

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

### III. Influence of Temperature on Kinetics and Equilibrium of the First Step

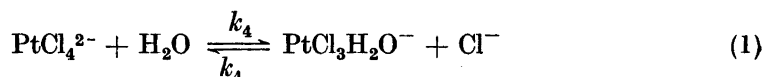
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Activation enthalpies and entropies of the aquation of  $\text{PtCl}_4^{2-}$  and of the chloride uptake of  $\text{PtCl}_3\text{H}_2\text{O}^-$  have been calculated from spectrophotometric measurements of the rate constants at 15, 25, and 35°C (*vide* Table 3). The ionic medium was 0.500 M  $\text{HClO}_4$ .

The dissociation constant of  $\text{PtCl}_4^{2-}$  may be obtained as the quotient of the rate constants. The enthalpy and entropy changes for the aquation have been calculated:  $\Delta H_4^\circ = 4.4$  (kcal mole<sup>-1</sup>) and  $\Delta S_4^\circ = 6.0$  (cal mole<sup>-1</sup>deg<sup>-1</sup>) at 25°C.  $\Delta H_4^\circ$  seems to be slightly dependent upon temperature in the interval 15–60°C.

In a previous paper,<sup>2</sup> the rate constants,  $k_4$  s<sup>-1</sup> and  $k_{4-}$  s<sup>-1</sup>M<sup>-1</sup>, of the forward and reverse reactions of the first aquation step of  $\text{PtCl}_4^{2-}$  were determined, at 25°C:



In order to obtain the activation parameters of the two reactions of (1), the rate constants have now been calculated at 15 and 35°C, using the method described in Ref. 2.

The enthalpy and entropy changes of the aquation reaction (1) may also be calculated from these measurements, since the dissociation constant,  $K_4$  M, is related to the rate constants by the expression

$$K_4 = k_4/k_{4-} \quad (2)$$

Only two previous investigations on this subject have been found in the literature (Table 3).

## EXPERIMENTAL

**Chemicals.**  $K_2PtCl_4$ , supplied by Heraeus, Hanau, was recrystallized twice from 1 M hydrochloric acid. Analysis (as in Ref. 1): Pt  $46.98 \pm 0.05$ , Cl  $33.8 \pm 0.1$ . Calc. for  $K_2PtCl_4$ : Pt 47.00, Cl 34.16. Analysis by coulometry (Ginstrup<sup>3</sup>): Pt 46.7 % by weight, Pt(IV) < 0.1 mole-% of the total amount of platinum.

The perchloric acid was Baker's *p.a.* and the hydrochloric acid Merck's *p.a.*

**Apparatus.** A Beckman DU Quartz Spectrophotometer with photomultiplier was used. The cell housing was furnished with double, heat insulated thermostatic systems (*cf.* Cigén<sup>4</sup>).

**Solutions.** Two stock solutions containing  $K_2PtCl_4$  ( $13.33 \times 10^{-3}$  and  $6.67 \times 10^{-3}$  M, respectively) and HCl (0.500 M) were used. They were stored in the dark at about 21°C. At this temperature and concentration of free chloride, there will be 97.7 % of  $PtCl_4^{2-}$  and 2.3 % of  $PtCl_3H_2O^-$  at equilibrium (*cf.* Ref. 1). No decomposition or oxidation was observed for a period of about two weeks.

By mixing 0.500 M HCl and 0.500 M  $HClO_4$ , solutions having the following concentrations (mM) of chloride were prepared: 1.250, 5.00, 10.00, 15.00, 20.00, 30.0, 40.0, and 50.0.

**Measurements.** 200.0 ml of the HCl- $HClO_4$ -solutions were thermostated at the desired temperature ( $\pm 0.02^\circ C$ ). The reaction was started by injecting 1.499 ml of one of the two HCl-platinum stock solutions by means of a calibrated glass syringe (reproducibility better than 0.1 %). The concentration of platinum became  $9.93 \times 10^{-5}$  or  $4.97 \times 10^{-5}$  M, and the additional concentration of free chloride  $3.72 \times 10^{-3}$  M. The decrease of absorbance *vs.* time was measured at 230 nm in 1.000 or 2.000 cm quartz cells, the samples being taken with thermostated pipettes. Light was excluded from the reaction vessels.

## RESULTS AND DISCUSSION

*a. Calculation of rate constants.* The notation and method of calculation have been presented in Ref. 2. In all experiments, the concentration of free chloride, *b* M, was much greater than the concentration of platinum. Then the rate expression is reduced to one of first order, and on integration we arrive at

$$(k_4 + k_4 - b)t = \ln(e_0 - e_\infty)/(e - e_\infty) \quad (3)$$

The first order rate constant  $(k_4 + k_4 - b) s^{-1}$  may be calculated from the slope of the line obtained by plotting  $\log(e - e_\infty)$  *vs.* *t*.

In solutions where  $b > 2 \times 10^{-2}$ , the only species present in detectable concentrations at equilibrium will be  $PtCl_4^{2-}$  and  $PtCl_3^-$  (*cf.* Ref. 1, Fig. 5). The measured value of  $e_\infty$  may then be used in the calculation.

Solutions where  $b < 2 \times 10^{-2}$ , on the other hand, will contain, at equilibrium, detectable amounts of  $PtCl_2$ , increasing with decreasing values of *b*. Then a value of  $e_\infty$ , calculated using known values of  $K_4$  and the molar absorptivities  $\epsilon_4$  and  $\epsilon_3 \text{ cm}^{-1} \text{ M}^{-1}$  of  $PtCl_4^{2-}$  and  $PtCl_3^-$ , has to be used instead of the measured  $e_\infty$  (*cf.* Ref. 2).

$\epsilon_4$  was obtained by extrapolating kinetic runs to zero time and correcting the extrapolated value for the 2.3 % of  $PtCl_3^-$  present in the platinum stock solutions. No effect of temperature on the molar absorptivities was found within the limits of experimental error. Obtained:  $\epsilon_4^{15^\circ C} = 8000 \pm 40$ ;  $\epsilon_4^{35^\circ C} = 8020 \pm 40$  ( $\text{cm}^{-1} \text{ M}^{-1}$ ). The value of  $\epsilon_3 = 2060 \pm 100$ , calculated in Ref. 2, was used, and the value of  $K_4$  was obtained by successive approximations.

Table 1. The rate constant  $(k_4 + k_{4-b})$  s<sup>-1</sup> at different values of the chloride concentration  $b$  M. Runs at two different concentrations of platinum, namely  $9.93 \times 10^{-5}$  and  $4.97 \times 10^{-5}$  M, were performed for each value of  $b$ .

$b \times 10^3$	15°C		35°C	
	Number of expts.	$(k_4 + k_{4-b}) \times 10^5$	Number of expts.	$(k_4 + k_{4-b}) \times 10^4$
4.96	9	$1.50 \pm 0.06$	6	$1.63 \pm 0.05$
8.68	8	$1.89 \pm 0.08$	3	$1.85 \pm 0.05$
13.65	7	$2.49 \pm 0.10$	3	$2.28 \pm 0.08$
18.61	6	$2.90 \pm 0.10$	—	—
23.57	9	$3.36 \pm 0.15$	2	$3.01 \pm 0.10$
33.5	6	$4.17 \pm 0.20$	3	$3.79 \pm 0.10$
43.4	7	$5.25 \pm 0.25$	10	$4.50 \pm 0.20$
53.4	7	$6.56 \pm 0.30$	4	$5.30 \pm 0.30$

In some cases, the rate constants were also evaluated according to Guggenheim<sup>5</sup>, p. 442 by plotting  $\log(e - e')$  against  $t$ . Here,  $e'$  is the absorptivity measured at time  $t + \tau$ , where  $\tau$  is a suitably chosen interval of time. Consistent results were obtained by the two methods.

In Table 1, a review of the measurements is given. In Figs. 1 and 2,  $(k_4 + k_{4-b})$  has been plotted *vs.*  $b$ . From these graphs,  $k_4$  is obtained as the ordinate-axis intercept, and  $k_{4-}$  as the slope. The constants are shown in Table 2.

b. *Thermodynamic parameters.* In Figs. 3 and 4, the logarithms of the rate constants have been plotted against  $1/T$  °K<sup>-1</sup>. The graphs are linear within

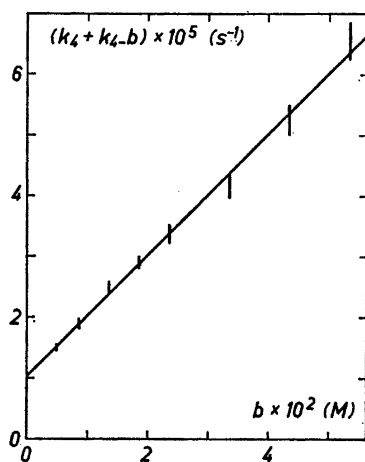


Fig. 1. The rate constant  $(k_4 + k_{4-b})$  at 15°C.

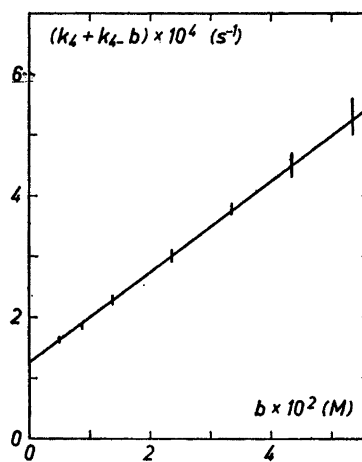


Fig. 2. The rate constant  $(k_4 + k_{4-b})$  at 35°C.

Table 2. The rate constants,  $k_4$  s<sup>-1</sup> and  $k_{4-}$  s<sup>-1</sup>M<sup>-1</sup>, and the dissociation constant,  $K_4$  M, of reaction (1). Values at 25°C from Ref. 2.  $K_4$  was calculated from eqn. (2), except for the value at 60°C, which has been obtained from equilibrium measurements at this temperature (Ref. 9).

	15°C	25°C	35°C	60°C
$k_4 \times 10^5$	1.02 ± 0.06	3.7 ± 0.2	12.5 ± 0.5	—
$k_{4-} \times 10^3$	1.00 ± 0.04	2.8 ± 0.1	7.5 ± 0.3	—
$K_4 \times 10^3$	1.0 ± 0.1	1.3 ± 0.1	1.7 ± 0.1	3.1 ± 0.2

the limits of experimental error. Accordingly, the rate constants conform to the Arrhenius equation

$$k = A \times \exp(-E_a/RT) \quad (4)$$

The activation energies  $E_a$  kcal mole<sup>-1</sup> obtained from the slopes of the lines are shown in Table 3.

The activation entropy  $\Delta S^\ddagger$  cal mole<sup>-1</sup>deg<sup>-1</sup> was calculated at 25°C from the transition-state theory,<sup>6</sup> according to which the frequency factor  $A$  s<sup>-1</sup> of eqn. (4) may be expressed as:

$$A = \kappa (kT/h) \times \exp(\Delta S^\ddagger/R) \quad (5)$$

where  $k$  is Boltzmann's constant,  $h$  Planck's constant and  $R$  the gas constant. The transmission coefficient,  $\kappa$ , was assumed to be unity. The standard state of complexes and chloride ions was chosen as unit concentration (M) and that of water as unit mole fraction. This means, of course, that the entropies calculated in Table 3 for the forward and reverse reactions are not directly

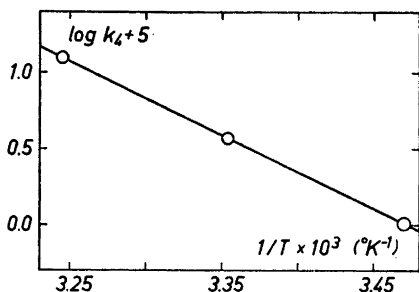


Fig. 3. Temperature dependence of the rate constant of the forward reaction.

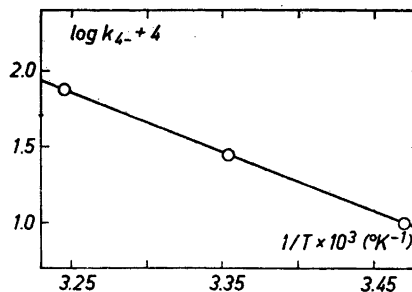


Fig. 4. Temperature dependence of the rate constant of the reverse reaction.

Table 3. Thermodynamic parameters at 25°C.  $E_a$ ,  $\Delta H_4^\circ$ ,  $\Delta H^\circ$ ,  $\Delta H^\ddagger$ ,  $\Delta H_4^\ddagger$  are in kcal mole<sup>-1</sup>,  $\Delta S^\circ$  and  $\Delta S^\ddagger$  in cal mole<sup>-1</sup> deg<sup>-1</sup>. Standard state of complexes and chloride ligands: unit concentration (M), and of water: unit mole fraction.

Reaction	Author	Temp. interval °C	$E_a$ Eqn. (4)	$\Delta H^\circ$ Eqn. (6)	$\Delta S^\circ$ Eqn. (5)	$\Delta H_4^\circ$	$\Delta S_4^\circ$
$\text{PtCl}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{PtCl}_3\text{H}_2\text{O}^- + \text{Cl}^-$	This paper	15–35	22.2	21.6	-6.4	4.4	6.0
	Martin <i>et al.</i> <sup>7</sup>	15–30	—	21	-8	5.1	—
	Babaeva and Rudyi <sup>8</sup>	20–40	23.4	—	—	—	—
$\text{PtCl}_3\text{H}_2\text{O}^- + \text{Cl}^- \rightarrow \text{PtCl}_4^{2-} + \text{H}_2\text{O}$	This paper	15–35	17.8	17.2	-12.4	—	—
	Martin <i>et al.</i> <sup>7</sup>	15–30	—	15	-18	—	—

comparable. If the standard state of water is chosen as 1 M instead,  $\Delta S^{\circ\ddagger}$  of the forward reaction will be  $-14.4$  e.u., *i.e.* a value of the same magnitude as that of the reverse reaction.

The activation enthalpy,  $\Delta H^{\circ\ddagger}$  kcal mole<sup>-1</sup>, finally, is related to the activation energy by the eqn.

$$\Delta H^{\circ\ddagger} = E_a - RT \quad (6)$$

In Table 3 the result may be compared with those of Martin *et al.*,<sup>7</sup> calculated from the rate of exchange of radioactive chloride, and of Babaeva and Rudyi,<sup>8</sup> who recently determined the rate constant of the forward reaction spectrophotometrically. The agreement is rather good, except for the values of the reverse reaction. For this reaction, however, Martin has not measured the rate constants, but has calculated them from equilibrium constants by means of eqn. (2). Therefore, his values might perhaps be somewhat less reliable (*cf.* Ref. 2).

In Fig. 5, the temperature dependence of the dissociation constant  $K_4$  may be studied. In this figure, a value of  $K_4$ , calculated from spectrophotometric equilibrium measurements at 60.0°C, has also been included.<sup>9</sup> The graph seems to show a slight curvature. If this deviation from the linear relationship is real, it would mean that  $\Delta H_4^{\circ}$  is not constant within the temperature interval 15–60°C. The mean value of  $\Delta H_4^{\circ}$  in the interval 15–35°C is 4.4 (kcal mole<sup>-1</sup>), and the enthalpy change  $\Delta S_4^{\circ}$  at 25°C is 6.0 (cal mole<sup>-1</sup> deg<sup>-1</sup>). The enthalpy value found by Martin *et al.*<sup>7</sup> is somewhat greater, but the uncertainty of his constants makes the calculation of  $\Delta H_4^{\circ}$  unsatisfactory, which has also been pointed out by Sanders and Martin in a later paper.<sup>10</sup>

At present, an investigation of the kinetics of the first aquation step of  $\text{PtBr}_4^{2-}$  is almost complete. The activation energy of the forward reaction turns out to be about 22.2 kcal mole<sup>-1</sup>, *i.e.* a value of the same magnitude as that of  $\text{PtCl}_4^{2-}$ . The activation energy of the reverse reaction is about 14.4 kcal mole<sup>-1</sup>, and  $\Delta H_4^{\circ}$  of the aquation about 7.8 (kcal mole<sup>-1</sup>). These measurements will be presented in a subsequent paper.

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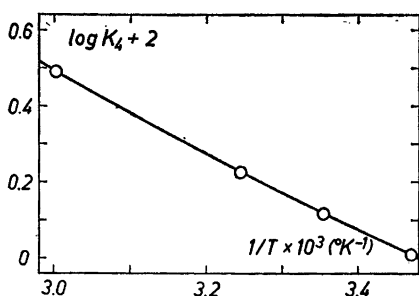


Fig. 5. Temperature dependence of the dissociation constant  $K_4$ .

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