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TRANS-DICHLORODIAMMINEPLATINUM(II). ACID HYDROLYSIS AND THE ISOTOPIC EXCHANGE OF THE CHLORIDE LIGANDS[*]

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ABSTRACT

The acid hydrolysis of trans-$[\mathrm{Pt(NH_3)_2Cl_2}]$ has been shown to occur to a measurable extent. For this reaction:

$$\mathrm{t-[Pt(NH_3)_2Cl_2]} + \mathrm{H_2O} \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} \mathrm{[Pt(NH_3)_2Cl(H_2O)]^+} + \mathrm{Cl^-} ,$$

the equilibrium quotient was measured at 15°, 25° and 35°C. At 25°C. the equilibrium quotient was 8.2×10^{-5} M. at μ (ionic strength) $= 0$ and 32×10^{-5} M. at $\mu = 0.318$. The indicated $\Delta H°$ for the reaction is 5.5 kcal. The rate constant, k_1, was found to be 9.8×10^{-5} sec.$^{-1}$ with an indicated $\Delta H^{\ddagger} = 20$ kcal. This rate constant was nearly independent of ionic strength. The acid hydrolysis provides a mechanism for the isotopic exchange between the chloride ligands and $\mathrm{Cl^-}$. Exchange experiments with $\mathrm{Cl^{36}}$ showed that in addition to the acid hydrolysis, a process, first-order in both $[\mathrm{Pt(NH_3)_2Cl_2}]$ and $\mathrm{Cl^-}$ with a rate constant of 7.8×10^{-4} sec.$^{-1}$ M.$^{-1}$, contributed to the exchange.

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[*] Contribution No. 1005. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

This is the first chloride-dependent exchange found for any of the chloro-complexes of platinum(II). For this process $\Delta H^{\ddagger} = 20$ kcal. The acid hydrolysis equilibrium for t-$[Pt(NH_3)_2Cl(H_2O)]^+$ was too slight for detection by the methods available. However it could be shown from the exchange experiments that the rate constant of any such reaction could not be substantially greater than k_1. The behavior of t-$[Pt(NH_3)_2Cl_2]$ was contrasted to the behavior of other chloroammine-complexes of platinum(II).

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INTRODUCTION

Previous studies in this Laboratory[1a-e] have utilized the potentiometric titration of the proton in the H_2O-ligands to characterize the kinetics and equilibria for acid hydrolysis of $[PtCl_4]^=$, $[Pt(NH_3)Cl_3]^-$ and cis-$[Pt(NH_3)_2Cl_2]$ in aqueous solutions. For each of the previous systems, the isotopic exchange of chloride ligands with chloride ion has been shown to occur by either an acid hydrolysis (aquation) or by processes independent of chloride ion concentration, which could possibly be acid hydrolysis. These techniques have now served to characterize the exchange of chloride ligands of trans-$[Pt(NH_3)_2Cl_2]$ and its acid hydrolysis,

$$\underline{t}\text{-}[Pt(NH_3)_2Cl_2] + H_2O \underset{R_1}{\overset{R_{-1}}{\rightleftarrows}} [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-, K_1 . \quad (1)$$

Materials. The usual preparation of t-$[Pt(NH_3)_2Cl_2]$ by heating $[Pt(NH_3)_4]Cl_2$ to 250°C. was used.[2,3] It was purified by fractional crystallization from solutions in dilute HCl.

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Solutions of the preparation, ca. 4×10^{-4} M., were found to attain rather rapidly a molar conductivity of ca. 35 l./ohm mole cm. Subsequently, fractional crystallizations of the compound were repeated as many as eight times without altering this behavior nor with any significant change in the ultraviolet absorption spectrum. Since divergent results have been reported for this compound and the absorption spectrum appears to provide the best criterion of purity, the ultraviolet absorption spectrum of a solution of our preparation is given in Fig. 1. The spectrum appears to agree closely with that published by Chatt, Gamlen and Orgel.[4]

Because of low solubility and the need for sufficient concentrations for titrations, the concentration range studied was severely limited. Also, crystals of t-$[Pt(NH_3)_2Cl_2]$ always dissolved slowly. For equilibrium titrations and the exchange studies a weighed quantity of the compound was shaken with the solution until solid was completely dissolved and a steady state attained. However, for a kinetics evaluation in which a freshly prepared solution was needed, a sample was shaken with the solution for 10 min. The undissolved crystals were then filtered out. The concentration was evaluated either by a chloride analysis of the solution or from the equilibrium titre.

EXPERIMENTAL RESULTS AND DISCUSSION

Acid Hydrolysis Equilibrium. Titres for equilibrium solutions at 15°, 25° and 35°C. are given in Table I. For several experiments, but not for all, the indicated titres represent averages of two to four titrations. If the hydrolysis of a second chloride were negligible, the equilibrium titre, T_{∞} (equiv. acid/l.) equals the concentration of $[Pt(NH_3)_2Cl(H_2O)]^+$. The equilibrium constant for Reaction (1) is then given by

$$K_1 = \frac{[Pt(NH_3)_2Cl(H_2O)^+][Cl^-]\gamma_{\pm}^2}{[Pt(NH_3)_2Cl_2]\gamma_o} = \frac{T_{\infty}(b+T_{\infty})\gamma_{\pm}^2}{(a-T_{\infty})\gamma_o} \tag{2}$$

a = Initial concn. $\underline{t}$-$[Pt(NH_3)_2Cl_2]$. (M.) (Before aging)

b = Initial concn. Cl^-. (M.) (Before aging).

(The γ's are the indicated activity coefficients.) For solutions in which the ionic strength was established at 0.318 M. by added Na_2SO_4, the concentration quotient, K_1' defined by Eq. (3),

$$K_1' = K_1\gamma_o/\gamma_{\pm}^2 \tag{3}$$

was considered to be constant. This quotient was calculated for each of the high ionic strength solutions in Table I. For solutions with no added salt, γ_o was taken as 1, and $\gamma_{\pm}$ was taken equal to the activity coefficient of HCl in a solution of KCl[5] with an ionic strength equal to T_{∞}. From these activity coefficients and T_{∞}, K_1 was calculated from the data for low ionic strength in Table I. The calculated equilibrium constants were substantially unchanged over the approximately 2.5-fold concentration range. Therefore the system appeared to be satisfactorily characterized by the equilibrium for Eq. (1). Accordingly, an upper limit of 2×10^{-5} M. was set for a second hydrolysis equilibrium quotient. The acid, $\underline{t}$-$[Pt(NH_3)_2Cl(H_2O)]^+$, was indicated from the titration curves to have a pK of approximately 6.

The magnitude of the constant, K_1', from the present work is considerably below the estimate given by Grinberg and Shagisultanova[6] and is probably too small to be measured accurately by their method.

Kinetics for Acid Hydrolysis. If the following rate expressions apply:

$$R_1 = k_1\,[\mathrm{Pt(NH_3)_2Cl_2}]\ , \tag{4}$$

$$R_{-1} = k_{-1}[\mathrm{Pt(NH_3)_2Cl(H_2O)^+}]\,[\mathrm{Cl^-}]\ , \tag{5}$$

and if acid hydrolysis of $[\mathrm{Pt(NH_3)_2Cl(H_2O)}]^+$ is negligible, the solution of the rate equation[1a] yields:

$$\ln(T_\infty - T)\left[T_o - T_\infty + \sqrt{(K_1' + b)^2 + 4K_1'a}\right] \Big/ (T_\infty - T_o)\left[T - T_\infty + \sqrt{(K_1' + b)^2 + 4K_1'a}\right]$$

$$= -k_{-1}\sqrt{(K_1' + b)^2 + 4K_1'a}\quad t\ . \tag{6}$$

It was found that titres of solutions of freshly dissolved t-$[\mathrm{Pt(NH_3)_2Cl_2}]$ increased rapidly with time; indeed, this method could not have been used satisfactorily had the acid hydrolysis rate been much higher. Values for k_{-1} were obtained from the plots of the function expressed in Eq. (6), and k_1 was calculated from the expression

$$k_1 = K_1' \cdot k_{-1}\ . \tag{7}$$

The reactions could be followed satisfactorily for about two half-times. Results for experiments under various conditions are in Table II. Rate constants could be duplicated generally to within about 15%. The exchange experiments described in the next section probably provided better values for the rate constants.

Since crystals of t-[$Pt(NH_3)_2Cl_2$] dissolve slowly it is believed that in the experiments of Banerjea et al.,[2] the rapid acid hydrolysis had attained equilibrium by the time they had complete solution. Thus, they observed no change in the small conductivity of the solutions which they probably attributed to a low concentration of electrolytic impurity.

Isotopic Exchange of Chloride Ligands. The rates of isotopic exchange were measured with Cl^{36} tracer only in solutions which were at chemical equilibrium. The solutions were contained in the dark, although in a few instances exposure to the laboratory lights did not change results. At various times, aliquots from a reaction solution were passed rapidly through anion exchange resins to replace Cl^- by NO_3^-. The columns had sufficient capacity to completely remove Cl^-, but a large excess of capacity was avoided. The effluent solutions were heated with excess NH_3 for 30 min. Acidification and the addition of $AgNO_3$ precipitated the chloride which had passed through the anion exchange in the neutral and positive complexes. The specific activity of the chloride in the precipitates was measured by methods which have been described in previous work.[1a,c,e]

For the description of isotopic exchange of chloride ligands the following terms are defined:

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

u = concn. of Cl^{36} in t-[$Pt(NH_3)_2Cl_2$], cts./min. l

v = concn. of Cl^{36} in t-[$Pt(NH_3)_2Cl(H_2O)$]$^+$, cts./min. l

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

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

$U = u/2[\mathrm{Pt(NH_3)_2Cl_2}]$

$V = v/[\mathrm{Pt(NH_3)_2Cl(H_2O)^+}]$

$Y = (u+v)/(2[\mathrm{Pt(NH_3)_2Cl_2}] + [\mathrm{Pt(NH_3)_2Cl(H_2O)^+}])$.

The experimental procedure yielded the quantity Y, and Y/Y_∞ was taken as F, the fraction of exchange. Normally, plots of log(1-F) vs t appeared linear over a period of at least twice the times of half-exchange. Conditions and results of the exchange experiments are collected in Table III. Chloride ion suppresses the acid hydrolysis, Reaction (1), so in many of the experiments $t\text{-}[\mathrm{Pt(NH_3)_2Cl_2}] \approx a >> t\text{-}[\mathrm{Pt(NH_3)_2Cl(H_2O)^+}]$. Under these conditions $Y \approx U$ and the exchange process can be treated as an exchange between the two components, $t\text{-}[\mathrm{Pt(NH_3)_2Cl_2}]$ and Cl^-. The well-known expressions for the rate of the exchange, R_{ex}, in such systems apply and

$$R_{ex} = (\ln 2)\ 2ab/T_{1/2}(b+2a)\ . \qquad (8)$$

The quantity, R_{ex}/a, calculated from Expression (8) for each of the experiments, has been plotted as a function of chloride ion concentration for 15°, 25° and 35°C in Fig. 2. For the experiments with $\mathrm{Cl}^- > 0.003$ M. the points for each temperature fall rather closely along straight lines. The straight lines extrapolate to values of the ordinate which agree satisfactorily with values for k_1, so for $\mathrm{Cl}^- > 0.003$ M. the expression can be written

$$R_{ex} = R_1 + R' = k_1[\mathrm{Pt(NH_3)_2Cl_2}] + k'[\mathrm{Pt(NH_3)_2Cl_2}][\mathrm{Cl}^-]\ . \qquad (9)$$

The exchange rate contains a second-order (chloride dependent) term, R', in addition to the expected acid hydrolysis term R_1. At $[Cl^-]$ = .1 M., the two processes contribute about equally to the exchange.

At very low chloride concentrations the points in Fig. 2 deviate badly from the straight line function because the condition that $[Pt(NH_3)_2Cl(H_2O)^+] << [Pt(NH_3)_2Cl_2]$ is no longer valid. The low chloride data provide information about the exchange of the $[Pt(NH_3)_2Cl(H_2O)]^+$ species. For example, in the solution at 25°C. in which the initial t-$[Pt(NH_3)_2Cl_2]$ concentration, a, was 7.59×10^{-4}M. and the KCl concentration, b, was 0.001 M., 13% of the complexed chloride was in the aquo-complex. The rate expressions for the introduction of Cl^{36} tracer into the complexes were taken as

$$du/dt = R_1 (S + V - 2U) + R' (S - U) \tag{10}$$

$$dv/dt = R_1 (U - V) + R'' (S - V) \quad . \tag{11}$$

R'' is considered to be the rate of exchange of chloride in $[Pt(NH_3)_2Cl(H_2O)]^+$ with Cl^-, and it contains any contribution from the acid hydrolysis of this complex. The solutions for these differential equations can be combined to yield the expression,

$$(1 - Y/Y_\infty) = C_1 e^{-\alpha_1 t} + C_2 e^{-\alpha_2 t} \quad . \tag{12}$$

The parameters, C_1, C_2, α_1 and α_2, are determined by a, b, K_1, k_1, k' and R''/R_1. Calculated values of $(1-Y/Y_\infty)$ were plotted for various values of R''/R_1 for the experiments with 0.001 M. KCl added at 15°, 25° and 35°C. The calculations have been summarized in Table IV. The times of half-exchange for each of the experiments have been tabulated with the assumption that $R''/R_1 = 0$. Also, the value of R''/R_1 which will account for the observed time of half-exchange is given for each experiment. It is apparent that times of half-exchange with $R''/R_1 = 0$ did not differ greatly from the observed quantities so that R'' is not indicated accurately by these experiments. An upper limit of 0.5 k_1 can be set for a first-order rate constant k''. At the very least it is safe to conclude that the acid hydrolysis or other chloride exchange process of $[Pt(NH_3)_2Cl(H_2O)]^+$ can not be large compared to that for the acid hydrolysis $[Pt(NH_3)_2Cl_2]$.

The rate constant, k_1, for the acid hydrolysis of t-$[Pt(NH_3)_2Cl_2]$ is 2.5 times larger than the value which Banerjea et al.[2] reported for the isotopic exchange rate. However it is approximately equal to the first-order rate constants for a number of substitution reactions for t-$[Pt(NH_3)_2Cl_2]$ which they determined. One can now satisfactorily attribute the first-order dependence of these substitutions by glycine, analine, pyridine, and hydroxide to a rate-determining acid hydrolysis followed by a rapid replacement of H_2O by the substituting group or neutralization in the case of OH^-.

A summary of the acid hydrolysis equilibrium quotients and constants for platinum(II) complexes is given in Table V, from which it can be seen that k_1 for t-$[Pt(NH_3)_2Cl_2]$ is larger than for any of the other chloro-ammine complexes. Only the rate constant for one of the chlorides of $[Pt(NH_3)(H_2O)Cl_2]$ is higher. Indeed, as Basolo and Pearson[7] have commented, the small range of variation in these constants is striking and argues against a simple dissociative mechanism with co-ordination number of 3. Also, the activation enthalpies, $\Delta H^{\ddagger}$ have all been within ±2 kcal of 19 kcal, which can hardly be evaluated more accurately. An ionic strength of 0.318 increases the equilibrium quotient K_1' to 4 times K_1. An increase would be expected because of the activity coefficient $\gamma_{\pm}^{2}$ in Eq. (3). However, the rate constant k_1 is substantially unchanged; all of the large ionic strength effect is reflected in k_{-1}. This feature strongly supports the hypothesis that the transition state for the hydrolysis has zero charge. A feasible scheme is shown in Fig. 3. It is proposed that the complex with its four square-planar ligands forms weaker bonds to solvent molecules along the normal to the plane which constitute labile ligands. The co-ordination figure is therefore a distorted octahedral arrangement. In the transition state one of the H_2O groups moves in displacing the chloride to yield approximately a trigonal bipyramid arrangement. The similarity in rate constants results from the feature that the process is the identical intramolecular step in each case with little dependence upon ionic charge, and differences in rate must be due to rather subtle differences in structure.

The chloride dependent exchange reaction with rate R' is the only such measurable process found with any of the chloroammine complexes of platinum(II) which have been studied. Instances in which chloride can compete with the solvent, which is present in such overwhelming excess, for displacing a chloride, are rather rare although Rich and

Taube[8] have found a chloride dependent contribution to the exchange of Cl^- with the square-planar $[AuCl_4]^-$. The rate constant k' for t-$[Pt(NH_3)_2Cl_2]$ must be at least 25 times the rate constant for $[PtCl_4]^=$ or for cis-$[Pt(NH_3)_2Cl_2]$, which were too small to be measured in the presence of the acid hydrolysis. This large factor is contrasted with the much smaller ratio of 2.3 in the acid hydrolysis rate constants.

The replacement of chloride ligands by Cl^- may be enhanced by changing the ionic charge on the complex in a positive sense. Thus the second-order reaction rate of the neutral complexes may be relatively more rapid than the acid hydrolyses of the anion species. There is evidence of such an effect in the k_{-1}'s for the various complexes, which are second-order rate constants for the replacement of H_2O ligands by chloride. However some of the variations in the k_{-1}'s as well as the difference in k_1 between cis- and t-$[Pt(NH_3)_2Cl_2]$ must be attributed to rather obscure structural causes which are commonly disguised under the labeling of trans-effect.

Table I. Equilibrium Quotients for the Acid Hydrolysis of <u>trans</u>-[$Pt(NH_3)_2Cl_2$] .

Ionic Strength "μ" (M.)	Initial [$Pt(NH_3)_2Cl_2$] "a" (M. x 10^4)	Equilibrium Titre "T" (M. x 10^4)	Free Chloride Added* "b" (M. x 10^4)	Equilibrium Quotient K' (M. x 10^4)
		For 15.0°C.		
0.318	5.00	2.40	0.013	2.22
0.318	5.60	2.51	0.13	2.14
0.318	5.94	2.61	0.13	2.15
			Average	2.2
		For 25.0°C.		
0	4.08	1.48	0	0.84
0	8.16	2.23	0	0.81
0	8.44	2.27	0	0.80
			Average	0.82
0.318	7.82	3.73	0.013	3.42
0.318	7.53	3.51	0.013	3.07
0.318	4.33	2.44	0.013	3.16
0.318	8.26	3.75	0.013	3.13
0.318	3.73	2.17	0.013	3.03
0.318	5.86	3.05	0.013	3.31
			Average	3.2
		For 35.0°C.		
0	8.13	2.55	0	1.12
0	8.29	2.70	0	1.25
0	8.43	2.55	0	1.09
			Average	1.1
0.318	4.06	2.53	0.13	4.41
0.318	8.16	4.17	0.13	4.49
0.318	8.26	4.14	0.13	4.31
0.318	8.63	4.24	0.13	4.22
			Average	4.4

$\Delta H° = 5.5$ kcal. $\Delta S° = 5$ e.u.

*The concentration of chloride was obtained from the analysis of the Na_2SO_4 added to adjust the ionic strength.

Table II. Rate Constants for the Reversible Acid Hydrolysis of trans-[$Pt(NH_3)_2Cl_2$].

Temp. °C.	Initial [$Pt(NH_3)_2Cl_2$] "a" M. x 10^4	initial Ionic Strength "μ" M.	Equilibrium [$Pt(NH_3)_2Cl(H_2O)^+$] "x" ∞	Half-Time min.	k_1 (x10^5) sec.$^{-1}$	k_{-1} sec.$^{-1}$ M.$^{-1}$
15°	2.68	0.318	1.56	147	3.2	0.145
25°	3.00	0.318	1.89	60	8.9	0.28
25°	5.23	0	1.70	22	10.0	1.2
35°	9.03	0.318	4.44	13.2	28	0.65
35°	6.27	0	2.14	8.8	27	2.5

Table III. Exchange of the Chloride Ligands of trans-[$Pt(NH_3)_2Cl_2$] .

Temp. (°C.)	Initial [$Pt(NH_3)_2Cl_2$] "a" (M. x 10^4)	Initial Added [Cl^-] * "b" (M.)	Equilibrium [$Pt(NH_3)_2(H_2O)Cl^+$] "x" (M. x 10^6)	Time of Half-exchange (min.)	Rate of Exchange † $R_{ex.}$ ($sec.^{-1}$ M.) x 10^8
15.0	5.95	0.001	100	390	1.6
	4.67	0.003	32	570	1.4
	4.98	0.040	2.7	560	2.0
	4.95	0.070	1.5	460	2.4
25.0	7.59	0.001	179	126	5.4
		0.003	81	160	7.3
		0.010	27	190	8.0
		0.040	6.9	160	10.6
		0.070	4.0	150	11.3
		0.100	2.8	130	13.2
	3.80	0.001	95	170	2.9
		0.003	41	190	3.7
		0.040	3.4	190	4.5
		0.100	1.4	130	6.6
35.0	7.59	0.001	194	42	16.5
		0.020	15	61	27.
		0.040	7.7	56	30.
		0.070	4.6	49	35.
		0.100	3.1	43	41.
	3.80	0.001	106	56	8.9
		0.040	3.8	58	14.9
		0.100	1.5	43	20.

*Ionic strength was adjusted to $\mu = 0.318$ by addition of Na_2SO_4 .

† $R_{ex.}$ calculated with assumption that $R'' = 0$ and that $x << a$.

Table IV. Chloride Exchange Experiments for trans-[$Pt(NH_3)_2Cl_2$] at Low Chloride Concentrations. (Added KCl = 0.001M., μ = 0.318M.)

Temp. °C.	Initial [$Pt(NH_3)_2Cl_2$] "a" M. x 10^4	Equilibrium [$Pt(NH_3)_2Cl(H_2O)^+$] "x" M. x 10^4	Time of Half-Exchange hrs. Obsd.	Calc. for $(R'/R_1) = 0$	Indicated R''/R_1
15.0	5.95	1.00	6.5	6.7	.04
25.0	3.80	.95	2.8	3.2	.1
25.0	7.59	1.79	2.1	2.4	.1
35.0	3.80	1.06	.93	1.03	.08
35.0	7.59	1.94	.70	.77	.09

Table V. Equilibrium and Rate Constants for Reactions of the Chloro-ammine complexes of Pt^{II}. Temp. = 25°C. μ = .318 M.

Complex.	Equil. Consts. Acid Hydrolysis		Rate Consts. Acid Hydrolysis		Direct Exchange of Chloride Ligands Rate Const. k_{Cl} sec^{-1} M^{-1} x10^5
	First K_1 x10^5	Second K_2 x10^5	First k_1 sec^{-1} x10^5	Second k_2^* sec^{-1} x10^5	
$[PtCl_4]^=$	1500	50	3.9	3.3	<3
$[Pt(NH_3)Cl_3]^-$	cis-1400 trans-<200	4	cis-3.6 trans-2.5	3 10	<3
cis-$[Pt(NH_3)_2Cl_2]$	330	40	2.5	3.3	~ 3
t-$[Pt(NH_3)_2Cl_2]$	32	<2	9.8	5	78
$[Pt(NH_3)_3Cl]^+$ (9)	25		2		

[*] Based on the rate of a chloride independent exchange of chloride ligand with Cl^-.

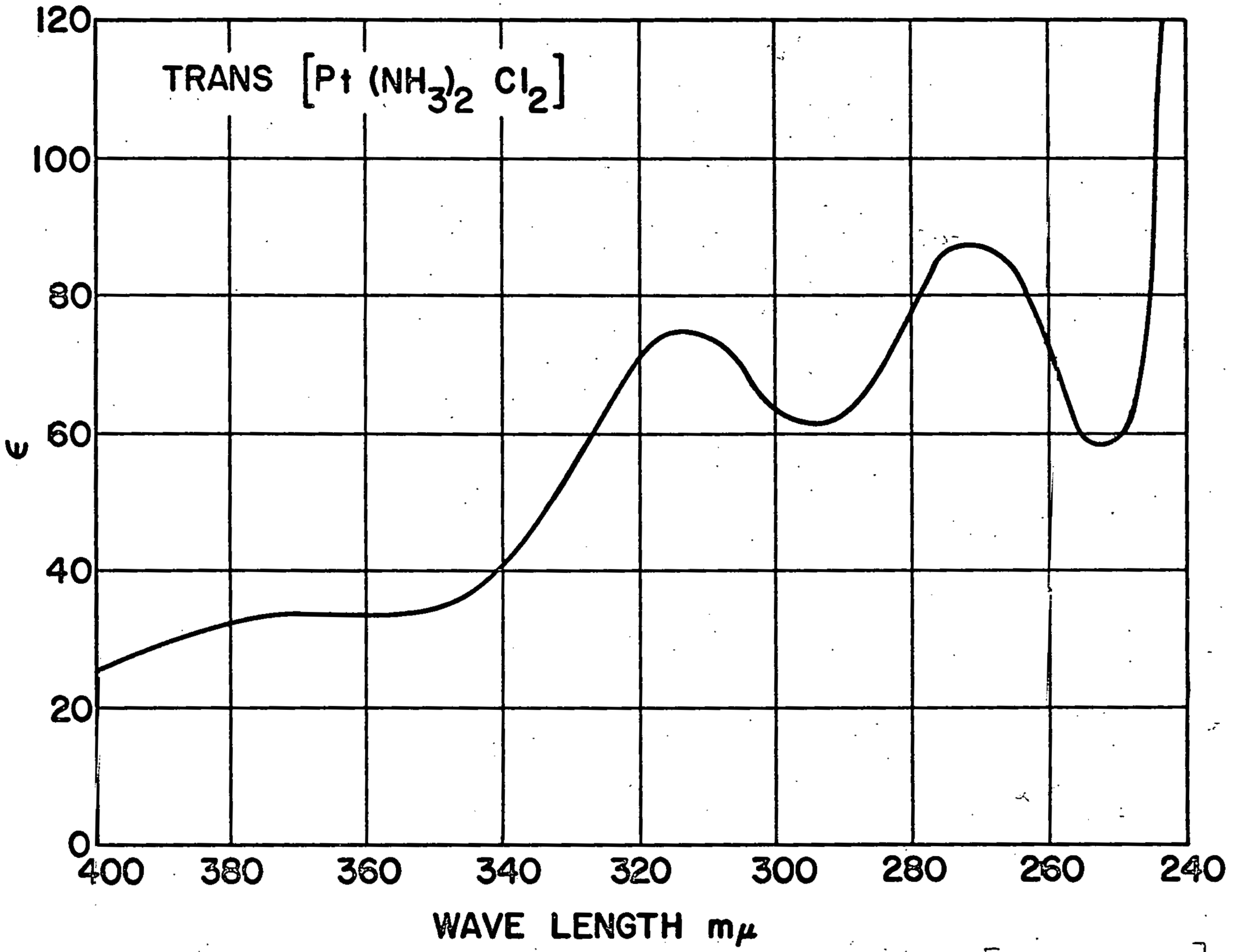

Fig. 1. Ultraviolet absorption spectrum of trans- $[Pt(NH_3)_2Cl_2]$. Extinction coefficient *vs* wave length. Spectrum obtained with a solution: 1.00×10^{-3}M. trans- $[Pt(NH_3)_2Cl_2]$, 0.200M. KCl (to suppress hydrolysis) in a 10 cm. cell in a Cary Recording Spectrophotometer, Model 12.

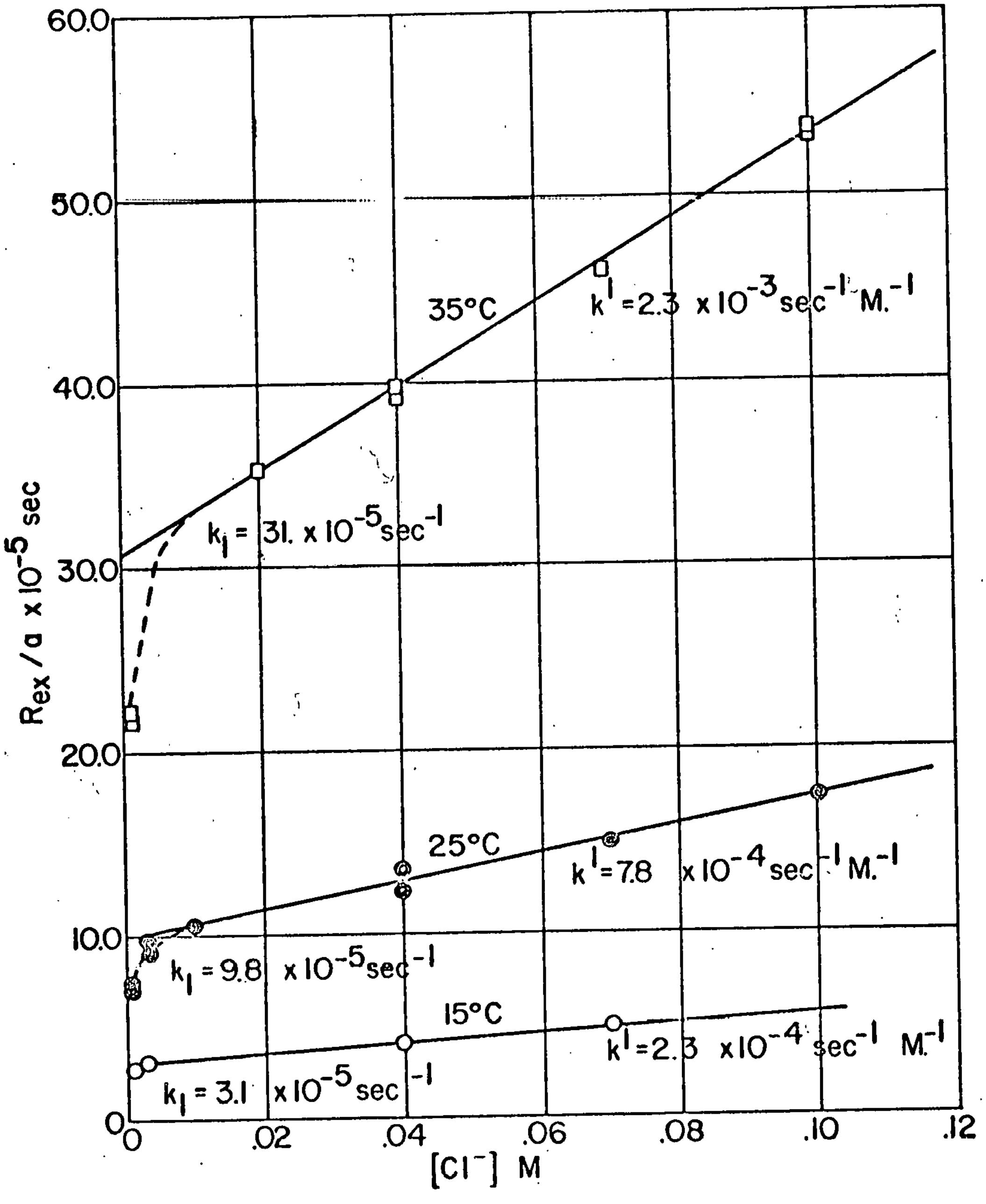

Fig. 2. Exchange Experiments. Plots of R_{ex}/a vs chloride concentration for 15°C., 25°C., 35°C. From the indicated rate constants $\Delta H^{\ddagger}$ (k_1) = 19.6 kcal., $\Delta S^{\ddagger}$ (k_1) = -11 e.u., $\Delta H^{\ddagger}$ (k') = 19.6 kcal., $\Delta S^{\ddagger}$ (k') = -7 e.u.

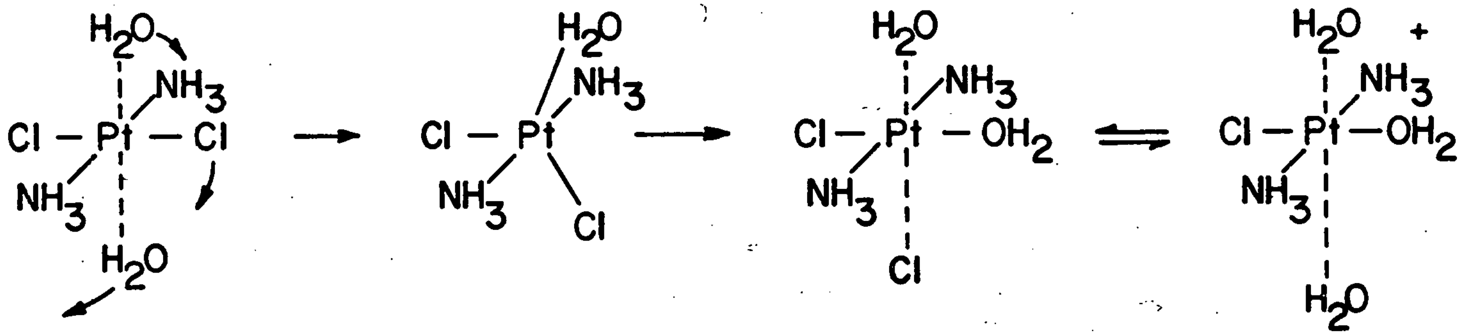

Fig. 3. Mechanism for the acid hydrolysis of trans- $[Pt(NH_3)_2Cl_2]$.

FIGURE CAPTIONS

Fig. 1. Ultraviolet absorption spectrum of trans-[$Pt(NH_3)_2Cl_2$] . Extinction coefficient vs wave length. Spectrum obtained with a solution: 1.00×10^{-3} M. trans-[$Pt(NH_3)_2Cl_2$] , 0.200 M. KCl (to suppress hydrolysis) in a 10 cm. cell in a Cary Recording Spectrophotometer, Model 12.

Fig. 2. Exchange Experiments. Plots of R_{ex}/a vs chloride concentration for 15°C., 25°C., 35°C. From the indicated rate constants $\Delta H^{\ddagger}(k_1) = 19.6$ kcal., $\Delta S^{\ddagger}(k_1) = -11$ e.u., $\Delta H^{\ddagger}(k') = 19.6$ kcal., $\Delta S^{\ddagger}(k') = -7$ e.u.

Fig. 3. Mechanism for the acid hydrolysis of trans-[$Pt(NH_3)_2Cl_2$].

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