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ABSTRACT

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The acid hydrolysis of $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ has been shown to occur to a measurable extent. For this reaction:

$$[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+ + \text{H}_2\text{O} \xrightleftharpoons[k_1]{k_{-1}} [\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^{++} + \text{Cl}^-$$

the equilibrium quotient was measured at 25°C and 35°C. At 25°C this quotient was 8.4×10^{-5} at μ (ionic strength) = 0 and 25×10^{-5} at $\mu = .318$ M. This variation is consistent with the expected changes in activity coefficients. ΔH° for the reaction was found to be approximately 0. The rate constant, k_1 was $2.3 \times 10^{-5} \text{ sec.}^{-1}$ at 25°C and it was nearly independent of ionic strength. The acid hydrolysis provides a mechanism for the exchange of the chloride ligand and Cl^- . Exchange experiments with Cl^{36} showed that in addition to the acid hydrolysis, a process, first order in both, $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ and Cl^- with a rate constant of $6 \times 10^{-5} \text{ sec.}^{-1} \text{ M.}^{-1}$ contributes to the exchange. The behavior of the entire series of chloro-ammines of platinum(II) toward acid hydrolysis and chloride exchange has been summarized, and a likely mechanism for the processes has been discussed.

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CHLOROTRIAMMINEPLATINUM(II) ION. ACID HYDROLYSIS AND
ISOTOPIC EXCHANGE OF CHLORIDE LIGAND*

by

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INTRODUCTION

The potentiometric titration of a proton in the H_2O -ligand has served to characterize the kinetics and the equilibria for the acid hydrolysis of $[PtCl_4]^-$, $[Pt(NH_3)Cl_3]^-$, cis-, and trans- $[Pt(NH_3)_2Cl_2]$ in aqueous solutions.^{1a-f}

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- 1 a. L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., J. Am. Chem. Soc. 77, 2965 (1955).
b. T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., Ibid., 80, 536 (1958).
c. T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., Ibid., 81, 10 (1959).
d. C. I. Sanders and D. S. Martin, Jr., Ibid., 83, 807 (1961).

*Contribution No. 1046. Work was performed in the Ames Laboratory, Institute for Atomic Research.

- e. J. W. Reishus and D. S. Martin, Jr., Ibid., 83, ---- (1961).
- f. D. S. Martin, Jr. and R. J. Adams, "Advances in the Chemistry of the Coordination Compounds" S. Kirschner, Editor, Paper No. _____, Macmillan Co., New York, N. Y., (1961).

For each of the previous complexes except trans-[Pt(NH₃)₂Cl₂] the isotopic exchange of chloride ligands with chloride ion has been shown to occur substantially by an acid hydrolysis (aquation) or by processes independent of chloride ion which could possibly be acid hydrolysis. With trans-[Pt(NH₃)₂Cl₂] an exchange process proportional to the complex concentration and the chloride ion concentration has been observed in addition to the acid hydrolysis. The present work includes an investigation of the ion [Pt(NH₃)₃Cl]⁺ by these techniques and completes studies for the entire series of the chloro-ammine-platinum(II) complexes.

Banerjea, Basolo and Pearson² reported that the acid hydrolysis

- 2 D. Banerjea, F. Basolo and R. G. Pearson, J. Am. Chem. Soc., 79, 4055 (1957).

equilibrium constant was immeasurably small in experiments designed to measure the increase of chloride ion concentration. From the isotopic exchange of chloride ion with the ligand, they obtained a first order rate constant of $1.5 \times 10^{-5} \text{ sec.}^{-1}$. Since this process was independent of chloride ion, it presumably characterized the acid hydrolysis. However, the present work has indicated that the equilibrium constant and the rate constant can be measured experimentally by the acid titration technique.

EXPERIMENTAL

The chlorotriammineplatinum sulfate was prepared by the method of Chatt, Gamlen and Orgel.³ The salt was crystallized twice from dilute

3 J. Chatt, G. A. Gamlen and L. E. Orgel, J. Chem. Soc., 486 (1958).

KCl solutions and was recrystallized several times from water until no changes in the ultraviolet spectrum of the product occurred. Analyses for a typical preparation were: Pt - 57.5 %, Cl - 10.6 %, which agree closely to the calculated values for $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2\text{SO}_4 \cdot \text{H}_2\text{O}$: Pt - 57.62% Cl - 10.46%. Since the ultraviolet absorption spectrum appears to give the best criterion for purity, the spectrum of our product is presented in Figure 1. This spectrum is similar to but not identical with the spectrum of Chatt et al.³ The extinction coefficient is somewhat lower over the spectrum than they reported. The low valley at 240 mμ of the present spectrum probably signifies a somewhat purer sample. The spectrum in Figure 1 was obtained with chloride to suppress the acid hydrolysis, and the solution of Chatt et al.³ may have contained appreciable quantities of $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^{++}$.

Procedures and equipment for the titrations have been described in earlier publications.^{1a-f} Isotopic exchange experiments involved only solutions which were at equilibrium with respect to the acid hydrolysis reaction. The exchange was initiated by the addition of a few microliters of HCl solution, tagged with Cl³⁶. At subsequent intervals aliquots

of the solution were removed and passed through an anion exchange resin to remove chloride ion, following the techniques used for the cis-, and trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. The chloride ligand from the complexes in the effluent was stripped by heating with ammonia and the chloride in solution was then precipitated as silver chloride. The procedures and precautions for preparing, weighing and counting the samples have followed those in the earlier work.

RESULTS AND DISCUSSION

Acid Hydrolysis Equilibrium. With $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ only a single acid hydrolysis of chloride is possible, according to Equation (1):

Equilibrium solutions were prepared by first dissolving the compound $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and an additional salt to establish the desired ionic strength in water. The solutions were then allowed to stand in a thermostat for at least 24 hours. The initial concentrations and the resulting titers for the equilibrium solutions, T_∞ , are included in Table I. The equilibrium constant for the acid hydrolysis is given by:

$$K = \frac{[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})^{++}][\text{Cl}^-]\gamma_2\gamma_{\text{Cl}}}{[\text{Pt}(\text{NH}_3)_3\text{Cl}^+]\gamma_1} = \frac{T_\infty(b + T_\infty)\gamma_2\gamma_{\text{Cl}}}{(a - T_\infty)\gamma_1} \quad (2)$$

where:

a = the initial conc. of $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ (M.) (before aging)

b = initial conc. Cl^- (M.) (before aging)

γ_2 = activity coefficient of $[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})]^{++}$

γ_{Cl^-} = activity coefficient Cl^-

γ_1 = activity coefficient of $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$.

For solutions in which the ionic strength was established by the addition of relatively large amounts of Na_2SO_4 or NaClO_4 the concentration quotient, K' , defined by Equation (3),

$$K' = K\gamma_1/\gamma_2\gamma_{\text{Cl}^-} \approx K/\gamma_2 \quad (3)$$

was considered to be constant. The quotient for each of the solutions has been included in Table I. For solutions with no added salt γ_2 was set equal to: $(f_{\text{C}_2\text{O}_4^{2-}}/f_{\text{HC}_2\text{O}_4^-}f_{\text{Cl}^-})\gamma_{\pm}$. The quantity $(f_{\text{C}_2\text{O}_4^{2-}}/f_{\text{HC}_2\text{O}_4^-}f_{\text{Cl}^-})$ was evaluated for a range of ionic strengths by Pinching and Bates⁴ in the

4 G. O. Pinching and R. G. Bates, J. Res. Nat. Bur. Stds., **40**, 405 (1948).

potentiometric determination of the ionization constants of oxalic acid, and $\gamma_{\pm}^2$ was obtained from the activity coefficient of HCl in a solution of KCl of the corresponding ionic strength.⁵

5 H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions", Reinhold Publishing Co., New York, N. Y. (1943) p. 575.

The equilibrium constant for the acid hydrolysis is comparable in magnitude to that for $\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. Accordingly, the acid hydrolysis is only important in rather dilute solutions which are free

of added chloride ion. The dependence upon ionic strength, which is opposite in sign of that for $\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and $[\text{PtCl}_4]^-$, is consistent with the expected variation in the activity coefficient, γ_2 . Since in solutions of 1 to 4×10^{-3} M. the extent of the acid hydrolysis amounts to 15 to 30%, the equilibrium constant is given rather precisely by the experiments. The indicated negligible temperature dependence for K indicates that ΔH° is small.

Kinetics for Acid Hydrolysis. The rate expressions for the two reactions indicated in Equation (1) have been taken as:

$$R_1 = k_1 [\text{Pt}(\text{NH}_3)_3\text{Cl}^+] , \quad (4)$$

$$R_{-1} = k_{-1} [\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})^{++}] [\text{Cl}^-] . \quad (5)$$

The solution of the kinetics is given by Equation (6) relating the titer, T , of a solution with the time, t .

$$\begin{aligned} \ln(T_\infty - T) [T_\infty - T_\infty + \sqrt{(K' + b)^2 + 4K'_1 a}] / (T_\infty - T_0) [T - T_\infty + \sqrt{(K' + b)^2 + 4K'_1 a}] \\ = -k_{-1} \sqrt{(K' + b)^2 + 4K'_1 a} \quad t . \end{aligned} \quad (6)$$

Titers of solutions were found to increase with time and plots of the function in Equation (6) vs. time were represented satisfactorily by straight lines. Values of k_{-1} were calculated from the slopes of these lines, and k_1 was calculated from the expression:

$$k_1 = k_{-1} K' . \quad (7)$$

Rate constants could be generally duplicated to within about 10%. The experimental conditions for the rate determinations together with the

indicated values of k_1 and k_{-1} have also been included in Table I. The acid hydrolysis rate constant, k_1 , was found to be $2.3 \times 10^{-5} \text{ sec.}^{-1}$. The value for k_1 is somewhat larger than the value of 1.5×10^{-5} inferred from the rates of exchange by Banerja *et al.*,² but it is rather close to the rate of some first order substitution reactions, *e.g.* with pyridine, which they observed. Although the equilibrium constant depends rather strongly upon ionic strength, it is apparent that the acid hydrolysis rate constant, k_1 , is independent of ionic strength, and the entire effect is reflected in k_{-1} . This feature has also been noted with $[\text{PtCl}_4]^-$ and $\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, for which ionic strength variations have been studied. It is consistent with the formation of a transition state which has a +1 charge and with the reaction path that is shown in Figure 2. In this mechanism the square complexes are considered to have labile solvent ligands bonded at the axial positions. The acid hydrolysis occurs as a solvent molecule from one of the axial positions moves in to displace a chloride. The transition state is approximately a trigonal bipyramid.

Isotopic Exchange of the Chloride Ligand. The isotopic exchange of chloride ion with the ligand was measured with Cl^{36} in solutions which were at chemical equilibrium with respect to the acid hydrolysis. The solutions were usually contained in flasks wrapped with opaque tape, although in a few instances exposure to the laboratory lights did not change results. At various times aliquots from an exchange solution were withdrawn for the determination of the specific activity in the chloride ligand. For the description of the isotopic exchange the terms are defined following the practice in the earlier work.

s = Conc. of Cl^{36} in Cl^- , cts/min. l

u = Conc. of Cl^{36} in $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$, cts./min. l

I = $u + s$ = total conc. of Cl^{36}

S = $s/[\text{Cl}^-]$ (specific activity of chloride ion)

U = $u/[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

The experimental procedure yielded the quantity U , and U/U_∞ represents F , the fraction of exchange. Some typical plots of $\log(1-F)$ vs. time appear in Figure 3. It can be seen from the plots that any separation-induced exchange was negligible and that the plots were satisfactorily linear over periods of more than a half-life. The rate of exchange R_{ex} was calculated from the well-known expression:

$$R_{\text{ex}} = (\ln 2)(a - T_\infty)(b + T_\infty)/\tau_{1/2}(b + a). \quad (8)$$

Experimental conditions for the exchange experiments and the indicated half-times and exchange rates are given in Table II. The quantity $R_{\text{ex}}/(a - T_\infty)$ has been plotted as a function of chloride ion concentration in Figure 4. At 25°C experiments have been performed at two concentrations of the complex. The plot in Figure 4 shows that the points follow along a straight line with an intercept on the ordinate satisfactorily close to k_1 .

The rate for the exchange can, therefore, be represented by the expression:

$$R_{\text{ex}} = R_1 + R' = k_1[\text{Pt}(\text{NH}_3)_3\text{Cl}^+] + k'[\text{Pt}(\text{NH}_3)_3\text{Cl}^+][\text{Cl}^-]. \quad (9)$$

These results indicate that there is a substantial contribution from a process which is first order in both the complex and chloride. The value of k' is $6 \times 10^{-5} \text{ M.}^{-1} \text{ sec.}^{-1}$ at 25°C. In this respect the $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ resembles $\text{trans-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ in possessing such a chloride dependent exchange and differs from the other chloro-ammine complexes.

The equilibrium constants for acid hydrolysis, and the rate constants for acid hydrolysis and the chloride exchange for the entire series of the chloro-ammine complexes of platinum(II) have been given in Table III.

Before a rational comparison between the equilibrium quotients and rate constants can be made, each needs to be divided by n , the number of equivalent chloride ligands in the complex, which serves as a statistical factor. It can be seen that K'_1/n for the cis-chloride in $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$, cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ and for $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ forms a series with a decrease of 4-5 for each unit increase in the charge on the complex. Such a trend is in the direction predicted by the coulombic interaction between the chloride and the complex. The K'_1/n for $[\text{PtCl}_4]^{2-}$ and trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ lie much below the trend established by the others. It is interesting that these two complexes are just the ones which from their symmetry do not possess a dipole moment. The low value of K'_2 for $[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$ appears puzzling.

Although k_1 for $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ is the lowest for any of the complexes; since $n = 1$, this chloride can be considered more labile than those in $[\text{PtCl}_4]^{2-}$, $[\text{Pt}(\text{NH}_3)\text{Cl}_3]$ and cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$. The small variation in the rate constants despite the wide variation in ionic charge is certainly striking and argues strongly against a simple dissociative mechanism. It is consistent with the mechanism shown in Figure 2 which forms a transition state via a similar intramolecular rearrangement together with the loss of a labile neutral solvent ligand for each of the complexes. The replacement of a chloride by chloride in a direct

exchange process is enhanced by a more positive charge on the complex. It is measurable only for $\text{trans-[Pt(NH}_3)_2\text{Cl}_2]$ and $[\text{Pt(NH}_3)_3\text{Cl}]^+$ and can not compete with acid hydrolysis for the other complexes. The lability of chloride in the $\text{trans-[Pt(NH}_3)_2\text{Cl}_2]$ appears quite exceptional.

Table I. Equilibrium Quotients and Rate Constants for the Acid Hydrolysis of $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$. No Chloride added, i. e., "b"=0.

Initial [Pt(NH ₃) ₃ Cl ⁺] "a" M. x 10 ³	Ionic Strength "M" (Added Salt)	Equilibrium Titer "T _∞ " M. x 10 ⁴	Equilibrium Quotient K' M. x 10 ⁴	Rate Constants	
				k_{-1} M. ⁻¹ sec. ⁻¹	k_1 sec. ⁻¹ x 10 ⁵
For 25°C					
4.38	.0079	6.65	1.10	0.19	2.3
	(-)		.83 (μ=0)		
4.00	.0072	6.22	1.14	.21	2.4
	(-)		.81 (μ=0)		
1.00	.0021	2.80	1.08	.21	2.3
	(-)		.88 (μ=0)		
			Ave. .84 (μ=0)		
4.00	.318	9.13	2.70	.82	2.2
	(Na ₂ SO ₄)				
1.00	.318	3.74	<u>2.30</u>	.96	<u>2.2</u>
	(Na ₂ SO ₄)				
			Ave. 2.5 (μ=.318)		2.3
For 35°C					
1.00	.0021	2.82	1.10	.69	7.6
	(-)		.90 (μ=0)		
2.00	.100	6.25	2.84	.27	7.7
	(NaClO ₄)				
2.00	.318	6.36	2.97	.26	7.7
	(NaClO ₄)				
4.00	.318	8.85	2.51		
	(Na ₂ SO ₄)				
1.00	.318	3.65	<u>2.10</u>		—
	(Na ₂ SO ₄)				
			Ave. 2.5 (μ=.318)		7.7

Table II. Exchange of the Chloride Ligand of $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ in Equilibrium Solutions.

$[\text{Pt}(\text{NH}_3)_3\text{Cl}^+][\text{Cl}^-]$ Before Aging "a" M. $\times 10^3$	$[\text{Pt}(\text{NH}_3)_3(\text{H}_2\text{O})^{++}]$ calcd "T _∞ " M. $\times 10^4$	Ionic Strength "μ" M.	Half-Time of Exchange Min ⁻¹	Rate of Exchange R _{ex} M. sec ⁻¹ $\times 10^8$
Before Aging "b" M. $\times 10^3$				
For 25°C				
1.75	1.0	2.90	0.318 ^a	263
1.75	10.0	0.43	.318 ^a	364
1.75	40.0	0.109	.318 ^a	396
3.50	70.0	0.124	.318 ^a	352
1.75	100	0.044	.318 ^a	350
1.75	150	0.029	.318 ^a	317
1.75	40	0.076	.043	370
For 35°C				
1.75	10	0.50	.100 ^b	123
1.75	100	0.05	.103 ^b	106
1.75	40	0.076	.043	130
1.75	100	0.050	.318 ^a	110
^a added salt - Na ₂ SO ₄				
^b added salt - NaClO ₄				

Table III. Equilibrium and Rate Constants of the Chloro-ammine Complexes of Platinum(II). Temp. = 25°C. μ = 0.318 M.

Complex	Equil. Quotients and Hydrolysis		Rate Constants Acid Hydrolysis		Rate Constant Direct Exchange of Chloride Ligands $k' \text{ sec}^{-1} \text{ M}^{-1} \times 10^5$
	First K_1' $\times 10^5$	Second K_2' $\times 10^5$	First $k_1 \text{ sec}^{-1}$ $\times 10^5$	Second $k_2 \text{ sec}^{-1}$ $\times 10^5$	
$[\text{PtCl}_4]^{2-}$	1500	50	3.9	3.3	<3
$[\text{Pt}(\text{NH}_3)\text{Cl}_3]^-$ cis-	1400	4	cis- 3.6	3	<3
trans-	<200		trans- 2.5	10	<3
cis- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	330	40	2.5	3.3	~3
trans- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$	32	<2	9.8	5	78
$[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$	25	-	2.3	-	6

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CAPTIONS FOR FIGURES

Figure 1. Ultraviolet absorption spectrum of $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2\text{SO}_4 \cdot \text{H}_2\text{O}$ in a 0.05 M. solution of KCl. Extinction Coefficient, based on one formula weight of the $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$ ion, vs wavelength. Cary Recording Spectrophotometer, Model 12.

Figure 2. Possible Mechanism for Acid Hydrolysis of $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+$.

Figure 3. Typical Exchange Experiments. Temp. = 25° $\mu = 0.318$
 $a = 1.75 \times 10^{-3}$ moles $[\text{Pt}(\text{NH}_3)_3\text{Cl}]^+/\text{l.}$

Figure 4. Chloride Dependence of Exchange Rates
 $R_{\text{ex}}/[\text{Pt}(\text{NH}_3)_3\text{Cl}^+] \text{ vs } [\text{Cl}^-]$

END