the solutions – the spectrum of $PtCl_4^{2-}$ reappeared when chloride was added in excess. However, even small concentrations of Pt(IV) or colloidal Pt(0) might act as catalysts. A catalyst might also form by the action of light, since it was observed that exposing the solutions to daylight increased the rate of reaction at these low concentrations. The reproducibility of the measurements was also less good than previously. The possibility of a simple dissociation

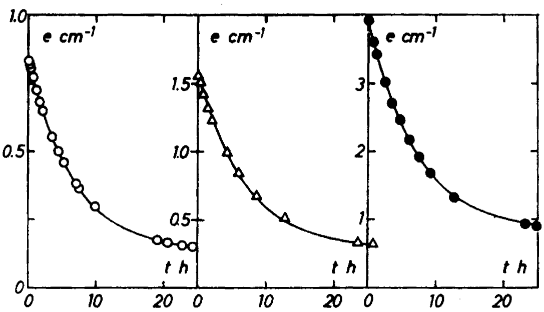

Fig. 7. The absorptivity at 230 nm as a function of time at 25°C for three aging solutions of K_2PtCl_4, 0.1035 (○), 0.1960 (△), and 0.489 (●) mM. The fulldrawn curves have been computed from eqns. (19) and (20). The following values of k_4 were used: 4.4×10^{-5} (○), 4.2×10^{-5} (△), and 3.9×10^{-5} (●) s^{-1}. The other parameters were: k_{4-} 2.8×10^{-3} s^{-1} M^{-1}; k_{3c} 5.6×10^{-5} s^{-1}; k_{3c-} 7.5×10^{-3} s^{-1} M^{-1}; ε_4 8020 cm^{-1} M^{-1}; ε_3 2060 cm^{-1} M^{-1} and ε_c 1100 cm^{-1} M^{-1}.

mechanism in addition to the usually suggested S_N2-mechanism seems less probable.[6,p.376]

The shape of the later parts (10–25 h) of the absorptivity *vs.* time curves of Fig. 7 is determined by the molar absorptivities ε_c and, less important, by ε_4 and ε_3, and by the rate constants k_4, k_{3c} and, to a small extent, k_{3c-}. Since ε_4, ε_3, and k_4 are already fixed, the fit between experimental and calculated curves may be improved by adjusting k_{3c} and ε_c. A variation of the former by 50 % only changes the curve slightly, whereas the value of ε_c has greater influence. Therefore, ε_c can be calculated by curve-fitting, using the value of k_{3c} determined in previous measurements (Table 5). ε_c was obtained as 1100 ± 100 cm^{-1} M^{-1}. A small systemic error in this value is possible because of the subsequent slow formation of *trans*-$PtCl_2$ and $PtCl^+$ (Fig. 8), and because of the error of ε_3. Since it has not been possible to calculate ε_c by some other method, no control of the rate constants k_{3c} and k_{3c-} can be obtained, using these measurements.

Table 5. Acid hydrolysis rate constants in s^{-1}, calculated from the equilibrium constants of Table 2 and the chloride anation rate constants given in Ref. 1, Table 5. The activation enthalpy, $\Delta H^{\circ\ddagger}$, is in kcal mol^{-1} and the activation entropy, $\Delta S^{\circ\ddagger}$, in cal mol^{-1}K^{-1} (standard state of water: unit mole fraction).

Constant	15°C	25°C	35°C	$\Delta H^{\circ\ddagger}$	$\Delta S^{\circ\ddagger}$
$k_{3c} \times 10^5$	1.7 ± 0.4	6 ± 1	17 ± 4	20	−11
$k_{3t} \times 10^8$	—	2.8 ± 0.7	11 ± 3	24	−12
$k_{2c} \times 10^{7a}$	—	2 ± 2	6 ± 6	—	—
$k_{2c} \times 10^{7b}$	—	5 ± 3	15 ± 6	—	—
$k_{2t} \times 10^{4c}$	—	~1	—	—	—

[a]The value of k_{2c-} used was obtained from the rate of chloride anation of *trans*-$PtCl_2$ and $PtCl^+$ (Ref. 1, Table 5). [b] k_{2c-} was obtained from the rate of formation of *trans*-$PtCl_2$ and $PtCl^+$ (this paper). [c] The value of k_{2t-} used was determined at the ionic strength 2.4 M.

DISCUSSION

The rate constants for the acid hydrolyses, k_{3t}, k_{3c}, k_{2t}, and k_{2c}, given in Table 5, were calculated from the equilibrium constants of Table 2 and the corresponding chloride anation rate constants determined previously.[1] The values of k_{2c} and k_{2t} are only approximate, because of the great experimental errors in the determination of k_{2c-} and k_{2t-}.

All parameters necessary to describe the equilibria and reaction rates of the platinum(II)-chloro complexes in aqueous solution have now been determined, except those of the final reaction step between $PtCl^+$ and Pt^{2+}. This has not been accessible, because of the difficulties of getting Pt^{2+} in measurable concentration in solution.[2] In Fig. 9, the reaction model and the rate constants obtained are given. Tentative values of k_1 and k_{1-} have also been included (*vide infra*). The change of concentration of the different com-

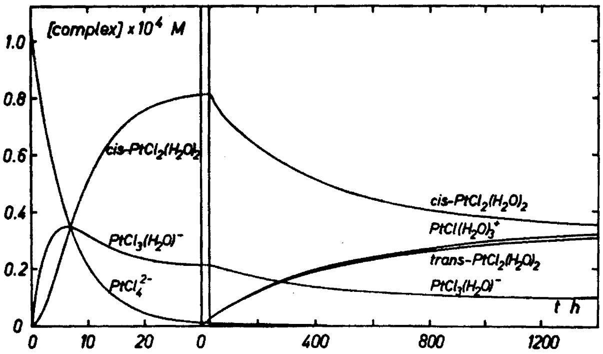

Fig. 8. Change of concentration of complex species with time in an aging solution of K_2PtCl_4 (1.035×10^{-4} M). Equilibrium is reached within about 1600 h.

Table 6. Comparison of rate constants in s^{-1}. The values for $L=NH_3$ have been determined by Martin *et al.*[7]

Reaction	Rate constant $\times 10^5$		Ratio
	$L=NH_3$	$L=H_2O$	
$PtCl_4^{2-}+H_2O\rightarrow PtCl_3(H_2O)^-+Cl^-$	3.9	3.7	
$PtCl_3L^-+H_2O\rightarrow$ *cis*-$PtCl_2L(H_2O)+Cl^-$	5.6	6	1:1
$PtCl_3L^-+H_2O\rightarrow$ *trans*-$PtCl_2L(H_2O)+Cl^-$	0.63	0.0028	200:1
cis-$PtCl_2L_2+H_2O\rightarrow PtClL_2(H_2O)^++Cl^-$	2.5	~0.03	100:1
trans-$PtCl_2L_2+H_2O\rightarrow PtClL_2(H_2O)^++Cl^-$	9.8	~10	1:1
$PtClL_3^++H_2O\rightarrow PtL_3(H_2O)^{2+}+Cl^-$	2	(~0.03)	(100:1)

plexes with time, as described by this model, is shown by Fig. 8 for a 10^{-4} M solution of K_2PtCl_4.

It might be interesting to compare the rate constants found for this system with the corresponding constants for the platinum(II)-chloro ammine complexes, which have been determined by Martin *et al.*[7] It is obvious from Table 6 that the rate constants are about the same when L ($L=NH_3$ or H_2O) is in *cis*-position to the leaving ligand, whereas the rates differ by a factor of about 100 to 200 when L is in *trans*-position. Thus, NH_3 and H_2O have *cis*-effects of about the same magnitude, whereas the *trans*-effect of NH_3 is about 100 – 200 times that of H_2O for these reactions.

Martin [7] found that his rate constants could be described within an uncertainty of about 20 % by the formula

$$k/m = 1.0\times10^{-5}\times0.5^p\times2.4^q \qquad (21)$$

Here, m is the number of equivalent chlorides in the complex, p the number of ammonia ligands *trans* to the replaced chloride, *i.e.* either 0 or 1, and q the number of ammonia ligands *cis* to the replaced chloride, *i.e.* 0, 1, or 2.

The ionic charge of the complex had no primary effect on the rate constants. There has been some discussion concerning the limitations of this formula.[10,11] A similar, empirical relationship may be derived for the present acid hydrolysis rate constants, however. k_4, k_{3c}, and k_{3t}, which are all determined with relatively good precision, satisfy the expression:

$$k/m = 9 \times 10^{-6} \times (3 \times 10^{-3})^r \times 3^s \quad (22)$$

where r is the number of water ligands *trans* to the replaced chloride, and s is the number of water ligands *cis* to it. From eqn. (22), k_{2c} may be calculated as 2×10^{-7} s^{-1} and k_{2t} as 2×10^{-4} s^{-1}. These values are in relatively good agreement with the experimental values given in Table 5, so the relation (22) seems to be approximately valid for these rate constants. A tentative value of $k_1 \sim 3 \times 10^{-7}$ (s^{-1}) may be predicted from eqn. (22). Since the equilibrium constant K_1 is about 1×10^{-5} M (Ref. 2), k_{1-} will be of the order of 3×10^{-2} s^{-1} M^{-1}. These values are also given in Fig. 9.

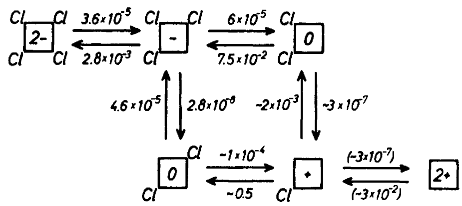

Fig. 9. The reaction model and the rate constants, given for 25°C in s^{-1} for the acid hydrolyses and in s^{-1} M^{-1} for the reverse chloride anations.

Comparisons similar to those of Table 6, using the rate constants of Fig. 9, show that the *trans*-effect of chloride is about 100 – 200 times greater than that of water, whereas the *cis*-effect of water is 2 – 3 times greater than that of chloride.

The extremely slow rate of formation and chloride anation of *trans*-$PtCl_2$ observed is thus due to the combination of the low *trans*-effect of water and the low *cis*-effect of chloride: in both cases the leaving ligand has water in *trans*-position and chloride in both *cis*-positions. These two slow reactions have high enthalpies of activation (24 and 23 kcal mol^{-1}, respectively). The entropies of activation, on the other hand, are quite similar to those of the corresponding reactions for the *cis*-isomer (*cf.* Table 5 and Ref. 1, Table 6). This fact supports the assumption that the slow-reacting species is really a simple complex like *trans*-$PtCl_2$, and not, for instance, a polynuclear complex.

The acid hydrolysis of *cis*-$PtCl_2$ is also a very slow reaction, since the leaving ligand has water in *trans*-position and chloride in one *cis*-position. The acid hydrolysis of $PtCl^+$ may also be expected to be a slow reaction for this reason, as is indicated by the calculated rate constant k_1.

Thus, the slow reacting species, which has been observed in aging solutions of K_2PtCl_4 and interpreted to be *trans*-$PtCl_2$, fits well into the reaction scheme when the *trans*- and *cis*-effects and the activation enthalpies and entropies are considered. Since it also has zero charge,[1] and is formed[1] by adding chloride to solutions containing $PtCl^+$, and since the consecutive stability constants[2] obtained from the model are reasonable, its existence in aged solutions seems to be beyond doubt. A species having analogous properties has been observed [12] in aged solutions of K_2PtBr_4.

To explain the experiments, it has not been necessary to presuppose a direct isomerisation *cis*-$PtCl_2 \longrightarrow$ *trans*-$PtCl_2$, taking place by an intramolecular process. According to the model used, the isomerisation occurs *via* $PtCl_3^-$ and $PtCl^+$. This is in accordance with Martin's *et al.*[7] observations for the isomerisation of $PtCl_2(H_2O)(NH_3)$, and also with recent investigations of the mechanism for the thermal isomerisations of the bis-(glycinato)-platinum (II)-complex [13] and of the diacidodiamminepalladium(II)-complexes.[14]

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