Pressure Effect on the Aquation Velocity of *cis*-$Pt(NH_3)_2Cl_2$ and $Pt(en)Cl_2$

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Activation volumes ($\Delta V^{\ddagger}$) have been obtained for the first acid hydrolysis of cis-$Pt(NH_3)_2Cl_2$ *and of* $Pt(en)Cl_2$*. The results are* $\Delta V^{\ddagger} = -9.5 \pm 1.2$ cm^3 mol^{-1} *at 45 °C and* $\Delta V^{\ddagger} = -9.2 \pm 1.0$ cm^3 mol^{-1} *at 41 °C. A hexacoordinate transition state with two* $Pt-OH_2$ *bonds can be inferred on the basis of* $\Delta V^{\ddagger}$*'s. The reaction volume of* 1.3 ± 0.1 cm^3 mol^{-1} *was dilatometrically obtained at 40 °C for the first acid hydrolysis of* $PtCl_4^{2-}$*.*

Introduction

It is generally accepted that the acid hydrolysis of six coordinate Co(III) complexes proceeds through the dissociative mechanism, whereas that of four coordinate Pt(II) complexes through the associative mechanism [1]. Values of $\Delta V^{\ddagger}$ have been obtained for many of the former reactions and their magnitudes have been discussed in relation to the dissociative mechanism [2]. On the other hand, $\Delta V^{\ddagger}$ has been known hitherto only for four of the latter reactions [3, 4] and more should be needed for the further understanding of the associative character of the aquation of Pt(II) complexes.

Reishus *et al.* first obtained the equilibrium and the rate constants for the first and second aquation of *cis*-$Pt(NH_3)_2Cl_2$ [5]. From their results at 25 °C, an initial 0.5 m*M* *cis*-$Pt(NH_3)_2Cl_2$ should yield 0.41 m*M* *cis*-$Pt(NH_3)_2ClH_2O^+$ and 0.03 m*M* *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ at equilibrium (1 m*M* = 10^{-3} mol dm^{-3}). Later, Panasyuk *et al.* found that the chloride ion liberation velocities from *cis*-$Pt(NH_3)_2Cl_2$ and from $Pt(en)Cl_2$ can be described as a first order reaction with respect to the complex ion [6]. In the present work we found that in the aquation of *cis*-$Pt(NH_3)_2Cl_2$ and of $Pt(en)Cl_2$, isosbestic points are maintained at 277 and 338 nm, and at 279 and 348 nm respectively, for up to two half lives. These data indicate that for both *cis*-$Pt(NH_3)_2Cl_2$ and $Pt(en)Cl_2$ one can effectively neglect the reverse step of the first aquation and the progress of the second aquation.

Thus, in this work the first aquations of *cis*-$Pt(NH_3)_2Cl_2$ and of $Pt(en)Cl_2$,

$$cis\text{-}Pt(NH_3)_2Cl_2 + H_2O \longrightarrow cis\text{-}Pt(NH_3)_2Cl(H_2O)^+ + Cl^- \quad (1)$$

$$Pt(en)Cl_2 + H_2O \longrightarrow Pt(en)Cl(H_2O)^+ + Cl^- \quad (2)$$

are followed spectrophotometrically at 307 and 303 nm respectively, under pressure up to 2 kbar. Rate constants were obtained by the Guggenheim plot of the optical density up to two half lives. Values of $\Delta V^{\ddagger}$ are calculated from the pressure dependence of the rate constants. The reaction mechanism of the aquation of Pt(II) complexes is discussed on the basis of $\Delta V^{\ddagger}$'s of reactions (1)–(6):

$$PtCl_4^{2-} + H_2O \longrightarrow PtCl_3(H_2O)^- + Cl^- \quad (3)$$

$$Pt(NH_3)Cl_3^- + H_2O \longrightarrow Pt(NH_3)Cl_2(H_2O) + Cl^- \quad (4)$$

$$Pt(dien)Cl^+ + H_2O \longrightarrow Pt(dien)(H_2O)^{2+} + Cl^- \quad (5)$$

$$Pt(dien)Br^+ + H_2O \longrightarrow Pt(dien)(H_2O)^{2+} + Br^- \quad (6)$$

In addition, the reaction volume (ΔV) of reaction (3) is obtained dilatometrically.

Experimental

The Pt(II) complexes, $K_2[PtCl_4]$ [7], *cis*-$Pt(NH_3)_2Cl_2$ [8] and $Pt(en)Cl_2$ [9] were obtained by published methods and identified by elemental analysis. The UV absorptions were [given as complex, $\lambda_{max}(\epsilon_{max})$]: $K_2[PtCl_4]$, 327(325), 389(281), 473(73); *cis*-$Pt(NH_3)_2Cl_2$, 304(177); $Pt(en)Cl_2$, 302.5(177). The absorption intensity of the complex solution (0.5 m*M* in 1 m*M* HNO_3) was followed using a thermostatted (±0.1 °C) Hawley and Chase type high pressure cell [10]. At this acid concentration, the contribution of the base hydrolysis can be neglected [6]. A 10 m*M* aqueous solution of $K_2[PtCl_4]$ was contained in a bulb (39.2 cm^3) with an upright capillary of 0.04 cm diameter. The temperature was maintained at 40.0 ± 0.004 °C. The solution level in the capillary was followed from 30 (34% reaction) to 80 min (64% reaction) after dissolution of $K_2[PtCl_4]$. The contribution of the second aquation

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step was neglected, since for this solution at 40 °C isosbestic points were maintained at 345, 380 and 431 nm up to 80 min after the dissolution. $\Delta V^\ddagger$ of reaction (3) was obtained using the rate constants at 25 °C [3] and the activation energies in the literature [11].

Results

The rate constants at each pressure are shown in Table I. The k values are fitted to $\ln k = aP + b$ by the least-squares method. The $\Delta V^\ddagger$'s are calculated by $\Delta V^\ddagger = -RT(d \ln k/dP) = -RTa$. The rate constants increase with the increase of pressure and the resultant $\Delta V^\ddagger$'s are negative (Table II). For reaction (3), $\Delta V = 1.3 \pm 0.1$ cm^3 mol^{-1} has been obtained. This value is comparable to $\Delta V = 4$ cm^3 mol^{-1} obtained previously from the pressure dependence of the equilibrium constant [3].

TABLE I. Rate Constants ($k/10^{-4}$ s^{-1}) of the First Aquation at Each Pressure (P/bar).

1[a], *cis*-$Pt(NH_3)_2Cl_2$, 45.3 °C[b]
$\ln(k/10^{-4}\ s^{-1}) = (1.14 \pm 0.05) + (3.59 \pm 0.46) \times 10^{-4}\ P$

P		1[c]	400	800	1200	1600	2000
k	3.30	3.20	2.90	4.49	4.54	5.42	6.90
	4.04	2.79	3.78	3.62	4.33	5.72	6.80

2[a], $Pt(en)Cl_2$, 40.7 °C[b]
$\ln(k/10^{-4}\ s^{-1}) = (1.15 \pm 0.04) + (3.53 \pm 0.37) \times 10^{-4}\ P$

P		1[d]	400	800	1200	1600	2000
k	3.30	3.39	3.72	4.48	5.67	5.55	5.86
	2.69	2.80	3.74	4.15	5.30	5.98	5.58

[a] Reaction number. [b] Reaction temperature. [c] $k = 3.30 \times 10^{-4}$ s^{-1} is reported at 1 bar and 45 °C in 0.01 *M* HNO_3 [6]. [d] $k = 3.05 \times 10^{-4}$ s^{-1} is reported at 1 bar and 40 °C in 0.01 *M* HNO_3 [6].

Discussion

The three possible mechanisms are illustrated in Fig. 1. Assuming that the mechanism is common throughout reactions (1)–(6), each possibility can be examined as follows. In mechanism *I*, a dipole moment is produced in the transition state by the partly dissociated n + 1 and −1 charges. This causes some electrostrictive contribution ($\Delta V^\ddagger_{el}$) in the $\Delta V^\ddagger$. In reactions (1)–(5), the leaving ligand is commonly Cl^-. Then, the difference between the electrostriction by the three coordinate complex and that by the initial complex should be critical for the relative magnitude of $\Delta V^\ddagger_{el}$ of reactions (1)–(5). According to the Drude–Nernst equation, the electrostriction is proportional to the square of the ionic valence [12]. Then, in reactions (1)–(5), $\Delta V^\ddagger_{el}$ and consequently $\Delta V^\ddagger$ should be smaller for larger value of $(n + 1)^2 - n^2$, where n is the charge on the

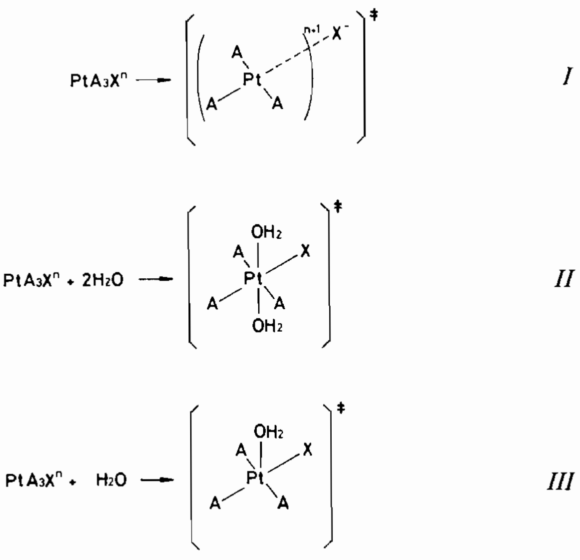

Fig. 1. Three possible mechanisms for the aquation of Pt(II) complexes: *I*: Dissociative. *II*: Associative via six coordinate intermediate. *III*: Associative via five coordinate intermediate.

TABLE II. $\Delta V^\ddagger$/cm^3 mol^{-1} (t/°C) for the First Aquation of Pt(II) Complexes.

a	Complex	$\Delta V^\ddagger$		
		Experimental	Estimated[e]	Estimated[f]
1	*cis*-$Pt(NH_3)_2Cl_2$	-9.5 ± 1.2 (45)[b]	−11.5	−5.8
2	$Pt(en)Cl_2$	-9.2 ± 1.0 (41)[b]	−9.5	−4.8
3	$PtCl_4^{2-}$	-17 ± 2 (25)[c]	−11.5	−5.8
4	$Pt(NH_3)Cl_3^-$	-14 ± 2 (26)[c]	−11.5	−5.8
5	$Pt(dien)Cl^+$	-10.5 ± 0.3 (25)[d]	−7.4	−3.7
6	$Pt(dien)Br^+$	-10.0 ± 0.3 (25)[d]	−7.4	−3.7

[a] Reaction number. [b] This work. [c] Ref. [3]. [d] Ref. [4]. [e] For mechanism *II*. ±1.1 cm^3 mol^{-1}. [f] For mechanism *III*. ±0.6 cm^3 mol^{-1}.

initial complex. This is in fact the case for the aquation of Co(III) complexes, where the mechanism is considered as dissociative [2]. However, this trend is not satisfied in reactions (1)–(5), and the possibility of mechanism *I* must be excluded.

In mechanism *II*, the activation process should be analogous to the spin state equilibrium of Ni(II) complex:

$$\mathrm{NiL^{2+} + 2H_2O \rightleftharpoons NiL(H_2O)_2{}^{2+}} \qquad (7)$$

where L is a tetraaza macrocyclic ligand. For four kinds of L ligand, ΔV's of equilibrium (7) have been obtained as -3.4 ± 1.1 cm^3 mol^{-1} at 20 °C [13]. This magnitude of ΔV has been interpreted to be composed of two competing contributions: one ($\Delta V^{\ddagger}_{\mathrm{coord}} = -11.5 \pm 1.1$ cm^3 mol^{-1}) due to the transfer of two water molecules from the bulk into the coordination sphere and the other ($\Delta V^{\ddagger}_{\mathrm{expa}} = 8.1$ cm^3 mol^{-1}) due to the expansion of the macrocyclic molecular plane. The latter should be caused by the enhanced coordination number. Correspondingly, in the case of mechanism *II*, there should be two contributions in the $\Delta V^{\ddagger}$ of reactions (1)–(6): $\Delta V^{\ddagger}_{\mathrm{coord}} = -11.5 \pm 1.1$ cm^3 mol^{-1} and $\Delta V^{\ddagger}_{\mathrm{expa}} <$ 8.1 cm^3 mol^{-1}. When L is a tetraaza macrocyclic ligand, there are four  rings in the NiL^{2+} complex. In reactions (1)–(6), the number of  rings in the initial complex may be critical for the magnitude of $\Delta V^{\ddagger}_{\mathrm{expa}}$. Then, in reactions (1), (3) and (4), $\Delta V^{\ddagger}_{\mathrm{expa}} = 0$ cm^3 mol^{-1}; in reaction (2), $\Delta V^{\ddagger}_{\mathrm{expa}} = 8.1 \times 1/4 = 2.0$ cm^3 mol^{-1}; in reactions (5) and (6), $\Delta V^{\ddagger}_{\mathrm{expa}} = 8.1 \times 2/4 = 4.1$ cm^3 mol^{-1}. The $\Delta V^{\ddagger}$'s for mechanism *II* have been estimated in this way and are illustrated in Table II. In mechanism *III*, $\Delta V^{\ddagger}$ may be estimated approximately as one half of $\Delta V^{\ddagger}$ for mechanism *II*. Thus, the $\Delta V^{\ddagger}$'s estimated for mechanism *II* agree fairly well with those obtained experimentally. Then, the associative mechanism via six coordinate intermediate should be most probable for reactions (1)–(6). In reaction (3), the experimental $\Delta V^{\ddagger}$ is rather smaller than the estimated value for mechanism *II*. In this case, the four $\mathrm{Cl^-}$ ions may attract the hydrogen atoms of the coordinated water in the transition state and this may cause the molar volume of the coordinated water to be smaller than the usual.

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