

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

II. Kinetics of the First Step

LARS IVAR ELDING

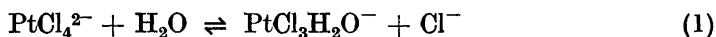
Department of Inorganic and Physical Chemistry, University of Lund, Lund, Sweden

Rate constants of the forward and reverse reactions of the first step of the aquation of the tetrachloridoplatinate(II) ion have been determined from spectrophotometric measurements at 230 nm. Excess of chloride reduced the rate expression to one of simple first order. The rate constant of the forward reaction was calculated also from the initial rate of the reaction, using measurements at 230 and 315 nm; *vide* Table 1. The forward reaction is first order with respect to platinum, the reverse reaction is first order with respect to platinum and to chloride.

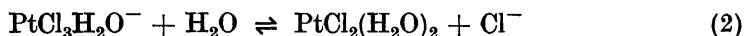
The equilibrium constant, K_4 M, of the aquation was obtained as the quotient of the rate constants, $K_4 = 1.3 \times 10^{-2}$. Spectra in the region 500–210 nm of PtCl_4^{2-} , $\text{PtCl}_3(\text{H}_2\text{O})^-$ and the equilibrium mixture of *cis*- and *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ have been obtained (Fig. 1).

The ionic strength was kept at 0.500 M by means of perchloric acid. The temperature was 25°C.

In a previous paper¹ the dissociation constants K_4 and K_3 of the aquation reactions



and



were determined from equilibrium measurements.

In this paper, the kinetics of reaction (1) is studied. This reaction may be almost completely separated from the second aquation step (2) if the concentration of free chloride is appropriately chosen. The rate constants, k_4 of the forward reaction and k_{4-} of the reverse reaction, may be measured. Then, from Guldberg's and Waage's relationship

$$K_4 = k_4/k_{4-} \quad (3)$$

Table 1. The rate constants k_4 sec⁻¹ and k_{4-} sec⁻¹M⁻¹ of reaction (1). All measurements were made at 25°C. The ionic strength is in M.

Author	Ref.	Method	Ionic strength	$k_4 \times 10^5$	$k_{4-} \times 10^3$
Martin <i>et al.</i>	3	Tit. with OH ⁻	0.318	3.86	2.14 ^a
Grinberg <i>et al.</i>	4	» » »	0.1	3.9	2.19 ^a
Grinberg and Kukushkin	5	» » »	?	3.9	—
Kivalo and Ulmanen	6	Polarogr.	0.1	3.3	1.61 ^b
This paper		Spectr.	0.500	3.69 ^c	2.81 ^c
» »		»	0.500	3.59 ^d	—

^a Calculated from eqn. (3) and a value of the equilibrium constant, obtained from measurements on aged solutions. ^b From eqn. (3) and Martin's equilibrium constant (Ref. 3). ^c From measurements having chloride in large excess. ^d From the initial rate of the reaction.

the equilibrium constant K_4 may be calculated. This kinetic method for determining equilibrium constants of inert complexes has been used only in few cases (Rosotti and Rosotti², p. 119).

The kinetics of reaction (1) have been studied earlier and Table 1 reviews these previous investigations. This will be discussed in the final part of this paper.

EXPERIMENTAL

Chemicals. Potassium tetrachloridoplatinate(II) supplied by Degussa, Hanau, was recrystallized twice from 1 M hydrochloric acid. This did not change the visible and UV spectrum in 0.5 M HCl. Analysis gave (as in Ref. 1): Pt (46.6 ± 0.3) %, Cl (33.9 ± 0.1) %. Calc. for K₂PtCl₆: Pt 47.00 %, Cl 34.16 %.

Perchloric acid (Baker's *p.a.*) and hydrochloric acid (Merck's *p.a.*) were used to prepare stock solutions.

Apparatus. The kinetic runs were made by a Beckman DU Quartz Spectrophotometer Model G 2400 equipped with a photomultiplier tube. The cell compartment was modified according to Cigén.⁷ Water thermostated at (25.00 ± 0.02)°C was pumped through the walls and the bottom of the cell housing and the apparatus was situated in a thermostated room (25.0 ± 0.5)°C.

The spectra were recorded at 25°C on a Beckman DK 1 Spectrophotometer.

Kinetic runs. Volumetric flasks were used as reaction vessels. The calculated quantity of chloride ions was added from stock solutions of 0.500 M HCl or mixtures of 0.500 M HCl and 0.500 M HClO₄. Then the flasks were filled almost up to the mark with 0.500 M HClO₄. They were thermostated over night at (25.00 ± 0.02)°C.

The reaction was initiated by transferring a weighed amount of K₂PtCl₆ to the flask and diluting rapidly to the mark with thermostated 0.500 M HClO₄. The flask was shaken and after about 1 min the mixing was complete. At intervals of time, samples were taken using thermostated pipettes and the absorbance was measured at 230 or 315 nm. For the choice of wavelengths see Ref. 1, Fig. 1. The reaction vessels in the thermostat were protected from light by a cover.

Spectra. For the calculation of the rate constant k_4 from the initial rate of reaction it was necessary to know the molar absorptivities, ϵ_4 and ϵ_3 , of PtCl₄²⁻ and PtCl₃⁻ at the wavelengths used. Four solutions of K₂PtCl₆ having varying concentrations of free chloride — Table 2 — were aged for three weeks at 25°C. The equilibrium concentrations of the complexes were calculated from the dissociation constants K_4 and K_3 of Ref. 1. The spectra of the solutions were recorded by means of the Beckman DK 1 spectrophotometer.

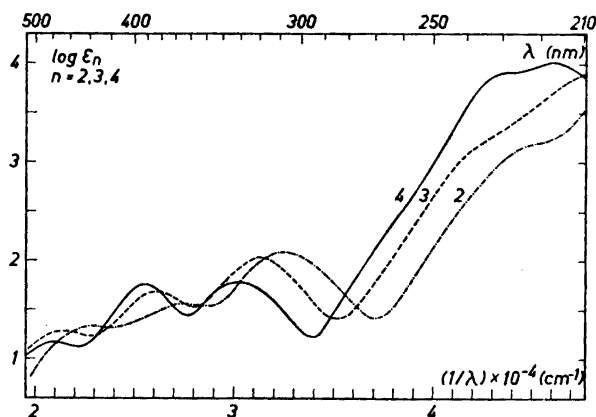


Fig. 1. Absorption spectra of $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$, $n = 2, 3, 4$. ϵ_n is in $\text{cm}^{-1}\text{M}^{-1}$.

Table 2. The composition (as obtained from Ref. 1, Fig. 5) of the solutions used to calculate the spectra. From the first one, an approximate spectrum of PtCl_4^{2-} was obtained. From the other three, the spectrum of $\text{PtCl}_3(\text{H}_2\text{O})^-$ was calculated. The concentrations are in M.

$C_{\text{Pt}} \times 10^{-3}$	$C_{\text{Cl}} \times 10^{-3}$	$[\text{PtCl}_4^{2-}] \times 10^{-3}$	$[\text{PtCl}_3(\text{H}_2\text{O})^-] \times 10^{-3}$	$[\text{PtCl}_2(\text{H}_2\text{O})_2] \times 10^{-3}$
1.000	504	0.975	0.025	0
1.000	29.00	0.655	0.328	0.017
1.000	20.00	0.543	0.421	0.036
1.000	15.00	0.450	0.492	0.058

Three of the solutions contained more than negligible amounts of $\text{PtCl}_2(\text{H}_2\text{O})_2$. The spectrum of this neutral complex (which may be a mixture of the *cis*- and *trans*-isomers) was recorded directly in the following manner:

A solution of K_2PtCl_4 (2×10^{-3} M) in HClO_4 (5×10^{-3} M) was aged. 100 ml of this solution was percolated through a column filled with anion exchanger Dowex 1 \times 4, 50–100 mesh in perchlorate form (same as used in Ref. 1). The perchloric acid concentration of the effluent was adjusted to 0.5 M and the spectrum was recorded using a 10 cm cell. 2 h later the spectrum was recorded again. No perceptible changes were observed. The concentration of platinum in the effluent was determined spectrophotometrically as in Ref. 1.

CALCULATIONS AND RESULTS

Notation

- a M concentration of PtCl_4^{2-} at time t_0
 b M » » Cl^- » » »
 x M » » PtCl_3^- » » t
 e cm^{-1} absorptivity
 ϵ_n $\text{cm}^{-1} \text{M}^{-1}$ molar absorptivity of the complex $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$, $n = 2, 3, 4$.
 The subscripts "0" and " ∞ " denote zero time and equilibrium, respectively.

Spectra

From the spectra of the solutions of Table 2 having the chloride concentrations 29, 20, and 15 mM, and the eqn.

$$e = \sum_{n=2}^4 \epsilon_n [\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}] \quad (4)$$

ϵ_3 was computed for the range 210–500 nm, using intervals of 3, 5, 10, or 20 nm. In the calculation, ϵ_4 was taken from the spectrum of the solution with $C_{\text{Cl}} = 0.504$ (M), and ϵ_2 was obtained from the spectrum of the solution that percolated through the anion exchanger.

Thus, three values of ϵ_3 were derived from eqn. (4), one for each of the three solutions. They usually agreed to within 5 %. The mean was used to construct the spectrum of $\text{PtCl}_3(\text{H}_2\text{O})^-$. Because of the low concentrations of $\text{PtCl}_2(\text{H}_2\text{O})_2$, the corresponding term of eqn. (4) became a correction term only. Even in the region 280–325 nm, where $\epsilon_2 > \epsilon_4$ and this term has its maximum influence, it did not exceed about 10 % of the total absorptivity. Therefore the calculation gave a good spectrum of $\text{PtCl}_3(\text{H}_2\text{O})^-$ even if ϵ_2 may have been erroneous.

Finally, the preliminary spectrum of PtCl_4^{2-} , obtained from the solution with $C_{\text{Cl}} = 0.504$ (M), was corrected for the 2.5 % of $\text{PtCl}_3(\text{H}_2\text{O})^-$ present. The three spectra are given in Fig. 1.

The kinetic measurements were performed at 230 and 315 nm. At these wavelengths, ϵ_3 was calculated more carefully in the manner described from two series of aged solutions, used for the determination of the equilibrium constants K_4 and K_3 of Ref. 1. The values of ϵ_3 given in Table 3 were calculated

Table 3. The values of the molar absorptivities $\epsilon_n \text{ cm}^{-1}\text{M}^{-1}$ at 230 and 315 nm.

λ	ϵ_4	ϵ_3	ϵ_2
230	8020 \pm 40	2060 \pm 100	990 \pm 50
315	45.0 \pm 1.0	104.7 \pm 1.2	110 \pm 5

from 27 solutions measured at 230 nm and 19 at 315 nm. ϵ_4 was obtained from the corrected spectrum of PtCl_4^{2-} and also from extrapolations of kinetic runs to zero time.

Kinetic runs

The experiments indicate that the forward reaction of (1) is first order with respect to platinum. The reverse reaction appears to be first order with respect to platinum and to chloride, *i.e.* second order over all. Then the rate of the reaction may be written

$$dx/dt = k_4(a-x) - k_4x(b+x) \quad (5)$$

The rate constants were calculated in two ways.

a. Evaluation of the rate constants from measurements with $b \gg a$. The initial concentration of chloride, b M, was chosen to be between 5×10^{-2} and 5×10^{-3} . In this range there is between 20 % and 60 % of $\text{PtCl}_3(\text{H}_2\text{O})^-$ at equilibrium. This is shown by Fig. 5 b of Ref. 1. In the interval $2 \times 10^{-2} > b > 5 \times 10^{-3}$ (M) there will be, in addition, a slight conversion into $\text{PtCl}_2(\text{H}_2\text{O})_2$ (*vide infra*).

The concentration of platinum, a , was about or less than 2 % of b , *i.e.* $b \gg a > x$. This condition could be fulfilled if the measurements were performed at 230 nm, where ϵ_4 is so high that the concentration of platinum may be lowered to 5×10^{-5} M and still give measurable absorbances.

If $b \gg x$ eqn. (5) may be written

$$dx/dt = k_4(a-x) - k_{4-b}x \quad (6)$$

Integration gives the first-order expression

$$(k_4 + k_{4-b})t = \ln \frac{x_\infty}{x_\infty - x} \quad (7)$$

Table 4. Measurements at 230 nm having chloride in excess. The first order rate constant $(k_4 + k_{4-b}) \text{ sec}^{-1}$ was calculated from the slope of the line $\log(e - e_\infty)$ vs. t . The concentrations a and b are in M.

$b \times 10^3$	$a \times 10^5$	$(k_4 + k_{4-b}) \times 10^5$	
		Each expt.	Mean
5.00	10.43	5.17	5.08 \pm 0.1
	4.71	5.08	
	4.55	5.00	
7.53	9.00	5.58	5.68 \pm 0.1
	4.53	5.78	
10.00	18.19	6.33	6.50 \pm 0.15
	10.19	6.50	
	4.49	6.67	
20.00	46.3	9.31	9.28 \pm 0.2
	9.89	9.25	
30.00	14.08	11.72	12.2 \pm 0.5
	9.60	12.63	
33.3	90.4	12.47	12.8 \pm 0.7
	88.0	13.47	
	46.7	12.53	
40.0	10.17	14.92	14.9 \pm 1
	9.33	16.11	
	6.98	13.61	
50.0	92.9	17.81	17.9 \pm 1
	14.78	18.92	
	10.27	17.42	
	8.38	18.44	
	7.82	17.08	

Introducing the absorptivities, which are given by

$$e_0 = \varepsilon_4 a \text{ and } e = \varepsilon_4(a-x) + \varepsilon_3 x \quad (8)$$

we arrive at

$$(k_4 + k_4 b)t = \ln \frac{e_0 - e_\infty}{e - e_\infty} \quad (9)$$

The first-order rate constant $(k_4 + k_4 b)$ was calculated from a plot of $\log(e - e_\infty)$ vs. t for a number of different values of b in the concentration range chosen. For each b , the concentration of platinum, a , was varied.

Fig. 2 shows three typical plots of kinetic runs for different values of b . Table 4 gives a review of the measurements. From this it is clear that the reaction is first-order with respect to platinum.

In the experiments with $b = (10.0, 7.5, \text{ and } 5.0) \times 10^{-3}$ (M) the measured values of e_∞ will become too low because of the presence of increasing amounts of $\text{PtCl}_2(\text{H}_2\text{O})_2$ at equilibrium (6, 8, and 13 %, respectively). For these experi-

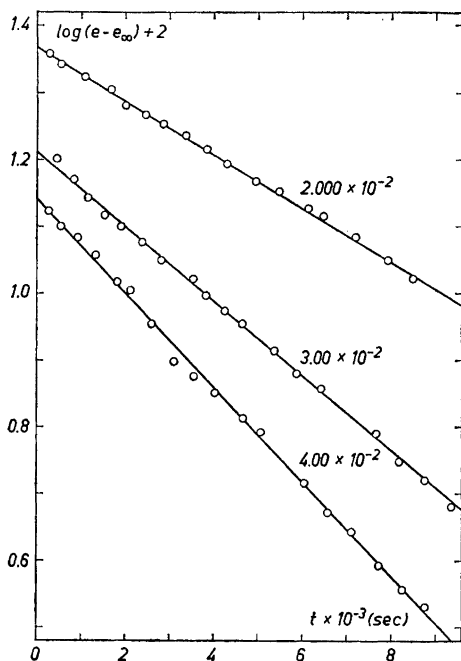


Fig. 2. Three typical kinetic runs having chloride in excess. The rate constant $(k_4 + k_4 b)$ was calculated from the slope of the lines. The number at each line gives the concentration of chloride, b M. The concentration of platinum, a M, was (from above) $(9.89, 9.60, \text{ and } 9.33) \times 10^{-5}$.

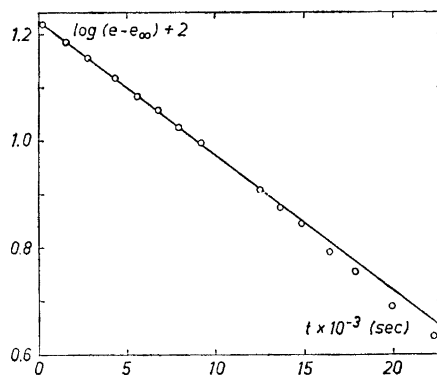


Fig. 3. A kinetic run having chloride in excess. In this instance the concentration of chloride, b , was not sufficiently high to suppress the second aquation. The rate constant was calculated from the first half-life of the reaction, where the second aquation may be neglected and the function is linear. $a = 4.53 \times 10^{-5}$ (M), $b = 7.53 \times 10^{-3}$ (M), $e_\infty, \text{ exp.} = 0.185$ (cm^{-1}). $e_\infty, \text{ calc.} = 0.196$ (cm^{-1}).

ments, a value of e_∞ was computed from K_4 , ε_4 and ε_3 according to eqn. (8). The second dissociation was thus neglected. This computed value of e_∞ was used to calculate $\log(e - e_\infty)$ instead of the experimental value obtained from the finally equilibrated solution.

Our present information on the kinetics of the second step (2), tells us that the reaction to the neutral complex may be neglected during the first half-life of the reaction studied here. In the solution with $b = 5 \times 10^{-3}$ (M), for instance, there will be only about 1.6 % of the platinum present as $\text{PtCl}_2(\text{H}_2\text{O})_2$ after 4 h. Thus, for these experiments, $(k_4 + k_{4-}b)$ could be calculated from the first half-life of the reaction in the same manner as before by using these calculated values of e_∞ . Fig. 3 shows an example of such a plot.

In Fig. 4, $(k_4 + k_{4-}b)$ has been plotted *vs.* b . The relation is linear within the experimental error, which means that the reverse reaction is first-order with respect to chloride. The rate constant k_4 was obtained by extrapolation to $b = 0$ and k_{4-} from the slope of the line

$$\begin{aligned} k_4 &= (3.69 \pm 0.20) \times 10^{-5} && (\text{sec}^{-1}) \\ k_{4-} &= (2.81 \pm 0.15) \times 10^{-3} && (\text{sec}^{-1}\text{M}^{-1}) \end{aligned}$$

In addition, we get the dissociation constant from eqn. (3):

$$K_4 = (13 \pm 1) \times 10^{-3} \quad (\text{M})$$

b. Calculation of k_4 from the initial rate of the reaction. Initially, the rate of the reverse reaction is low. Eqn. (5) may then be written

$$dx/dt = k_4(a-x) \quad (10)$$

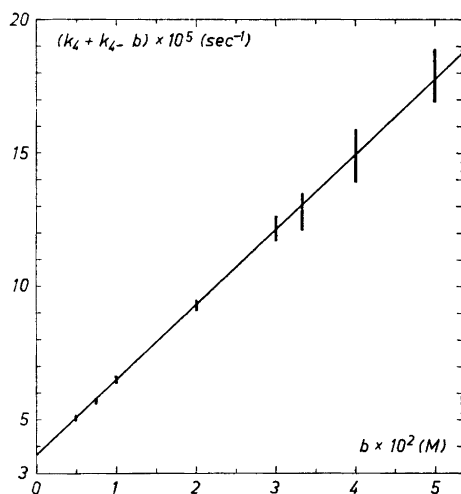


Fig. 4. The rate constant $(k_4 + k_{4-}b)$ at different b 's. The rate constants k_4 and k_{4-} were obtained from the ordinate axis intercept and the slope of the line, respectively.

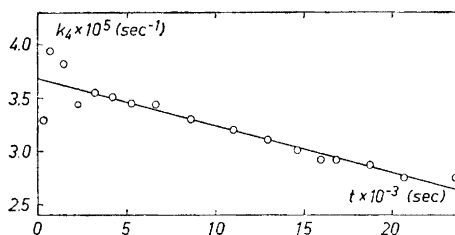


Fig. 5. Calculation of k_4 from the initial rate of the reaction by extrapolation of the values of k_4 from eqn. (11) to zero time.

Integrating and introducing the absorptivities (8) gives

$$k_4 t = \ln \frac{e_0(\varepsilon_4 - \varepsilon_3)}{e\varepsilon_4 - e_0\varepsilon_3} \quad (11)$$

From this expression, k_4 has been calculated for each measurement and then plotted *vs. t*. The rate constant was obtained by extrapolation of this function to zero time. Fig. 5 shows an example.

Measurements were made at 230 and 315 nm, with and without addition of extra chloride. Table 5 contains the results. The concentration of platinum was varied from 10^{-2} to 5×10^{-5} M, *i.e.* by a factor greater than 10^2 . The constancy of k_4 proves that the reaction to the right is first-order with respect to platinum.

The value of k_4 calculated in this manner agrees well with the one obtained by extrapolating the function $(k_4 + k_{-4}b)$ to $b = 0$.

Table 5. The rate constant k_4 sec $^{-1}$ calculated by means of eqn. (11) from the initial rate of the reaction. The values of ε_n were taken from Table 3. The concentrations a and b are in M.

$a \times 10^3$	$b \times 10^3$	$k_4 \times 10^5$	λ
10.02	10.00	3.56	315
10.00	0	3.78	315
5.01	10.00	3.67	315
3.06	10.00	3.68	315
3.00	10.00	3.47	315
3.01	0	3.81	315
0.929	20.00	3.53	230
0.463	20.00	3.53	230
0.0989	20.00	3.58	230
0.1819	10.00	3.53	230
0.1019	10.00	3.58	230
0.0449	10.00	3.72	230
0.0900	7.53	3.36	230
0.0453	7.53	3.47	230
0.1043	5.00	3.64	230
0.0471	5.00	3.56	230
0.0455	5.00	3.61	230

Mean 3.59 ± 0.11

DISCUSSION

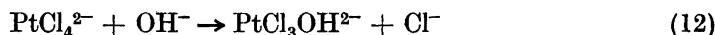
The equilibrium constant K_4 of the first aquation step (1) calculated by the kinetic method, is in good agreement with the one obtained from measurements on equilibria (Ref. 1).

In Table 1, earlier kinetic investigations have been summarized. In all these, the rate constant actually measured was k_4 , since the first term of eqn. (5) greatly dominated the rate expression during the first part of the reaction, used by these authors. k_{-4} was then calculated by means of eqn. (3) from k_4 and some value of the equilibrium constant K_4 , obtained from equilibrium measurements. The discrepancies in k_{-4} therefore reflect the differences

in the values of the equilibrium constants used. The rate constant, k_4 , on the other hand, is relatively unaffected by the value of K_4 used in the calculation (if it is used at all). This explains the good agreement between the values of k_4 .

In the present measurements which have chloride in excess, both terms of the rate expression (5) are important, *i.e.* k_{4-} will affect the rate even at the beginning of the reaction. This is also evident from the decreasing values of k_4 obtained when calculated by means of eqn. (11) from solutions with chloride in excess (*vide* Fig. 5).

Some authors⁸⁻¹⁰ have calculated the rate constant of the reaction



The rate determining step of this reaction may be the slow aquation (1), followed by a rapid neutralisation of the acidic aquo complex. The values of this rate constant given in literature (Banerjea *et al.*,⁸ $3.3 \times 10^{-5} \text{ sec}^{-1}$; Grinberg *et al.*,⁹ $3.9 \times 10^{-5} \text{ sec}^{-1}$; and Colvin,¹⁰ $3.8 \times 10^{-5} \text{ sec}^{-1}$) agree well with those k_4 's in Table 1.

The rate constant k_4 appears to be independent of the ionic strength. This might be expected according to the activity-rate theory of Brønsted¹¹ and Bjerrum¹², since one of the reactants, the water molecule, is uncharged. However, the ionic strengths are really too high for this theory to be strictly valid (Frost and Pearson¹³, p. 151).

The kinetics of the first step (1) studied here, are now investigated at other temperatures in order to calculate the activation energies and entropies of the reactions. The kinetics of the second step (2) will also be described in a paper to follow.

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