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AQUATION AND ISOTOPIC EXCHANGE OF THE CHLORIDE LIGANDS OF THE *CIS*-DICHLORODIAMMINEPLATINUM(II) COMPLEX

by

John William Reishus

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

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Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1960

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I. INTRODUCTION

The subject of this thesis is the acid hydrolysis (aquation) and isotopic exchange of the chloride ligands in the cis-dichlorodiammine-platinum(II) complex.

Platinum(II) compounds have been studied for over a hundred years. Among the early workers Jorgensen (1) and Peyrone (2) investigated the reactions

$$[PtA_4]^{++} + 2X^- \longrightarrow [PtA_2X_2] + 2A \qquad (I.1)$$

and

$$[PtX_4]^{=} + 2A \longrightarrow [PtA_2X_2] + 2X^- \qquad (I.2)$$

respectively, where A was NH_3 or an organic amine and X^- was a halide. It was noted that different isomers with the formula $[PtX_2A_2]$ were obtained from the two preparations. Werner (3) was the first to explain the existence of the two isomeric forms by the proposal of a square planar configuration for Pt(II) complexes.

It has been proposed that in aqueous acid solutions cis-$[Pt(NH_3)_2Cl_2]$ undergoes the following aquation:

$$\underline{cis}\text{-}[Pt(NH_3)_2Cl_2] \rightleftharpoons [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^- \qquad (I.3)$$

$$[Pt(NH_3)_2Cl(H_2O)]^+ \rightleftharpoons [Pt(NH_3)_2(H_2O)_2]^{++} + Cl^- \qquad (I.4)$$

Werner and Miolati (4) observed conductivity evidence of this aquation; however, they did not interpret their results in this way. More recently Drew *et al.* (5), Jensen (6), and King (7,8), used conductivity measurements to study the extent of aquation in Pt(II) ammines. King in particular carried out extensive experiments with compounds of the general type $[Pt(NH_3)_2X_2]$ and $[Pt(NH_3)_3X]X$. He found two calsses of di- and triammines: the first in which $X=Cl^-$, Br^-, and NO_2^- dissolved in water as such and behaved as nonelectrolytes in the diammine case and as salts of univalent cations in the triammine case while the second class ($X=NO_3^-$, $SO_4^=$, picrato, etc.) dissolved with complete or substantial conversion into the aquo di- and triammines. Ryabchikov (9) investigated the isomeric bases of cis- and trans-$[Pt(NH_3)_2Cl_2]$. He prepared the hydroxo complexes by treatment of the chloro compounds with $AgNO_3$ and by titration of the resulting nitrato complex with NaOH. It was observed that although both complexes required two equivalents of acid, the cis-dihydroxo compound behaved as a monoacidic substance in that only one break was observed in the titration curve while the trans-dihydroxo complex behaved as a diacidic substance. A quantitative treatment of the hydrolysis of $K_2[PtCl_4]$ by Grantham et al. (10) was later reinvestigated with respect to the second aquation equilibrium by Sanders and Martin[1]. The acid hydrolysis of $K[PtNH_3Cl_3]$ was examined by Elleman et al. (11). And Grinberg and Kukushkin (12) investigated the hydrolysis kinetics of $K[PtNH_3Cl_3]$, $K_2[PtCl_4]$, and $[Pt(NH_3)_3Cl]Cl$. Leden and Chatt (13) found that the aquation equilibrium

$$[Pt(C_2H_4)Cl_3]^- + H_2O \rightleftharpoons \text{trans-}[Pt(C_2H_4)Cl_2(H_2O)] + Cl^- \qquad (I.5)$$

was established within two minutes. Gelman et al. (14) cited evidence for the formation of aquo species of halide pyridine platinum complexes.

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[1] Sanders, C. I. and D. S. Martin, Jr., Ames, Iowa. Acid hydrolysis of $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$. Private communication. 1960.

The exchange and rates of substitution of ligands in transition metal complexes was the subject of a review article by Taube (15). He defined labile complex ions as ones in which the ligand exchange substantially established equilibrium in not more than two minutes and inert complex ions as ones in which the equilibrium required longer periods of time to be attained. Furthermore it was stated that the rates of substitution were influenced predominantly by the electronic configuration of the complex ion. Labile complexes were found to be ones in which the central metal atom had vacant d orbitals to accommodate the electron pair of the incoming ligand; inert complexes were characterized by filled d orbitals on the central atom.

With this definition Pt(II) complexes would be classified as inert. And in general the ligand exchange of many Pt(II) complexes have very convenient half-times to measure experimently. Early exchange studies were done primarily by the Russian school of chemists. Grinberg and Filinov (16) investigated the $[PtBr_4]^{=}$-Br^{*-} system and a year later Grinberg (17) reported on the applications of radioactive tracers to problems concerning complex compounds. He studied several Pt(II) and Pt(IV) systems among them the one above and $[PtBr_6]^{=}$-Br^{*-}. Exchange in the $[PtX_4]^{=}$-X^{*-} system was investigated more thoroughly and systematically by Grinberg and Nikol'skaya (18). They let X be CN^-, I^-, Br^-, and Cl^-, and found that the rates of exchange decreased in the series $CN^- > I^- > Br^- > Cl^-$ but also that the stabilities of the $[PtX_4]^{=}$ complexes toward dissociation were in the same order. The significance of this reversal in the thermodyamic stabilities of Pt(II) complexes was discussed by Leden and Chatt (13). They also found that the affinities of the halides and thiocyanate ion for

Pt(II) increased in the order $F^- << Cl^- < Br^- < I^- < SCN^-$ whereas for most metals the order of halide stability is the reverse of that given above. It was noted that the metals of reverse order were Cu(I), Pd(II), Ag, Pt(II), Au, and Hg and that these all had low valences but formed strongly covalent bonds with donor atoms of low electronegativity. Metals in this group are also known to have filled d orbitals under the valence shell. The reverse stability of the $[MX_4]^=$ ions was attributed to $d\pi$-$p\pi$ or $d\pi$-$d\pi$ bonding between the d electrons of the metal and vacant p or d orbitals on the ligand atoms

Grantham et al. (10) examined the exchange of Cl^{*-} in the $K_2[PtCl_4]$ system and reported that the exchange with $K_2[PtCl_4]$ occurred by only the observable first acid aquation while the exchange with $[PtCl_3(H_2O)]^-$ occurred by a chloride independent process. Sanders and Martin[2] later showed that the first and second aquation equilibria can explain the observed exchange. The $K[Pt(NH_3)Cl_3]$-Cl^{*-} system was investigated by Elleman et al. (19). They found that exchange occurred by the hydrolysis equilibria and by a chloride independent process. The latter could also have been an aquation reaction with a small equilibrium constant. Grinberg and Shagisultanova (20) reexamined the $[PtBr_4]^=$-Br^{*-} exchange and found that it proceded through an aquo species. The same mechanism for the exchange between halides and Pd(II) complexes was indicated in work done by Grinberg et al. (21), and Ettle and Johnson (22) also concluded that Cl^- exchanged with $[Co(NH_3)_4Cl_2]^+$ by a slow aquation process. In fact both

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[2] Ibid.

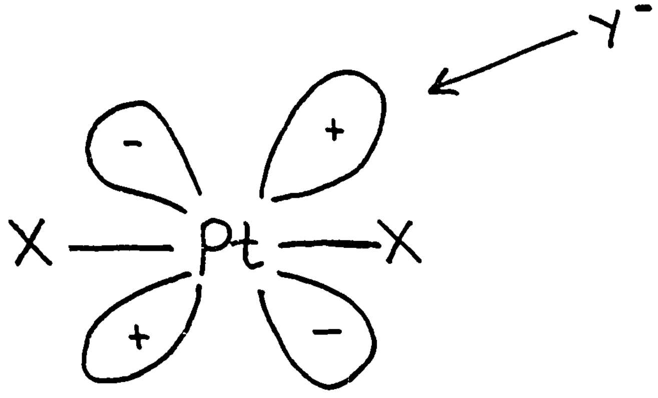
Taube (15) and Stranks and Wilkins (23) point out in general that there are very few unambiguous examples of direct ligand exchange of transition metal complexes in solution because of the excellent complexing power of the water molecule.

Banerjea *et al.*(24) investigated, rather extensively, kinetics for the reaction of various Pt(II) complexes with a variety of nucleophilic reagents. They found that the reactions fell roughly into two categories. In the first category the reactions were first order in complex, zeroth order in reactant, and they reacted at approximately the same rate; in the second category the reactions were first order in both complex and reactant and the rates were faster than those in the first group. In general the nucleophilic reagents in category 1 were conspicuous by their low position in the *trans*-effect series while those in category 2 had high *trans*-effects. For the substitution reactions of square planar complexes the authors proposed a "dissociation" mechanism which was later described in a more generalized form in a book by Basolo and Pearson (25, pp. 188-189). Before discussion their mechanism, it will be helpful to explain what is meant by the *trans*-effect and to discuss briefly the various theories that have been proposed to explain it.

The early workers in platinum chemistry were concerned primarily with the preparation of various compounds. They noticed that the substitution of ligands into the inner coordination sphere of Pt(II) complexes was not statistical in nature, but rather, seemed to be governed by some directional effect. Werner (3) mentioned in passing that the position of substitution of a ligand in Pt(II) complexes seemed influenced by the coordinated ligand in the position *trans* to the incoming group. The term "*trans*-

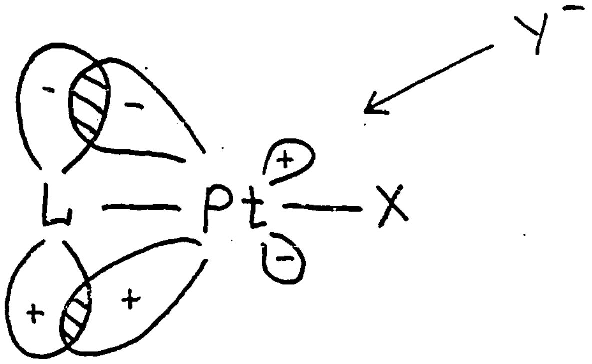
effect" was so designated initially by Chernyaev (26) and it stated that the bond holding a ligand trans to an electronegative or otherwise labilizing ligand was weakened. Quagliano and Schubert (27) discussed the trans-effect qualitatively and illustrated its use in preparations of numerous isomeric Pt(II) complexes. The first fairly general theory of this effect was an electrostatic explanation proposed by Grinberg (28). For ligands unable to form π-bonds with the metal atom, he found a correlation between the polarizability of the ligand and its trans-effect. Grinberg theorized that if one ligand of a square planar complex had a greater polarizability than the other ligands, it would induce a dipole in the central atom oriented away from the group trans to the labilizing ligand. This he concluded weakened to a relatively greater extent the bond trans to the polarizing ligand than the two bonds cis to it. Hence substitution was favored in the trans position. Grinberg's proposal served as a pattern for other purely electrostatic theories by Syrkin (29) and Cardwell (30). These later hypotheses were more general in that they were based on a greater induced replusive potential at the trans-position from a negative ligand than at the cis-positions.

While these theories correlated the trans-effect of groups such as H_2O, NH_3, and Cl^-, they could not explain the large trans-effect of such ligands as Br^-, I^-, C_2H_4, R_3P, R_2S, CO, NO, etc. Chatt et al. (31) and Orgel (32) independently utilized π-bonding between the d electrons of Pt(II) and vacant p or d orbitals on the ligands to explain the trans-effect. Contrasted to the previous theories, a π-bonding ligand would not necessarily weaken the bond to the group opposite it but instead would remove the d electrons of Pt from the area about that ligand. In this way the trans position is made more accessible to an incoming negative ligand; that is, the energy of the transition state for an S_{n2} attack by a ligand at the trans ligand is lowered. Pictorially it may be represented as follows. For a complex trans-$[PtA_2X_2]$ in which the ligands X are unable to π- or double-bond, the spacial distribution of the d_{xz} or d_{yz} orbitals of the platinum atom is



(I.6)

For a complex $[PtA_2LX]$ where L can π-bond with the platinum's electrons, the $d\pi$ -$p\pi$ bond might be represented as



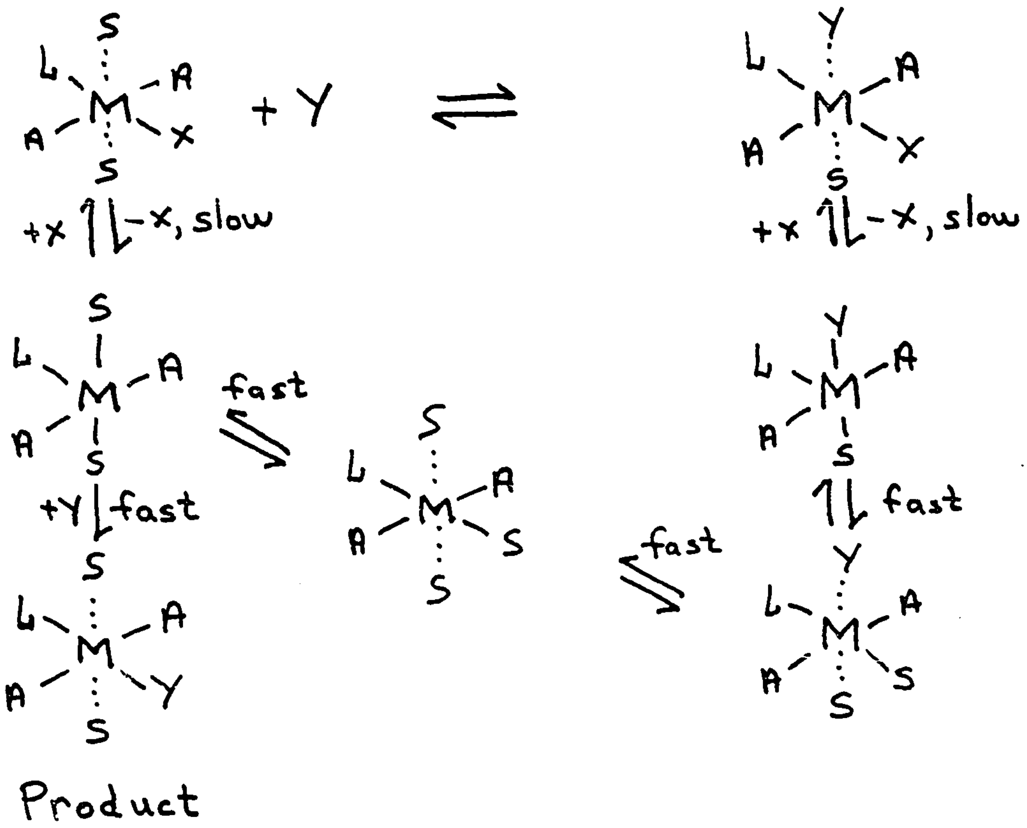
(I.7)

This π-bonding hypothesis and the electrostatic theory for non-π-bonding ligands qualitatively predicts the following observed order of decreasing trans-effect rather well: $CN^- \sim C_2H_4 \sim CO \sim NO > SC(NH_2) \sim R_2S \sim R_3P \sim NO_2^- \sim I^- \sim CNS^- > Br^- > Cl^- >$ pyridine $> NH_3 > OH^- > H_2O$.

To return to Basolo and Pearson's book (25, pp. 188-189), they proposed the mechanisms below for substitution of square planar complexes in solution. For complexes with non-π-bonding ligands the authors proposed the following "dissociation" mechanism of substitution through a square pyramid intermediate.

$$[MLA_2X] + Y \text{ ——— } [MLA_2Y] + X$$

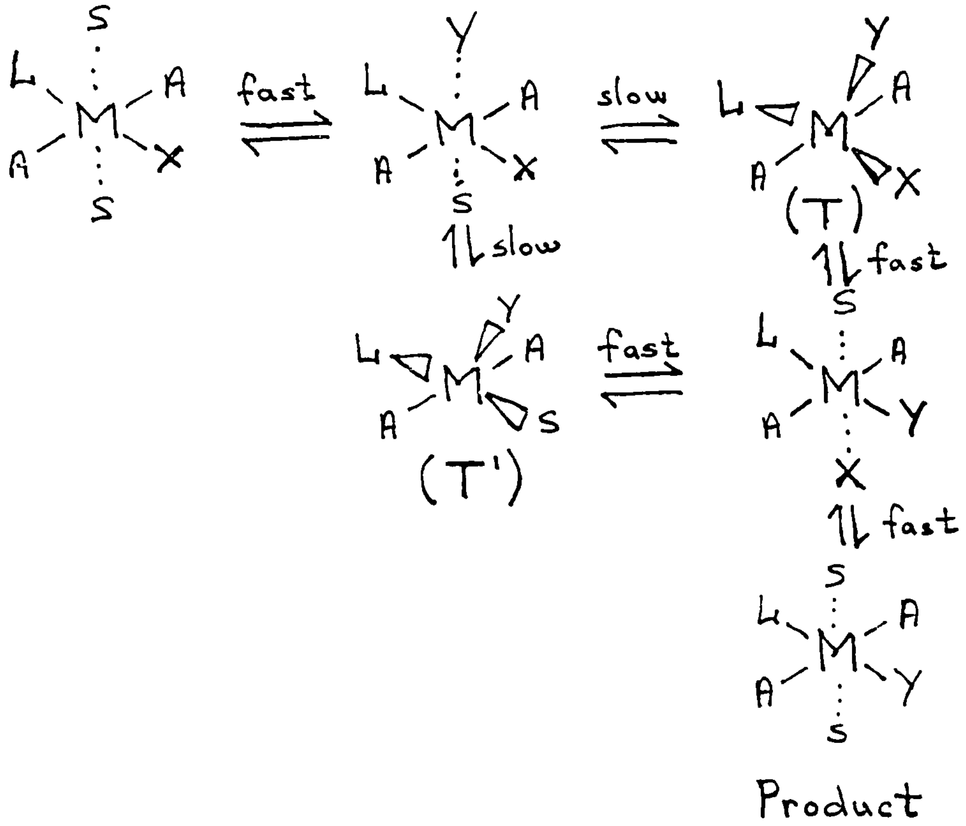
Path I Path II



(I.8)

By Path I the kinetics of the substitution would be first order in complex and zeroth order in the reactant. Path II would be first order in both complex and reactant because of the top equilibrium. Both paths are characterized by a stable solvated complex, $[MA_2LS]$.

If L or Y is capable of π-bonding, the authors proposed a "dissociation" mechanism of substitution through a trigonal bipyramid intermediate as given below:



(I.9)

When L or Y is capable of π-bonding, this path (first order in complex and Y) will be favored because the trigonal bipyramid intermediate will be stabilized by double bonding between L or Y and the $d_{x^2-z^2}$ and/or the d_{xz} orbitals of Pt. This is the same concept introduced by Chatt and Orgel except that it is applied to the incoming ligand instead of a coordinated ligand. The path through intermediate (T') considers the possibility that

X may be lost initially during the formation of the trigonal bipyramid. It is obvious that by both "dissociation" mechanisms the solvent plays an important role in aiding the displacement of X. And indeed when Pearson et al. (33) studied the rate of chloride exchange of trans-[Pt(py)$_2$Cl$_2$] in a variety of solvents, they found that the rates were influenced in a manner explainable by a strong interaction of the solvent and metal ion in the rate determining step.

Exchange in Pt(IV) complexes will be discussed only briefly. It is significant to note that exchange is believed not to proceed via the stable aquo intermediates but by a redox mechanism. Rich and Taube (34) showed that exchange between $[PtCl_4]^=$ and $[PtCl_6]^=$ was catalyzed by Pt(III). Grinberg and Shagisultanova (20) supported this mechanism for exchange while Basolo et al. (35) cited evidence that could indicate exchange in Pt(IV) complexes is catalyzed by Pt(II).

II. EXPERIMENTAL

A. Materials

1. Pt

Platinum was obtained from the Fisher Scientific Company in the form of $K_2[PtCl_6]$.

To obtain iridium-free platinum all of the purchased material was treated in the following manner. Aqueous solutions of $K_2[PtCl_6]$ were made basic (pH 11) with NaOH and the $[PtCl_6]^=$ was reduced to Pt by addition of a small excess of hydrazine. After the filtrate was removed, the platinum was treated with hot concentrated HNO_3 followed by hot concentrated HCl to remove the less noble metals. After the metal was washed with water, it was converted to $H_2[PtCl_6]$ by treatment with hot aqua regia as described by Vezes (36) in his method for preparing $K_2[PtCl_4]$. The solution of $H_2[PtCl_6]$ was then converted to $H_2[PtBr_6]$ by heating to near dryness three times with concentrated HBr. The $[PtBr_6]^=$ was precipitated as $K_2[PtBr_6]$ by the addition of aqueous KCl and this violet-colored salt was then recrystallized at least three times from hot water.

The iridium-free $K_2[PtBr_6]$ was recycled through the same reduction procedure to obtain iridium-free platinum.

Any waste solutions that were believed to contain platinum were also treated as above to reclaim the platinum for future preparations.

2. $K_2[PtCl_4]$

$K_2[PtCl_4]$ was prepared according to the method described by Vezes (36). $H_2[PtCl_6]$, prepared from platinum by treatment with hot aqua regia, was converted to the insoluble $K_2[PtCl_6]$ by the addition of KCl and reduced to $K_2[PtCl_4]$ by refluxing the Pt(IV) salt with stoichiometric amounts of $K_2C_2O_4$. The reflux solution yielded reddish crystals of $K_2[PtCl_4]$ which were recrystallized from hot water.

3. Cis-$[Pt(NH_3)_2Cl_2]$

Cis-$[Pt(NH_3)_2Cl_2]$ was prepared by an adaptation of a method proposed by Lebedinskii and Golovnya (37). Six grams of KCl and six grams of $K_2[PtCl_4]$ were dissolved in 50 ml. of a 20% $NH_4C_2H_3O_2$ solution and refluxed for half an hour. After the solution cooled, the greenish-yellow precipitate was recrystallized three times from hot water, acidified with HCl; the final product was the yellow cis-$[Pt(NH_3)_2Cl_2]$.

4. Chlorine-36

Chlorine-36 was obtained from the Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee. The isotope was delivered in the form of approximately 2 N. HCl. It decays by emission of a 0.71 Mev beta with a half-life of approximately 3.5×10^5 years (38).

5. Water

All water used in experiments was distilled water redistilled from alkaline permanganate solutions.

6. Additional reagents

All other reagents such as $NaNO_3$, used in recharging exchange resins, Na_2SO_4, KCl, $K_2C_2O_4$, N_2H_4, $NH_4C_2H_3O_2$, etc. were reagent grade chemicals purchased either from the Baker Chemical Company or the Fisher Scientific Company.

B. Equipment

1. Constant temperature bath

All solutions were kept within 0.1° C. of the desired temperature by a Sargent constant temperature bath. A series of intermittant heaters balanced the cooling effect of tap water run through a cooling coil.

2. Exchange columns and resins

Ion-exchange columns, 30 cm. long, were made with a coarse sintered glass filter for rapid flow. The columns were packed with approximately 12 to 14 cm. of 50-100 in. mesh resin.

The anion resin used was Doxew-1 and the cation resin was Amberlite IR-120.

3. Filtering equipment

Smooth uniform counting samples were obtaized from exchange runs by directly filtering the AgCl precipitates onto a round filter paper. The apparatus consisted of two parts: a round sintered glass disk with an inside diameter of 2.8 cm. fused into the top of a funnel and a glass chimney of the same diameter. With the filter paper on top of the sintered glass disk, the chimney and disk were held together by rubber bands. Uniform samples of 6.16 cm.^{2} area were obtained by pouring the AgCl slurry into the chimney.

4. Geiger-Muller counter

Activities of samples were measured with a TCG-1 Geiger-Muller counter manufactured by Tracerlab Inc. The tube had a dead time of approximately 300 microseconds and was housed in a lead shield. The pulses from the tube were recorded by a Berkeley decimal scalar, model 100. All samples were placed 7 mm. vertically below the window of the counting tube.

5. Analytical apparatus

To titrate acid species, standardized solutions of NaOH were added from a Machlett Auto-Burette, a self-filling burette calibrated to hundredths of a milliliter. The change in pH was followed with a Beckman model "G" pH meter standardized against a pH 7 buffer. Shielded electrodes, model 1190-80, allowed pH determinations outside the shielded cabinet.

If the absorbance of a reaction solution at a particular wavelength was desired, a Beckman Model D.U. spectrophotometer with 1 cm. silica cells was used. For situations in which the uv spectrum from 220 mu to 400 mu was desired, a Cary Recording Spectrophotometer, Model 12, manufactured by Applied Physics Corp., Pasadena, California, was used with 10 cm. silica cells. No temperature control of the reaction solution was possible with this latter instrument.

A 700° C. muffle furnace manufactured by Schaar and Company, Chicago, Illinois, was used in the combustion analysis for platinum in cis-$[Pt(NH_3)_2Cl_2]$. Platinum content was also determined by plating the metal out of solution onto a platinum electrode with a Sargent-Slomin Electrolytic Analyzer.

C. Procedures

1. Analysis of cis-$[Pt(NH_3)_2Cl_2]$

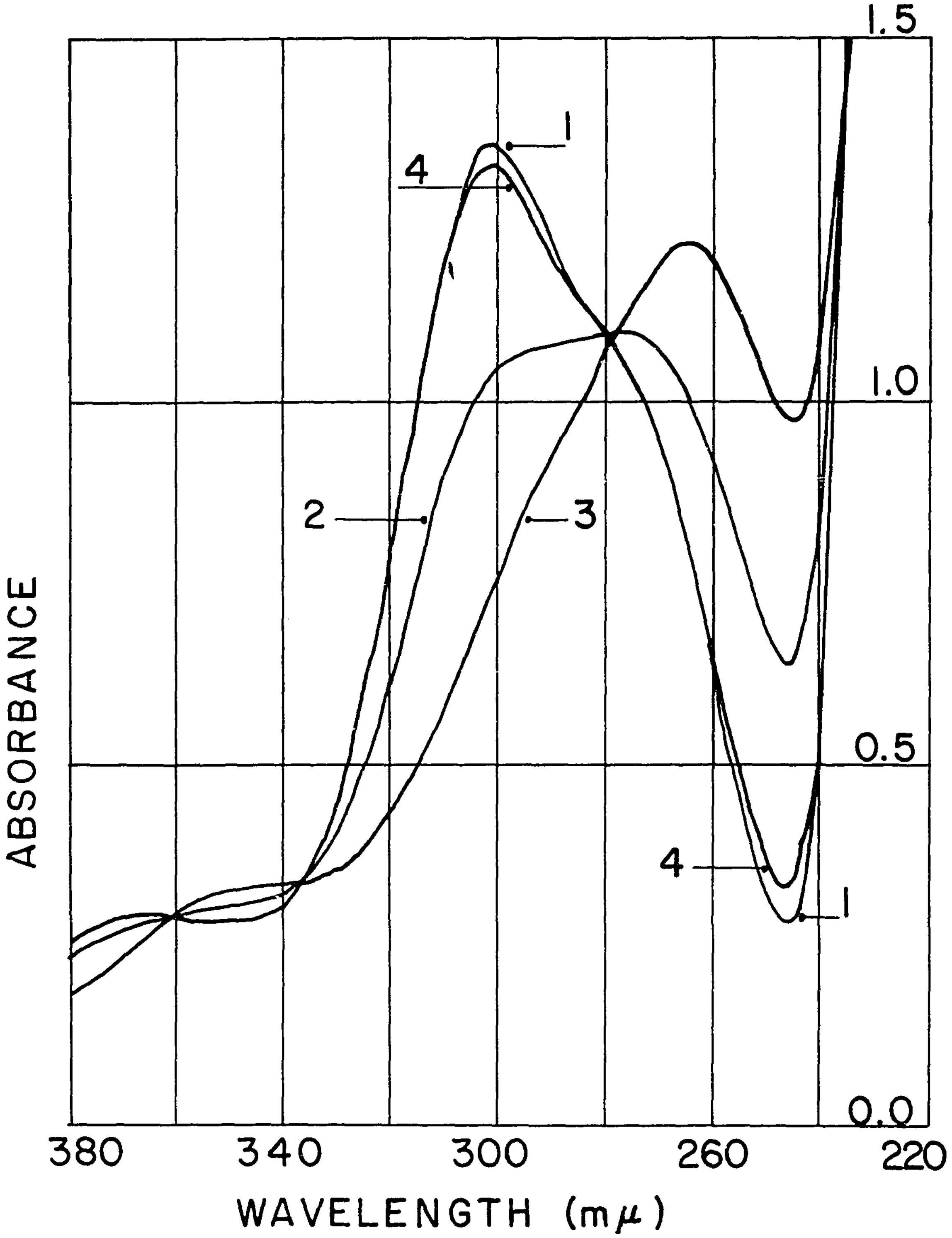
Each preparation of the platinum complex was usually analyzed for platinum and chloride and the spectrum was taken with a Cary recording spectrophotometer. The analysis for the metal was performed by the electrolysis of a solution of a weighed amount of the compound for 1.5 to

2.0 hrs. The solution was acidified with sulfuric acid and a drop of nitric acid was added as a depolarizing agent. A current of little less than 0.1 amp. was used. (When a faster method was desired, the platinum was determined by combustion analysis.) After the electrolysis was completed, excess $AgNO_3$ was added to precipitate the chloride. From the spectrum of the compound particular attention was paid to the ratio of the absorbance of the peak at 300 mu to that of the valley at 247 mu. Any value greater than 4.5 in this ratio was considered to correspond to cis-$[Pt(NH_3)_2Cl_2]$ of acceptable purity. A spectrum of the compound appears in Fig. 1.

2. Determination of equilibrium titre

A weighed amount of cis-$[Pt(NH_3)_2Cl_2]$ was dissolved in the desired volume of water to which enough Na_2SO_4 had been added for an ionic strength of 0.318. The contribution of the ions produced by the hydrolysis of the complex to the ionic strength of a solution was neglected in all reactions conducted in this research. The solution was then allowed to equilibrate in a water bath of the desired temperature. To several solutions a weighed amount of KCl was added also. All aliquots were titrated with approximately 0.1 N. or 0.05 N. NaOH. The initial aliquot was generally titrated slowly to obtain a rather complete picture of the titration curve. The second and third aliquots were titrated more rapidly with points concentrated around the endpoint indicated by the first aliquot. Finally a single point titration was taken by the addition of nearly the exact amount of base required to reach the endpoint. This was used as the endpoint of the titrations and it gave an estimate of the amount of base-induced aquation that occurred during the titrations. A typical titration

Fig. 1. Spectra for the aquation of an 0.00102 M. *cis*-$[Pt(NH_3)_2Cl_2]$ solution. Temp. = 25.0° C., μ = 0.318. 1, 10 min. after dissolving complex; 2, 240 min.; 3, approximately 22 hrs., *i.e.*, at equilibrium; 4, approximately 45 hrs. after adding KCl to solution, [KCl] = 0.134 M.


1.5
1.0
0.5
0.0
1
4
2
3
4
1
ABSORBANCE
380
340
300
260
220
WAVELENGTH (mμ)

curve with a single point titration is shown in Fig. 2. The average titre obtained from these titrations was then used to find the first and second aquation equilibrium constants from Eq. III.5.

3. Determination of first aquation rate constant

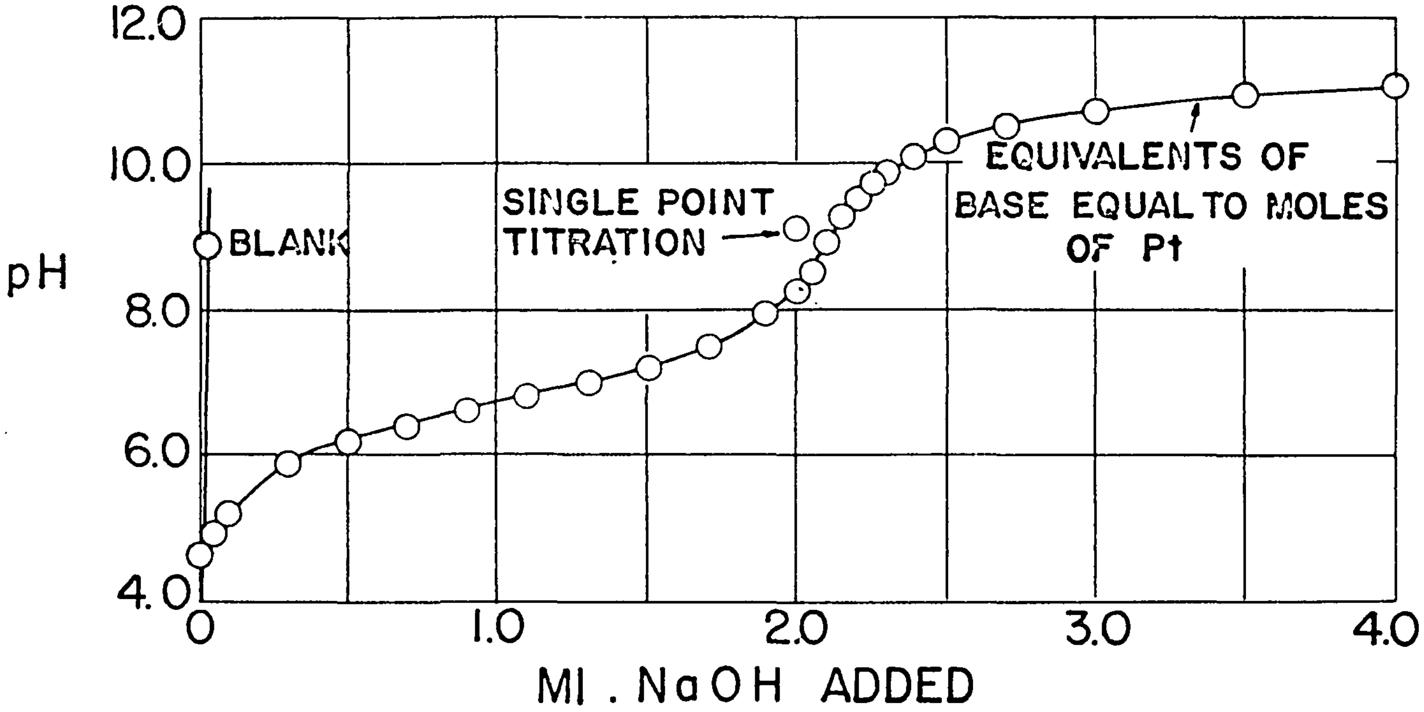
The rate constant for the first aquation was determined by titration of the acidic $[Pt(NH_3)_2Cl(H_2O)]^+$ species formed during approximately the first 100 min. of hydrolysis. A weighed amount of the compound was dissolved in an aqueous Na_2SO_4 solution (ionic strength 0.318) of the proper volume and temperature. Zero time was taken to be the moment when the compound was added to the solution. Aliquots, taken over a period of about 60 to a 100 min., were then titrated with NaOH as rapidly as possible to minimize any base-induced hydrolysis. The amount of $[Pt(NH_3)_2Cl(H_2O)]^+$ formed was then plotted versus time. The initial slope of the curve was used to find the rate constant.

4. Exchange experiments

The success of the exchange experiments rested on the clean separation of the platinum complexes from the ionic chloride in solution. Anion exchange resins in the NO_3^- cycle proved an acceptable method for this separation. $AgNO_3$ was found to be unsuitable because of a fast induced exchange between the complex and ionic chloride caused by the precipitation of AgCl.

Exchange experiments were conducted in two types of solutions: "aged" solutions and "fresh" solutions. The former were ones in which the cis-$[Pt(NH_3)_2Cl_2]$ was allowed to reach equilibrium with its hydrolysis species before the exchange was initiated by the addition of radioactive chloride; the latter were ones in which the platinum compound, KCl, and

Fig. 2. Titration curve for aged solution of *cis*-[$Pt(NH_3)_2Cl_2$] with approximately 0.1 N. NaOH. Temp. = 25.0° C., μ = 0.318, initial concentration of complex = 0.005 M.


12.0
10.0
8.0
6.0
4.0
pH
0
1.0
2.0
3.0
4.0
Ml . NaOH ADDED
BLANK
SINGLE POINT TITRATION
EQUIVALENTS OF BASE EQUAL TO MOLES OF Pt

Na_2SO_4 were dissolved in solution simultaneously with the addition of radioactive chloride.

The object in both types of exchange experiments was to follow the rate of introduction of Cl^{36} into either the cis-$[Pt(NH_3)_2Cl_2]$ alone or into the combined cis-$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_2Cl(H_2O)]^+$ species.

The introduction of chloride into cis-$[Pt(NH_3)_2Cl_2]$ in an aged solution was determined in the following way. The desired amounts of the complex, KCl, and Na_2SO_4 were weighed out and dissolved in water of the proper temperature and volume. The solution was allowed to equilibrate at this temperature. After the reaction flask was wrapped with black electrical tape to prevent any light-induced exchange, 5 to 20 lambda of 2 N. HCl^{36} were introduced into the reaction solution. This moment was taken as the zero time of exchange. After five minutes, the first aliquot of the solution (generally 15-25 ml.) was pipetted into an anion exchange column in the NO_3^- cycle to remove all the ionic chloride and effectively quench the exchange reaction. Directly from the anion column the solution passed into a cation exchange column in the Na^+ cycle to remove the $[Pt(NH_3)_2Cl(H_2O)]^+$ species. The aliquot was finally eluted from the exchange resins with 100 ml. of water. The effluent solution was made basic by the addition of excess aqueous NH_3 and boiled for 30 min. to replace all the chloride ligands on the neutral complex with NH_3. In the process ionic chloride and $[Pt(NH_3)_4]^{++}$ were formed. The solution was then acidified with H_2SO_4 and an excess of $AgNO_3$ was added to precipitate the chloride. The AgCl was counted and its specific activity determined (cts./min. mg. Cl^-). The specific activity at infinite time, i.e., at equilibrium, was found by direct treatment of a small aliquot with NH_3 and the precipitation of the chloride present in all species. The fraction of exchange for the cis-$[Pt(NH_3)_2Cl_2]$ species only, F_u, at five minutes was, therefore, $S_{5\ \text{min.}}/S_\infty$. The other aliquots, taken periodically over at least one time of half-exchange, were treated in the same manner.

If the time of half-reaction for the exchange of chloride in the cis-$[Pt(NH_3)_2Cl_2]$ and the $[Pt(NH_3)_2Cl(H_2O)]^+$ species together had been desired, the procedure would have been the same except that the aliquots would not have been passed through the cation resin.

Fresh solution exchange experiments were handled in an identical manner, but all the aliquots were taken within the first two hours of exchange.

III. MATHEMATICAL TREATMENT OF DATA

A. Aquation Equilibrium Constants

Research by other workers (4,5,6,7,9) have indicated that cis-$[Pt(NH_3)_2Cl_2]$ undergoes an acid hydrolysis. The aquation of the complex may be described by the equations:

$$\underset{(a-x-y)}{\underline{cis}\text{-}[Pt(NH_3)_2Cl_2} \underset{R_{-1}}{\overset{R_1}{\rightleftharpoons}} \underset{(x)}{[Pt(NH_3)_2Cl(H_2O)]^+} + \underset{(b+x+2y)}{Cl^-} \qquad \text{(III.1)}$$

$$\underset{(x)}{[Pt(NH_3)_2Cl(H_2O)]^+} \underset{R_{-2}}{\overset{R_2}{\rightleftharpoons}} \underset{(y)}{[Pt(NH_3)_2(H_2O)_2]^{++}} + \underset{(b+x+2y)}{Cl^-} \qquad \text{(III.2)}$$

where a = initial concn. of cis-$[Pt(NH_3)_2Cl_2]$, moles/l.

x = concn. of $[Pt(NH_3)_2Cl(H_2O)]^+$, moles/l., at time t

y = concn. of $[Pt(NH_3)_2(H_2O)_2]^{++}$, moles/l., at time t

$(a-x-y)$ = concn. of cis-$[Pt(NH_3)_2Cl_2]$, moles/l., at time t

b = initial concn. of ionic chloride, moles/l.

$(b+x+2y)$ = concn. of ionic chloride, moles/l., at time t

The expressions for the rates were taken to be

$R_1 = k_1(a-x-y)$, moles/l.sec.

$R_{-1} = k_{-1}x(b+x+2y)$, moles/l.sec.

$R_2 = k_2x$, moles/l.sec.

$R_{-2} = k_{-2}y(b+x+2y)$, moles/l.sec.

Concentration equilibrium constants for reactions III.1 and III.2, respectively, can be written as

$$K_1 = \frac{x_e(b + x_e + 2y_e)}{(a - x_e - y_e)} \qquad \text{(III.3)}$$

and

$$K_2 = \frac{y_e(b + x_e + 2y_e)}{x_e} \qquad \text{(III.4)}$$

where the subscript e on the x and y indicate steady state equilibrium concentrations of those species.

To be completely rigorous, activity coefficients for each species in solution should be included to obtain thermodynamic equilibrium constants; however, all reaction solutions were conducted at a constant ionic strength of 0.318. Therefore, it was expected that all activity coefficients were constant and that any concentration ratios would remain constant also under these conditions.

With the assumption that each water ligand has one acidic hydrogen atom, the total observed equilibrium titre, T_e, would be $(x_e + 2y_e)$. Now the equilibrium constants can be rewritten as

$$K_1 = \frac{x_e(b + T_e)}{(a-x_e-y_e)} \qquad \text{(III.3a)}$$

and

$$K_2 = \frac{y_e(b + T_e)}{x_e} \quad . \qquad \text{(III.4a)}$$

After x_e and y_e are eliminated from the product K_1K_2, a relation between the measurable quantities a, T_e, and $(b + T_e)$ and the unknown equilibrium constants is obtained:

$$[(b + T_e)T_e - (b + T_e)a]K_1 + (T_e-2a)K_1K_2 = -(b + T_e)^2T_e \qquad \text{(III.5)}$$

Therefore from two titrations that differ in a and/or b, two different equilibrium titres can be found and the two equilibrium constants can be determined by simultaneously solving the two equations of type III.5.

B. Rate Constant for First Aquation

From reactions III.1 and III.2 the expression for the rate of formation of $[Pt(NH_3)_2Cl(H_2O)]^+$ is given by

$$dx/dt = k_1(a-x-y)-k_{-1}x(b+x+2y)-k_2x+k_{-2}y(b+x+2y) \qquad (III.6)$$

If, during the early stages of aquation, the amount of x and y formed is small, the approximation can be made that

$$dx/dt = k_1a$$

or, upon integration,

$$x = k_1at \qquad (III.7)$$

If the derivative $(dx-dt)_{t=0}$ is the initial slope of the graph of x versus t, then k_1 is given by

$$k_1 = [(dx/dt)_{t=0}]/a. \qquad (III.8)$$

C. Exchange Equations

1. Aged solution exchange equations

It is obvious that Eqs. III.1 and III.2 represent a path by which radioactive chloride can be introduced into both cis-$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_2Cl(H_2O)]^+$. An alternate path of exchange exists also if either of the above platinum species exchange directly with the chloride ion. If the rates of these alternate paths are designated R' and R'', the total chloride exchange scheme can be written as:

$$\underset{\substack{(a-x_e-y_e),\\ u,\ S_u}}{\underline{cis}\text{-}[Pt(NH_3)_2Cl_2]} \underset{R_{-1}}{\overset{R_1}{\rightleftharpoons}} \underset{\substack{(x_e),\\ v,\ S_v}}{[Pt(NH_3)_2Cl(H_2O)]^+} + \underset{\substack{(b+x_e+2y_e),\\ s,\ S_s}}{Cl^-} \qquad (III.9)$$

$$[Pt(NH_3)_2Cl(H_2O)]^+ \underset{R_{-2}}{\overset{R_2}{\rightleftharpoons}} [Pt(NH_3)_2(H_2O)_2]^{++} + Cl^- \qquad (III.10)$$

$$\underline{cis}\text{-}[Pt(NH_3)_2Cl_2] \xrightarrow[Cl^*]{R'} \underline{cis}\text{-}[Pt(NH_3)ClCl^*] + Cl^- \qquad (III.11)$$

$$[Pt(NH_3)_2Cl(H_2O)]^+ \xrightarrow[Cl^*]{R''} [Pt(NH_3)_2Cl^*(H_2O)]^+ + Cl^- \qquad (III.12)$$

where $u = Cl^{36}$, Cl^*, atoms/ml. in $\underline{cis}$-$[Pt(NH_3)_2Cl_2]$

$S_u = u/2(a-x_e-y_e)$, specific activity at time t of the chloride in $\underline{cis}$-$[Pt(NH_3)_2Cl_2]$

$v = Cl^*$ atoms/ml. in $[Pt(NH_3)_2Cl(H_2O)]^+$

$S_v = v/x_e$, specific activity of chloride in $[Pt(NH_3)_2Cl(H_2O)]^+$ at time t

$s = Cl^*$ atoms/ml. in ionic Cl^-

$S_s = s/(b+x_e+2y_e)$, specific activity of the ionic Cl^- at time t

$I = u + v + s$, total number of Cl^* atoms/ml.

The general expression for the rate of increase of u is given by

$$\frac{du}{dt} = -2R_1S_u + R_{-1}(S_v + S_s) + R'(S_s - S_u) \ . \qquad (III.13)$$

Since for a steady state system $R_1 = R_{-1}$, division of du/dt by $R_{\pm 1}$, substitution of $s = I-u-v$, and rearrangement yields

$$\frac{1}{R_{\pm1}}\frac{du}{dt} + \left[\frac{(1+\gamma)}{(a-x_e-y_e)} + \frac{(1+\gamma)}{(b+x_e+2y_e)}\right]u + \left[\frac{1}{x_e} - \frac{(1+\gamma)}{(b+x_e+2y_e)}\right]v = \left[\frac{(1+\gamma)}{(b+x_e+2y_e)}\right]I \qquad \text{(III.14)}$$

where γ is defined as the ratio of $R'/R_{\pm1}$.

Likewise the general expression for the rate of increase of v is

$$\frac{dv}{dt} = R_1S_u - R_{-1}S_v - R_2S_v + R_{-2}S_s + R''(S_s - S_v). \qquad \text{(III.15)}$$

Again for a steady state system this expression becomes

$$\frac{1}{R_{\pm1}}\frac{dv}{dt} + \left[\frac{1}{2(a-x_e-y_e)} - \frac{(\beta+\omega)}{(b+x_e+2y_e)}\right]u + \left[\frac{(1+\beta+\omega)}{x_e} + \frac{(\beta+\omega)}{(b+x_e+2y_e)}\right]v = \left[\frac{(\beta+\omega)}{(b+x_e+2y_e)}\right]I \qquad \text{(III.16)}$$

where β is defined as $R_{\pm2}/R_{\pm1}$ and ω is defined as $R''/R_{\pm1}$. The general solutions for differential Eqs. III.14 and III.16 are

$$u - u_\infty = A_1e^{-\alpha_1t} + A_2e^{-\alpha_2t}$$

and

$$v - v_\infty = B_1e^{-\alpha_1t} + B_2e^{-\alpha_2t}$$

where u_∞ and v_∞ are the values of u and v at infinite time or equilibrium. These equations can be written in terms of fractions of exchange for each separate species as follows:

$$(1 - F_u) = A_1'e^{-\alpha_1t} + A_2'e^{-\alpha_2t} \qquad \text{(III.17)}$$

and

$$(1 - F_v) = B_1'e^{-\alpha_1 t} + B_2'e^{-\alpha_2 t} \qquad (III.18)$$

where $F_u = u/u_\infty$ and $F_v = v/v_\infty$ are the fractions of exchange at time t for the cis-$[Pt(NH_3)_2Cl_2]$ and the $[Pt(NH_3)_2Cl(H_2O)]^+$ species, respectively. The constants A_1', A_2', B_1', B_2', α_1, and α_2 are functions of the known equilibrium solution concentrations, k_1, and the parameters γ, β, and ω. The rate of exchange of chloride with both platinum species together is given by

$$(1 - F_{u+v}) = C_1e^{-\alpha_1 t} + C_2e^{-\alpha_2 t} \qquad (III.19)$$

Thus if a, b, K_1, K_2, k_1, γ, β, and ω are known, the constants in the above equations can be calculated to give the functions in III.17, III.18, and III.19 which can then in turn be compared with the experimental curves. It should be pointed out that although the functions in the above expressions are double exponential, they frequently cannot be resolved over the region which is measured experimentally, i.e., $0 < F < .6$. In this region they are not distinguishable from single exponentials. Moreover, if, for example, the value of F_u is known at some instant of time, this knowledge gives you no information concerning the value of F_v at that time because this system has three exchanging species--cis-$[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_2Cl(H_2O)]^+$, and Cl^-. Therefore at any particular time the fraction of exchange of the system is not uniquely described by F_u, F_v, or F_s but rather any two of the three. It is also interesting to note that if either of the platinum species were to exchange rapidly with Cl^-, it is possible, before equilibrium is established between the three species, for the fraction of exchange of that species to be greater than unity.

2. Fresh solution exchange equations

For fresh solutions the exchange scheme can be written as III.9 and III.11. Now, however, the rates R_1 and R_{-1} are no longer equal, but they together with R' are variables. Moreover, during short times, x and y can be considered negligible compared to a and b; therefore $(a-x-y) \simeq a$ and $(b+x+2y) \simeq b$. With these restrictions $dx/dt = k_1a$ and $x = k_1at+x_0$ where x_0 is the value of x at zero time, i.e., the time when the Cl^* was added. The expressions for the rate were taken as

$$R_1 = k_1a \tag{III.20}$$

$$R_{-1} = k_{-1}xb = k_{-1}x_0b + k_{-1}(k_1at)b \; . \tag{III.21}$$

The rate of appearance of u is given by

$$\frac{du}{dt} = -2R_1S_u + R_{-1}(S_s + S_v) + R'(S_s - S_u) \; . \tag{III.22}$$

Since it is assumed that $S_u = S_v = 0$ and $S_s = I/b$, the above can be rewritten in the integrated form as

$$u = k_{-1}x_0It + k_1k_{-1}aIt^2/2 + R'It/b \; . \tag{III.23}$$

Because $S_u = u/2a$ and $S_{oo} = I/(b + 2a)$, the fraction of exchange at time t can be expressed as

$$\frac{S_u}{S_\infty} = \frac{k_{-1}x(b+2a)t}{2a} + \frac{k_1k_{-1}(b+2a)t^2}{4} + \frac{R'(b+2a)t}{2ab} \tag{III.24}$$

This equation is an approximation which is valid for short times and it is generally satisfactory for values of S_u/S_∞ up to approximately 0.2.

IV. RESULTS

A. Aquation Equilibrium Constants

The aquation of cis-$[Pt(NH_3)_2Cl_2]$ in aqueous solutions is described by reactions III.1 and III.2. Experimentally this aquation was indicated by several phenomena. The pH of the solutions decreased gradually over approximately 20 hrs. to an equilibrium value because of the dissociation

$$[Pt(NH_3)_2Cl(H_2O)]^+ \rightleftharpoons [Pt(NH_3)_2Cl(OH)] + H^+ . \qquad (IV.1)$$

For 0.005 M. solutions of the complex a steady state pH of 4.6 was attained after 22 hrs. Further evidence was the change in the absorption spectrum of the solutions over an interval of time as shown in Fig. 1 and the increase in the conductivity of the solutions upon aging. In addition, the second aquation was indicated by fluctuations in the value of the equilibrium constant, calculated from titres of solutions with different initial concentrations of the complex, when just a single equilibrium constant was used to describe the system. A typical titration curve with a single point titration is shown in Fig. 2.

The possibility that the NH_3 ligands were replaced instead of the chloride ligands can be eliminated since such a substitution would cause the solutions to become basic whereas they were observed to become more acidic.

In Table 1 are presented the observed equilibrium titres each of which is an average of three titrations. By means of Eq. III.5 values of the first and second equilibrium constants were obtained from these experimental titres. The average values of the constants are given in Table 2.

Table 1. Observed titres used to calculate average K_1 and K_2 and calculated titres as test of self-consistancy of the average constants

Temp., °C.	Initial $[\underline{cis}\text{-}[Pt(NH_3)_2Cl_2]]$, a, M. x 10^3	Initial [KCl], b, M. x 10^3	Equil. $[Pt(NH_3)_2Cl(H_2O)^+]$, x, M. x 10^3	Equil. $[Pt(NH_3)_2(H_2O)_2^{++}]$, y, M. x 10^4	Titres T_e, M. x 10^3 Obsd.	Titres T_e, M. x 10^3 Calcd.
35.0	1.5	0.00	1.01	1.6	1.32	1.31
	2.5	0.00	1.57	1.6	1.90	1.90
	5.0	0.00	2.71	1.8	3.06	3.06
25.0	5.0	0.00	2.40	3.4	3.08	3.10
	5.0	1.03	2.21	2.6	2.72	2.73
	2.5	0.00	1.36	3.1	1.97	1.98
	2.5	1.00	1.27	2.1	1.68	1.68
15.0	1.50	0.00	1.00	1.2	1.24	1.25
	2.5	0.00	1.56	1.4	1.83	1.80
	3.0	0.00	1.76	1.4	2.04	2.04
	4.0	0.00	2.21	1.4	2.49	2.49

Table 2. Average values of first and second aquation equilibrium constants[a]

Temp., °C.	K_1, moles/l., x 10^3	K_2, moles/l., x 10^4
35.0	3.9	2.0
25.0	3.3	4.4
15.0	3.3	1.6

[a]Ionic strength was 0.318 in all experiments

The self-consistancy of the average K_1 and K_2 was checked by finding calculated titres with the average values of the constants for comparison with the observed titres. These calculated titres are also presented in Table 1. It is felt that the value of K_1 is known rather well, to within 10%; however, the uncertainty in K_2 is at least 30% and perhaps larger. This large uncertainty and indeed the question of whether K_2 is needed at all to explain the experimental data is discussed in some detail in section V.

From the temperature dependence of K_1, ΔH^0 was found to be approximately 0 ± .3 kcal./mole.

B. Rate Constant for First Aquation

$$\underset{(a-x)\sim a}{\underline{cis}\text{-}[Pt(NH_3)_2Cl_2]} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{x}{[Pt(NH_3)_2Cl(H_2O)]^+} + Cl^- \qquad (IV.2)$$

Graphs of x versus time, obtained in the titration of fresh solutions of cis-$[Pt(NH_3)_2Cl_2]$ at 35.0, 25.0, and 15.0° C., are shown in Figs. 3, 4, and 5, respectively. From the initial slopes of these graphs were calculated k_1. The value of k_{-1} was then obtained from the expression $k_{-1} = k_1/K_1$. In Table 3 values of k_1 and k_{-1} are tabulated. Fig. 6 shows the temperature dependence of k_1 graphically. From the slope of the line the enthalpy of activation, $\Delta H^{\ddagger}$, was calculated to be 17.4 kcal/mole. The entropy of activation, $\Delta S^{\ddagger}$, was -12 cal./mole deg.

Despite the use of a micro-buret, titration of the acidic $[Pt(NH_3)_2Cl(H_2O)]^+$ species was not a very accurate method for the determination of k_1 because of the very small amounts of the species formed during the early stages of hydrolysis. It will be shown below that the high chloride exchange experiments in some cases afforded a somewhat more accurate method for the determination of k_1.

C. Exchange of chloride with *cis*-$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_2Cl(H_2O)]^+$

Possible paths for the exchange of chloride with the two platinum species consist of the acid hydrolysis reactions and also a direct exchange process. It was possible to show experimentally that exchange which may have occurred by the direct reaction

$$\textit{cis-}[Pt(NH_3)_2Cl_2] \xrightarrow[Cl^*]{R'} \textit{cis-}[Pt(NH_3)_2ClCl^*] + Cl^- \qquad (IV.3)$$

was negligible compared to that which proceded via the aquation process. This feature was indicated by fresh solution exchange experiments in which the direct exchange would be most noticeable because of the small quantities of the hydrolysis products present. In Fig. 7 fraction of exchange points are plotted versus time and compared with a calculated fraction of

Fig. 3. $[Pt(NH_3)_2Cl(H_2O)^+]$ versus time graphs from the titration of fresh solutions of *cis*-$[Pt(NH_3)_2Cl_2]$. Temp. = 35.0° C., μ = 0.318, a = initial concn. of *cis*-$[Pt(NH_3)_2Cl_2]$

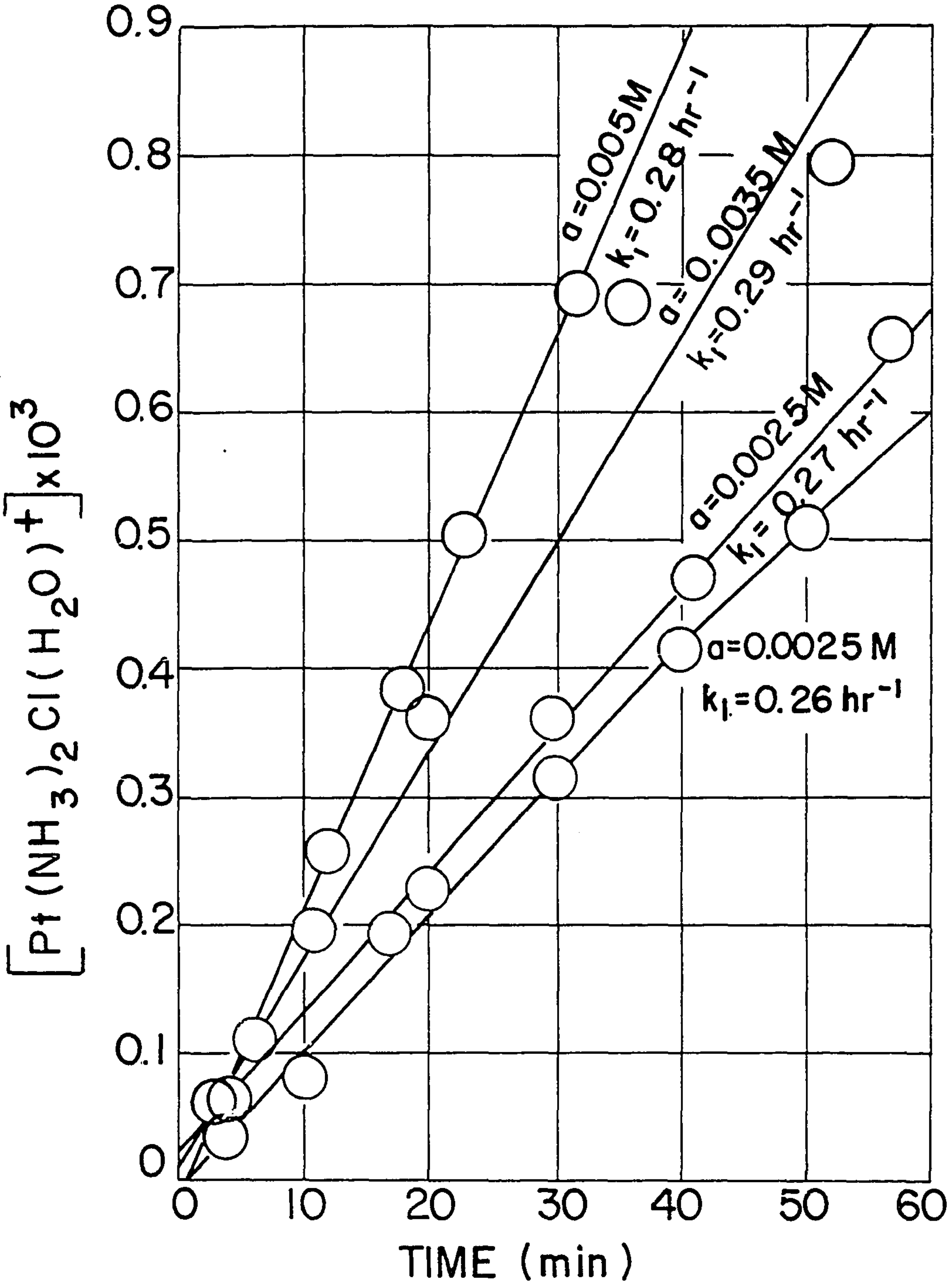

$[Pt(NH_3)_2Cl(H_2O)^+] \times 10^3$
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
10
20
30
40
50
60
TIME (min)
a=0.005M
k_1=0.28 hr^{-1}
a=0.0035 M
k_1=0.29 hr^{-1}
a=0.0025M
k_1=0.27 hr^{-1}
a=0.0025 M
k_1=0.26 hr^{-1}

Fig. 4. $[Pt(NH_3)_2Cl(H_2O)^+]$ versus time graphs from the titration of fresh solutions of <u>cis</u>-$[Pt(NH_3)_2Cl_2]$. Temp. = 25.0° C., μ = 0.318, a = initial concn. of <u>cis</u>-$[Pt(NH_3)_2Cl_2]$

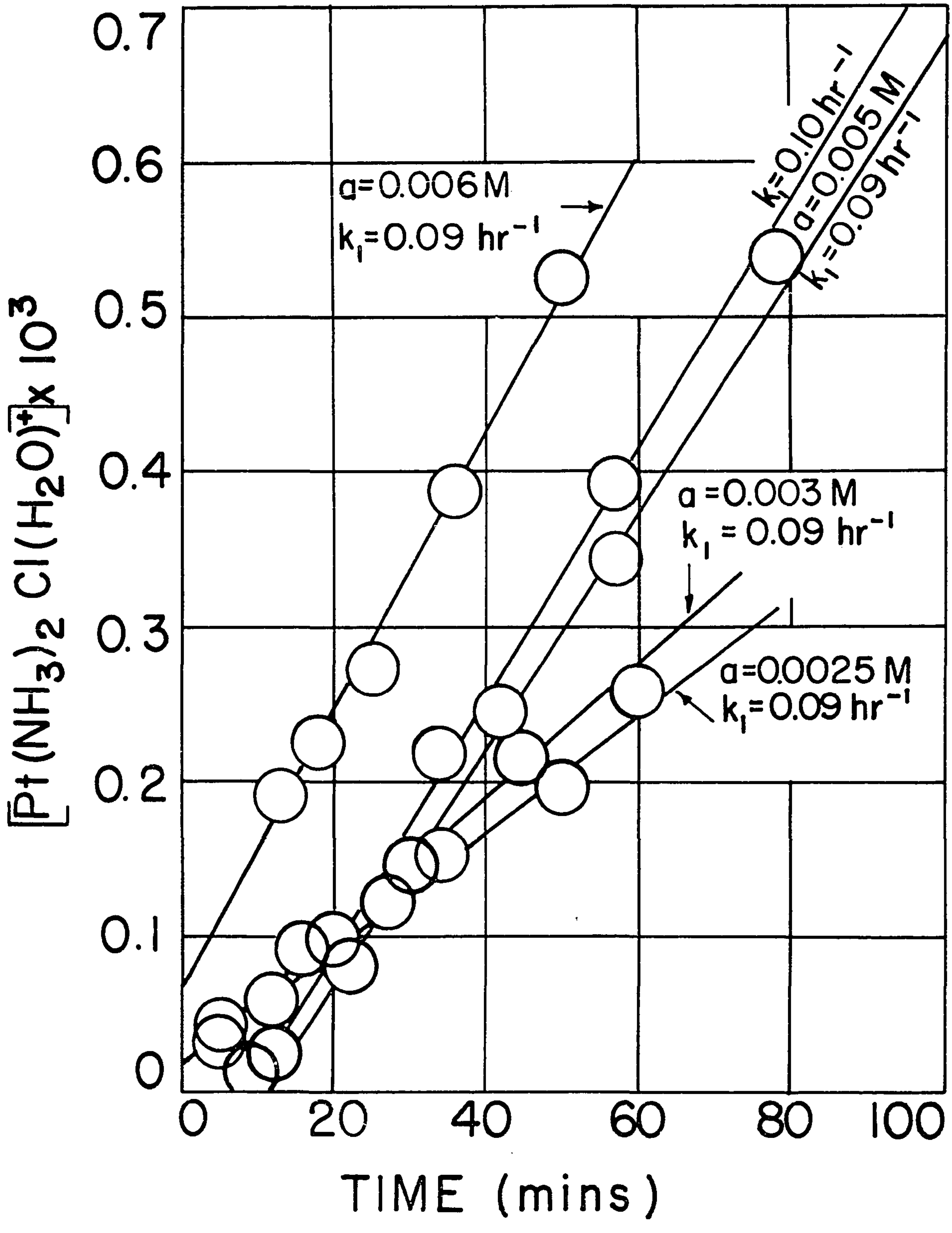

0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
20
40
60
80
100
TIME (mins)
$[Pt(NH_3)_2Cl(H_2O)]^+ \times 10^3$
a=0.006 M
k_1=0.09 hr^{-1}
k_1=0.10 hr^{-1}
a=0.005 M
k_1=0.09 hr^{-1}
a=0.003 M
k_1 = 0.09 hr^{-1}
a=0.0025 M
k_1=0.09 hr^{-1}

Fig. 5. $[Pt(NH_3)_2Cl(H_2O)^+]$ versus time graphs from the titration of fresh solutions of <u>cis</u>-$[Pt(NH_3)_2Cl_2]$. Temp. = 15.0° C., μ = 0.318, a = initial concn. of <u>cis</u>-$[Pt(NH_3)_2Cl_2]$

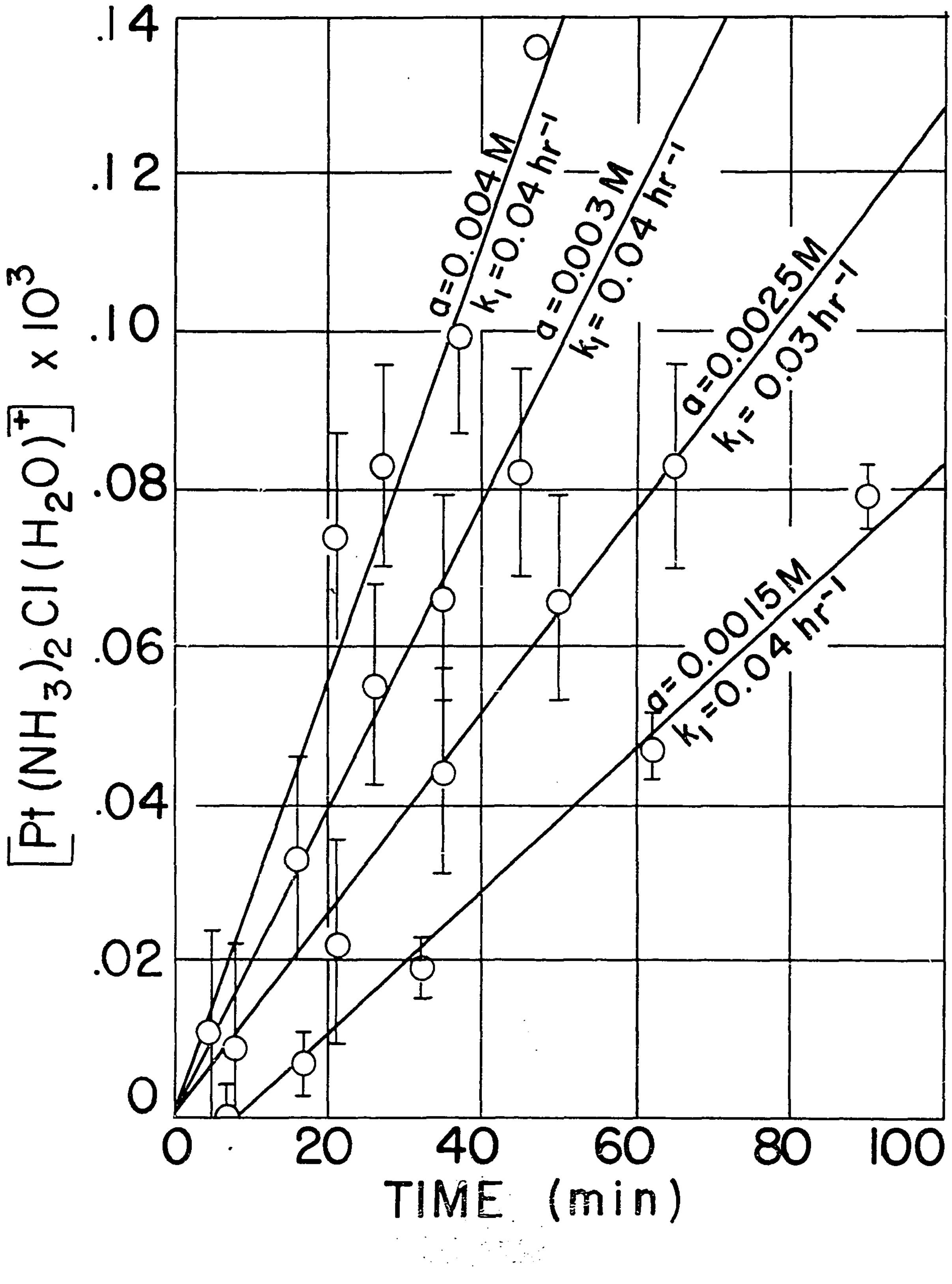

$[Pt(NH_3)_2Cl(H_2O)]^+ \times 10^3$
.14
.12
.10
.08
.06
.04
.02
0
0
20
40
60
80
100
TIME (min)
a=0.004 M
k_1=0.04 hr^{-1}
a=0.003 M
k_1= 0.04 hr^{-1}
a=0.0025 M
k_1= 0.03 hr^{-1}
a= 0.0015 M
k_1=0.04 hr^{-1}

Fig. 6. Temperature dependence of the first aquation rate constant. $\Delta H^{\ddagger} = 17.4$ kcal./mole, $\Delta S^{\ddagger} = -12$ cal./mole deg.

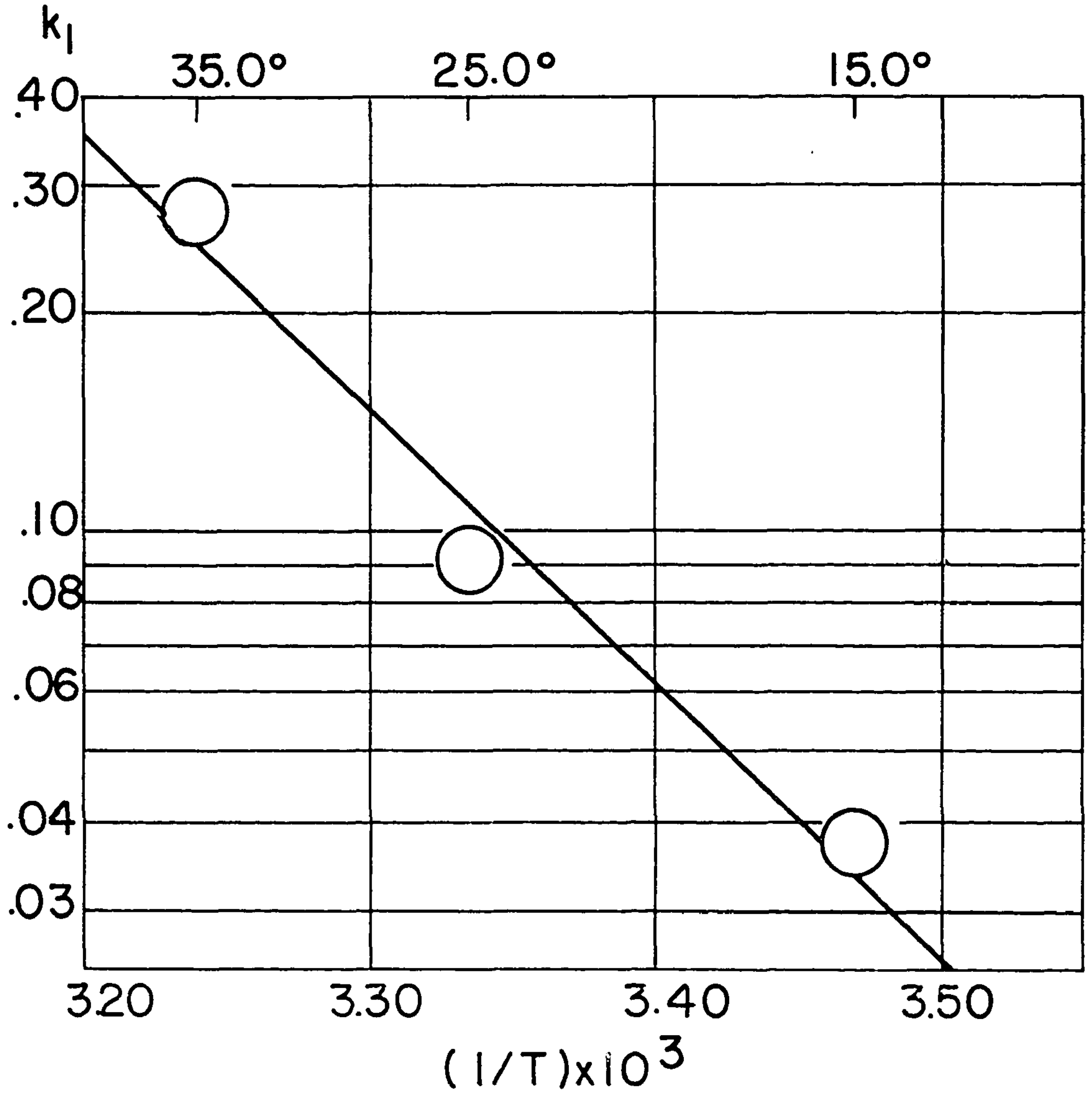

k$_1$
35.0°
25.0°
15.0°
.40
.30
.20
.10
.08
.06
.04
.03
3.20
3.30
3.40
3.50
(1/T)x10^3

Fig. 7. Fresh solution exchange curves. Temp. = 25.0° C., $\mu = 0.318$. ○, $a = b = 0.005$ M., S_u/S_∞; ◑, $a = b = 0.005$ M., S_{u+v}/S_∞; ●, $a = 0.005$ M., $b = 0.0025$ M., S_{u+v}/S_∞. ——— calcd. curve from

$$S_u/S_\infty = \frac{k_{-1}x_o(b+2a)t}{2a} + k_1k_{-1}(b+2a)t^2/4$$

where $a = .005$ M., $b = .0025$ M., and $x_o = .00015$ M.

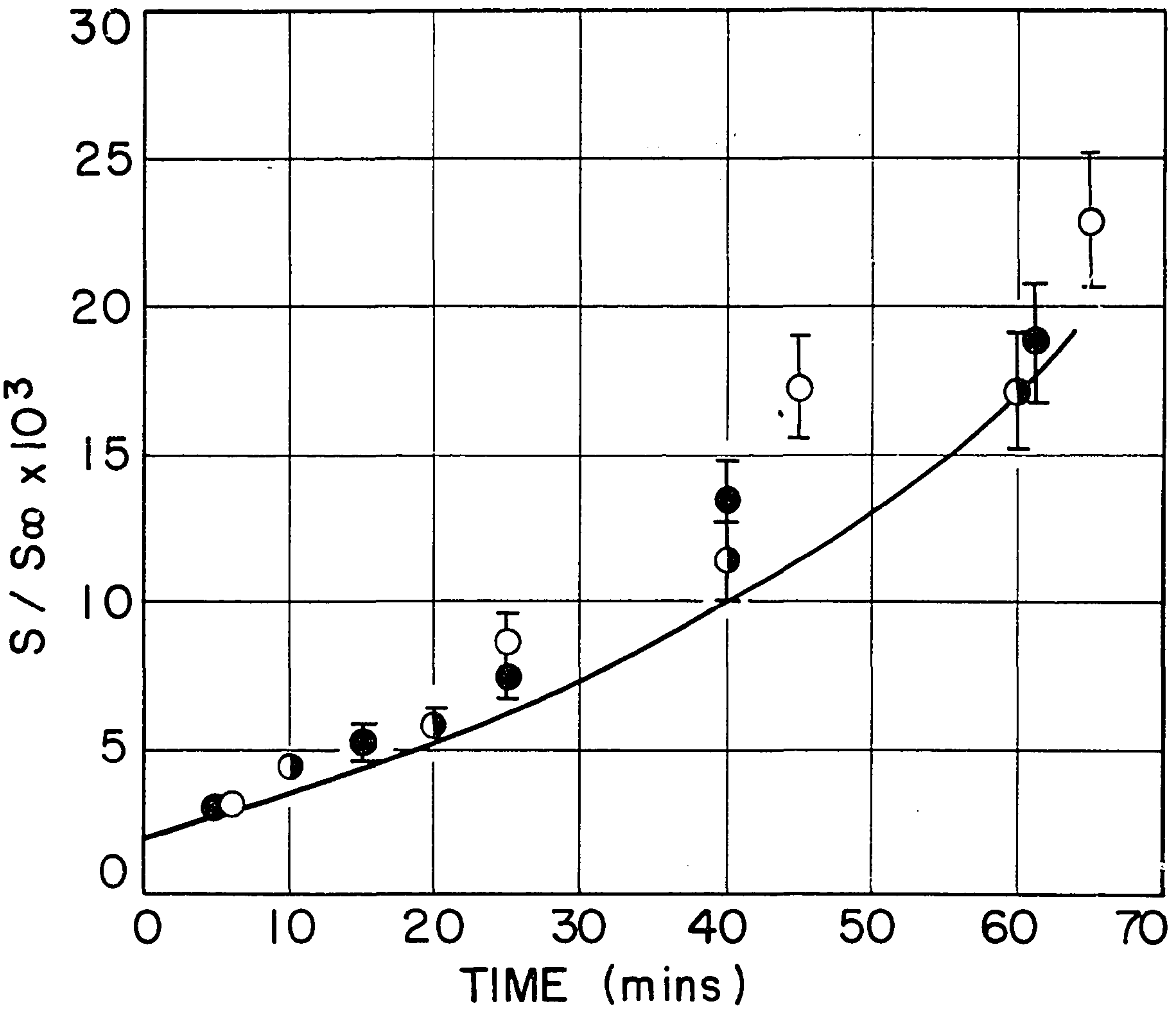

30
25
20
15
10
5
0
S / S∞ x 10³
0
10
20
30
40
50
60
70
TIME (mins)

Table 3. Values of first aquation rate constants by titration[a]

Temp., °C.	Concn. <u>cis</u>-[Pt(NH_3)$_2$$Cl_2$], M. x 10^3	k_1 sec^{-1} x 10^4	k_{-1} l./mole sec x 10^2
35.0	5.0	.78	2.00
	3.5	.81	2.06
	2.5	.75	1.92
	2.5	.72	1.86
25.0	6.0	.25	.75
	5.0	.28	.83
	5.0	.25	.75
	3.0	.25	.75
	2.5	.25	.75
15.0	4.0	.11	.33
	3.0	.11	.33
	2.5	.08	.25
	1.5	.11	.33

[a] Ionic strength was 0.318 in all experiments

exchange curve. This curve, which is seen to describe the fresh solution exchange rates adequately, is given by

$$\frac{S_u}{S_\infty} = \frac{k_{-1}x_0(b+2a)t}{2a} + \frac{k_1k_{-1}(b+2a)t^2}{4} \quad . \qquad (IV.4)$$

This is Eq. III.24 in which $a = 0.005$, $b = 0.0025$, $x_0 = 0.00015$, and $R' = 0$. If R' were not zero, the above would indicate it to be less than 5% of k_1a. Therefore it was concluded that the amount of this direct exchange was negligible compared to the exchange proceding through the aquation process.

All of the experimental aged solution exchange curves, i.e., $\ln(1-F_u)$ or $\ln(1-F_{u+v})$, were found to be linear with time over the period of exchange studied. The results of all these experiments are given in Table 4.

The method of exchange in solutions of high chloride concentration could be explained in terms of the first aquation step along and the times of half-exchange were calculated within 10% by the first term of Eq. III.17 (that is, by a single exponential function). The constants A_1' and α_1 were considered to be functions of the known equilibrium solution concentrations and the rate constant k_1 only; the parameter γ, corresponding to the direct exchange of chloride, was set equal to zero in Eq. III.14 because of the observations discussed above.

Before discussing the low chloride exchange experiments, a few words will be said about the statement made previously that the high chloride exchange experiments offered another method, and perhaps a somewhat more accurate one than the titration method, for the determination of k_1. At 15.0° C. k_1 was titrated to be approximately $.11 \times 10^{-4}$ sec^{-1} (see Table 3). However, with this value in Eq. III.17, a calculated time of half-exchange of 33 hrs. was obtained as compared to the observed 47 hrs. Without abandoning the aquation equilibria mechanism of exchange, the only error that could explain such a discrepancy was an incorrect value for k_1. And it was found that when $k_1 = .08 \times 10^{-4}$ sec^{-1}, the calculated

Table 4. Exchange between chloride and cis-$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_2Cl(H_2O)]^+$ in aged solutions

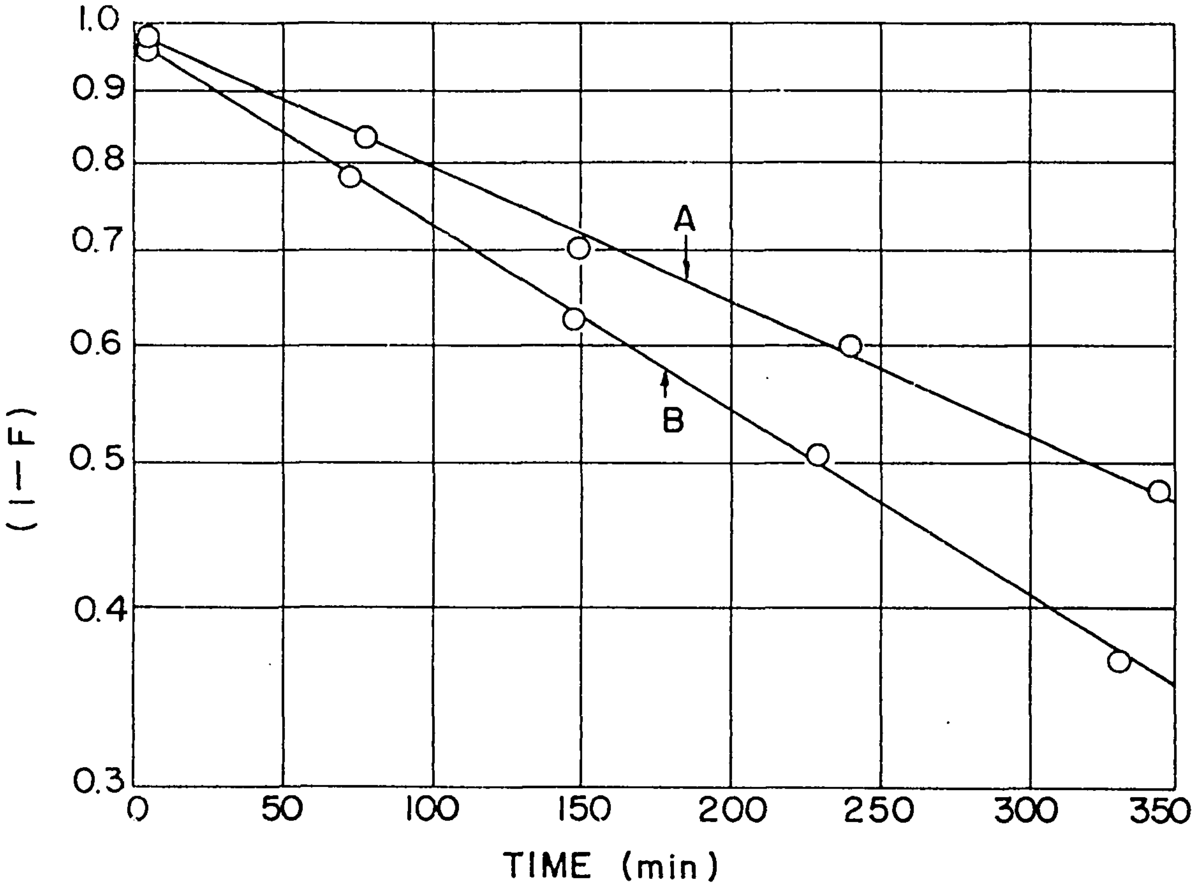
Temp., °C.,	Initial $[Pt(NH_3)_2Cl_2]$, M. x 10^3	Initial [KCl], M. x 10^3	Equil. $[Pt(NH_3)_2$-$Cl(H_2O)^+]$, M. x 10^3	Equil. $[Pt(NH_3)_2$-$(H_2O)_2^{++}]$, M. x 10^3	Time of half-exchange (u)		(u+v)		β
					Obsd. hrs.	Calcd. hrs.	Obsd. hrs.	Calcd. hrs.	
15.0	2.5	134	.06	-	47	45	-	45	0.0
25.0	5.0	1.0	2.22	.26	5.32	5.00	3.90	3.80	1.0
		2.5	1.96	.18	5.50	5.50	4.33	4.30	0.9
		5.0	1.60	.10	6.40	6.20	-	5.20	0.7
		10	1.13	.04	7.45	7.40	6.90	6.80	0.5
		134	.12	-	13.3	14.5	-	14.5	0.0
		268	.06	-	12.1[a]	14.9	-	14.9	0.0
		268	.06	-	13.8	14.9	-	14.9	0.0
	2.5	134	.06	-	10.5[a]	15.0	-	15.0	0.0
		134	.06	-	13.8	15.0	-	15.0	0.0
35.0	5.0	2.5	2.19	.09	2.32	2.00	1.48	1.53	1.0
		10	1.28	.02	2.75	2.54	2.36	2.32	0.6
		134	.14	-	4.33	5.04	-	5.04	0.0

[a] Anion resin did not remove all the ionic chloride from the aliquots before the complex chloride was precipitated

time of half-exchange was 45 hrs. which is in good agreement with the observed time. Likewise at 35.0° C., the average value for the rate constant was .76 x 10^{-4} sec^{-1} by titration while the exchange rates indicated a value nearer .72 x 10^{-4} sec^{-1}. At 25.0° C. the value of k_1 obtained by titration was consistant with that indicated by the exchange experiments. To summarize then, the values of k_1 used in Eq. III.17 to describe the high chloride aged solution exchange experiments were .08 x 10^{-4} sec^{-1} at 15.0° C., 25 x 10^{-4} sec^{-1} at 25.0° C., and .72 x 10^{-4} sec^{-1} at 35.0° C. These constants were then, of course, used to describe the low chloride exchange experiments also.

In the latter experiments the exchange was attributed to both the first and second aquation reactions. Typical plots of low chloride aged solution exchange runs are given in Fig. 8. The time of half-exchange for chloride and cis-$[Pt(NH_3)_2Cl_2]$ was calculated within 10% by the complete form of Eq. III.17 (that is, a double exponential) while the exchange rate for chloride with cis-$[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_2Cl(H_2O)]^+$ together was given within 10% by Eq. III.19. The constants A_1', A_2', B_1', B_2', α_1, and α_2 of these two expressions were functions of the equilibrium concentrations, k_1, and β. The parameter ω, corresponding to the direct exchange of chloride and $[Pt(NH_3)_2Cl(H_2O)]^+$, was set equal to zero in Eq. III.16 as the parameter γ had been in Eq. III.14. However, in the case of ω this was somewhat more arbitrary than for γ in that it could not be shown experimentally that ω was zero. The exchange experiments would measure the introduction of Cl* into $[Pt(NH_3)_2Cl(H_2O)]^+$ by both the direct exchange and the second aquation process since these two reactions are experimentally indistinguishable; hence it might be more realistic

Fig. 8. Plots of low chloride aged solution exchange experiments. Temp. = 25.0° C., u = 0.318, a = .005 M., b = .001 M. **A**, $\ln(1-F_u)$; B, $\ln(1-F_{u+v})$


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
(I — F)
0
50
100
150
200
250
300
350
TIME (min)
A
B

to describe the times of half-exchange of chloride into both platinum species by the parameter ($\beta+\omega$). However, all of the exchange was considered to proceed via the second hydrolysis for two reasons: (1) the existance of the second aquation equilibrium was indicated by experiments in this research and by investigations of other workers and (2) because there are very few examples of a transition metal complex exchanging directly with a ligand in aqueous solutions. Before discussing the parameter β in more detail, it should be restated here that the low chloride exchange experiments were not carried out over an interval of time long enough to distinguish the two components of Eqs. III.17 and III.19. Rather, β was arbitrarily varied until the times of half-exchange indicated by the above equations agreed within 10% with the observed times of half-exchange.

In section III the parameter β was defined as the ratio of the rate of the second aquation to the rate of the first aquation:

$$\beta = {}^{R_{\underline{+2}}}/R_{\underline{+1}} \qquad \text{(IV.6)}$$

The values of β necessary to calculate times of half-exchange in agreement with the observed times for exchange experiments that differed in the initial concentrations of chloride are tabulated in Table 5. In Fig. 9 is shown a plot of β versus total chloride concentration. It is seen that the curve approximates the equation

$$\beta = {}^{C}/[Cl^-] \qquad \text{(IV.7)}$$

where C is a constant. Eq. IV.6, which defines β, can be put in such a form:

Table 5. Values of β and the corresponding second aquation rate constants from low chloride exchange experiments[a]

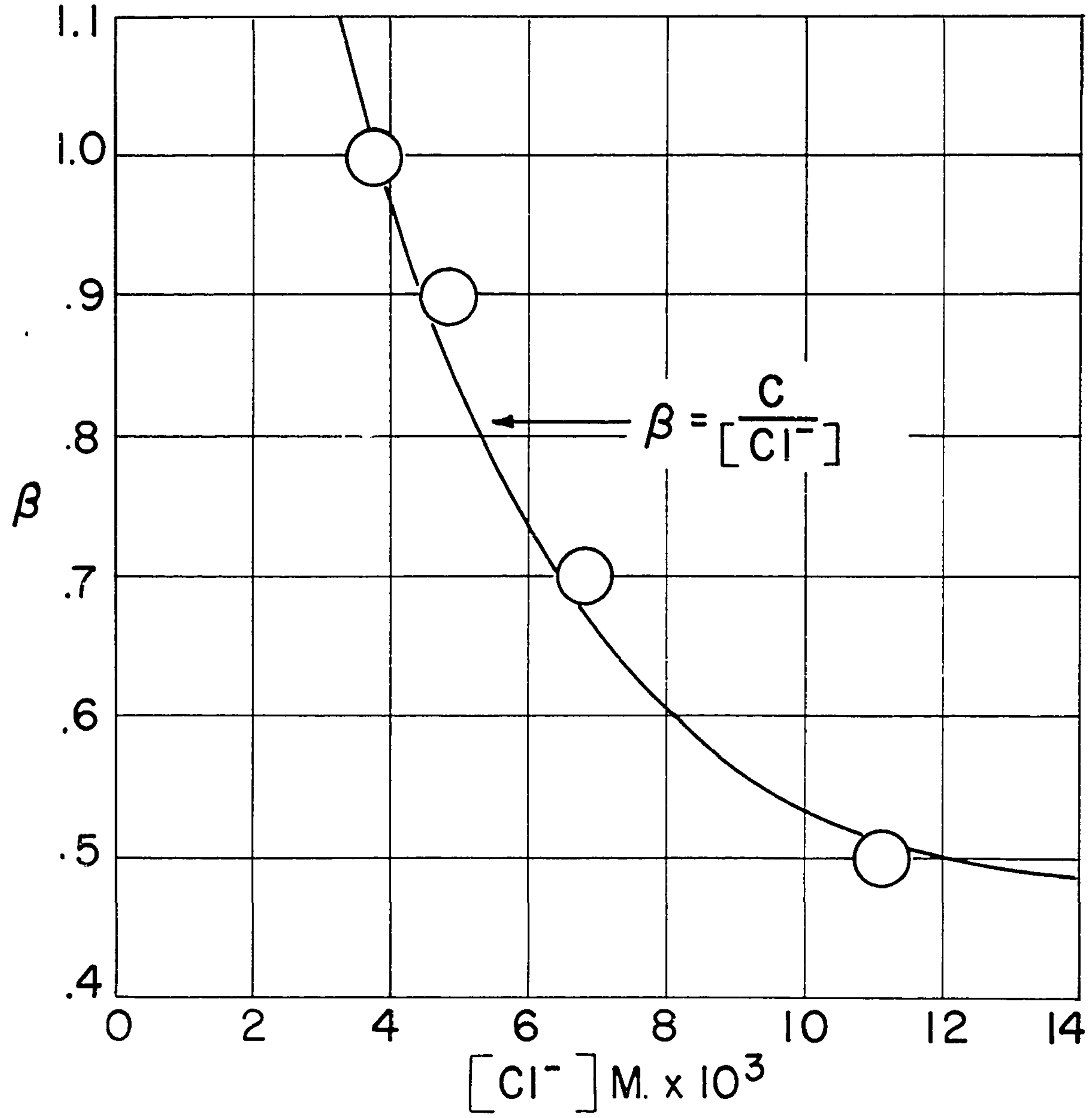
Temp., °C.	Initial [cis-[Pt(NH$_3$)$_2$Cl$_2$]] M. x 10^3	Initial [KCl], M. x 10^3	β	k_2 sec^{-1} x 10^4
25.0	5.0	1.0	1.0	.28
		2.5	0.9	.33
		5.0	0.7	.36
		10.0	0.5	.42
35.0	5.0	2.5	1.0	.92
		10.0	0.6	1.25

[a] Ionic strength of 0.318 for all experiments

$$\beta = \frac{R_2}{R_{-1}} = \frac{k_2 x_e}{k_{-1} x_e (b + x_e + 2y_e)} = \left(\frac{k_2}{k_{-1}}\right) \frac{1}{[Cl^-]} \qquad (IV.8)$$

where the value of the second aquation rate constant, k_2, is the only unknown. The values of k_2 obtained from the exchange experiments are listed in Table 5 also.

Fig. 9. Plot of β versus concentration of chloride


1.1
1.0
.9
.8
.7
.6
.5
.4
β
$\beta = \frac{C}{[Cl^-]}$
0
2
4
6
8
10
12
14
$[Cl^-]$ M. x 10^3

V. DISCUSSION

The exchange of chloride in the cis-[$Pt(NH_3)_2Cl_2$]-Cl^- system was found to proceed through the acid hydrolysis steps illustrated in reactions III.1 and III.2. As previously mentioned in section IV, the first equilibrium constant was fairly accurately known, within 10%, but the value of the second equilibrium constant possessed a large uncertainty. This uncertainty is not too surprising when one realizes that the experimental titres are on the order of $1.24-3.08 \times 10^{-3}$ M. (see Table 1) and that the $[Pt(NH_3)_2(H_2O)_2]^{++}$ species contributes only about 10% or 20% of these totals. Since the concentration of the diaquo species is so small in these solutions, what then would be the result if the second aquation step was just ignored? In Table 1 the four observed titres at 25.0° C. are given as 3.08, 2.72, 1.97, and 1.68×10^{-3} M. If the second aquation is assumed non-existant, these four titres would give values for K_1 of 4.94, 4.46, 7.32, and 5.49×10^{-3} moles/l., respectively. This variance is hardly consistant with a single equilibrium constant system and does indicate the existance of a second aquation. If the second aquation is included now, the four observed titres can be paired up in six different combinations to give as values of K_1, 3.31, 3.28, 3.22, 3.13, 3.53, and 2.95×10^{-3} moles/l. This method then gives a fairly constant value for K_1. At the same time, however, the corresponding values obtained for K_2 were 4.2, 4.3, 4.6, 5.1, 3.7, and 5.8×10^{-4} moles/l. Thus, although K_2 cannot be determined with much accuracy, it is still necessary to include the second aquation in order to make sense of the experimentally obtained data. Further evidence of the uncertainty of K_2 is the sensitivity of its value towards changes in the observed titres. Thus, if one of the two titres used to calculate K_1 and K_2 by Eq. III.5 is altered by 2%, the corresponding change in K_2 is 30% or more.

The value of the first aquation rate constant, k_1, was determined by two methods: (1) titration of the acidic aquo species as it formed during the early stage of aquation and (2) comparison of the calculated times of half-exchange for high chloride aged solution exchange experiments with the observed times. The second method was possible because _cis_-$[Pt(NH_3)_2Cl_2]$ only exchanges with Cl^- through the aquation processes, and since the high $[Cl^-]$ effectively suppressed the second aquation, the rates of exchange were proportional to only one rate constant--k_1. The value of k_1 found from both of these methods at 25.0° C. was $.25 \times 10^{-4}$ sec^{-1}. Banerjea _et al_. (24) reported a value for k_1 at 25.0° C. of $.38 \times 10^{-4}$ sec^{-1}. They obtained their data from the potentiometric titration of the chloride formed during aquation, but the value of the constant was calculated from the usual first order equation. This may in part account for the difference in the two values because the first order expression actually applies to only a single irreversible step and not to a reversible reaction between two species much less to the case of three species as exists in the _cis_-$[Pt(NH_3)_2Cl_2]$-$[Pt(NH_3)_2Cl(H_2O)]^+$-$[Pt(NH_3)_2(H_2O)_2]^{++}$ system. As a check to determine how large a difference this method for the evaluation of k_1 would cause, some titration data for the _cis_-$[Pt(NH_3)_2Cl_2]$ system, which gave a value for k_1 of $.25 \times 10^{-4}$ sec^{-1} from the initial slope of x vs. t, indicated a k_1 of $.43 \times 10^{-4}$ sec^{-1} from the time of half-reaction from the usual first order plot. It was also possible to compare the value of the constant with that derived from the conductivity data of

Drew <u>et al</u>. (5). Their data, when applied to the same first order expression used by Banerjea <u>et al</u>. indicated that k_1 was $.48 \times 10^{-4}$ sec^{-1}.

The entropy of activation for the first aquation process (-12 cal./mole deg.) is consistant with the expectation for a neutral molecule dissociating into two ions.

The rate constant for the second aquation, k_2, was determined indirectly from the dependence of the exchange parameter β on the concentration of chloride. The values of k_2 obtained at 25.0° C. are listed in Table 3. It is noted that as β decreases from 1.0 to 0.5, k_2 increases from .28 to $.42 \times 10^{-4}$ sec^{-1}. A cursory glance might suggest that this small but definite increase indicates that k_2 is not constant. However the calculated half-times of exchange are rather insensitive towards the value of β, especially when β becomes much less than 1.0. This is expected since a low value of β corresponds to the situation in which the second aquation contributes less and less to the overall chloride exchange process. When, moreover, the value of k_2 is seen to depend rather strongly on β (see Eq. IV.8), the small increase in the rate constant is not considered to be significant. The average value of k_2 was $.35 \times 10^{-4}$ sec^{-1}. It is possible to compare this with the rate constant Banerjea <u>et al</u>. (24) obtained for the reaction

$$\underline{cis}\text{-}[Pt(NH_3)_2Cl(OH)] + OH^- \longrightarrow \underline{cis}\text{-}[Pt(NH_3)_2(OH)_2] + Cl^- \qquad (V.1)$$

since this reaction is believed to proceed via the second aquation process, <u>i.e</u>., H_2O reacts initially with the $[Pt(NH_3)_2Cl(OH)]$ complex to form $[Pt(NH_3)_2(OH)(H_2O)]^+$. They reported a value for the rate constant of $.22 \times 10^{-4}$ sec^{-1}. The difference in two values probably reflects the fact that the reactions are not strictly analogous in that water reacts with $[Pt(NH_3)_2Cl(H_2O)]^+$ in one case and $[Pt(NH_3)_2Cl(OH)]$ in the other. Also the former reaction occurs in acidic solutions while the latter reacts in a basic medium.

Before leaving the discussion of the second aquation rate constant, a few words will be said about an attempt to evaluate k_{-2} directly by preparing $[Pt(NH_3)_2(H_2O)_2]^{++}$ and following the rate at which the spectrum of the solution changed after chloride was added to it. However the results were inconclusive, primarily it is thought, because a solution of pure $[Pt(NH_3)_2(H_2O)_2]^{++}$ could not be prepared. The method of preparation was one used by Ryabchikov (9) and entailed treating a solution of <u>cis</u>-$[Pt(NH_3)_2Cl_2]$ with Ag_2O.

The kinetics for chloride exchange in the <u>cis</u>-$[Pt(NH_3)_2Cl_2]$ - Cl^- system were found to be similar to the exchange kinetics for the $[PtCl_4]^=$, $[Pt(NH_3)Cl_3]^-$, and $[Pt(NH_3)_3Cl]^+$ complexes in that all of these substitutions were first order in complex, zeroth order in chloride, and proceeded by either an observable acid hydrolysis equilibria or by a process zero order in chloride. The values of the aquation and chloride exchange rate constants for these complexes are given in Table 6. Also summarized in Table 6 are the known concentration equilibrium constants for the acid hydrolysis equilibria. From these results it is apparant that Cl^- cannot compete with H_2O as a complexing agent in these aqueous systems. It is also noticed that the rate constants all fall within the range .15 to .38 x 10^{-4} sec^{-1} despite the fact that the charges on the complexes vary from -2 to 1. Such a behavior is inconsistant with a S_N1 reaction, but is compatible with a reaction in which a bond-making step occurs simultaneously

Table 6. Acid hydrolysis equilibrium constants, first aquation rate constants, and chloride exchange rate constants for the chloroammineplatinum(II) complex series at 25.0° C.

Complex	k_{Cl^*}, x 10^4 sec^{-1}	k_{H_2O}, x 10^4 sec^{-1}	K_1, x 10^3	K_2, x 10^3
$[PtCl_4]^=$	.38[a]	.38[a]	11.4[b]	1.92[b]
$[Pt(NH_3)Cl_3]^-$[c]	.37	.36	14.0	.05
cis-$[Pt(NH_3)_2Cl_2]$	.25	.25	3.3	.44
$[Pt(NH_3)_3Cl]^+$[d]	.15	.22	—	—

[a] (10)

[b] Sanders, C. I. and D. S. Martin, Jr., Ames, Iowa. Acid hydrolysis of $[PtCl_4]^=$ and $[PtCl_3(H_2O)]^-$. Private communication. 1960

[c] (19)

[d] (24)

with the bond-breaking between the platinum atom and a chloride ligand.

The above observations are accounted for by Path I of mechanism I.8 proposed by Basolo and Pearson (25). They stated that the exchange of ligands such as NH_3, Cl^-, and H_2O, which are unable to form double bonds with the central metal atom, could proceed by this path which is characterized by first order kinetics in the complex, zeroth order kinetics in chloride, and a stable solvated intermediate. The apparent insensitivity of the rate constants to the charge on the complexes is accounted for by the two rather loosely coordinated water molecules, above and below the plane of the complex, moving towards the Pt(II) ion and bonding with it in a square pyramid transition state as the chloride ligand is released.

VI. SUMMARY

The acid hydrolysis of <u>cis</u>-$[Pt(NH_3)_2Cl_2]$ may be described as

$$\text{\underline{cis}-}[Pt(NH_3)_2Cl_2] \rightleftharpoons [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^- \qquad (VI.1)$$

$$[Pt(NH_3)_2Cl(H_2O)]^+ \rightleftharpoons [Pt(NH_3)_2(H_2O)_2]^{++} + Cl^- \qquad (VI.2)$$

The concentration equilibrium constant for the first hydrolysis step, K_1, was determined, within 10%, to be 3.9, 3.3, and 3.3 x 10^{-3} moles/l. at 35.0°, 25.0°, and 15.0° C., respectively. Also the rate constant for this initial aquation step, k_1, was found to be .72, .25, and .08 x 10^{-4} sec^{-1} at the three temperatures, respectively. The temperature dependence of k_1 indicated that $\Delta H_1^{\ddagger}$ = 17.4 kcal./mole and $\Delta S_1^{\ddagger}$ = -12 cal/mole deg.

The concentration equilibrium constant for the second hydrolysis step was determined, within 30%, to be 2.0, 4.4, and 1.6 x 10^{-4} moles/l. at 35.0°, 25.0°, and 15.0° C., respectively. The second aquation rate constant, k_2, at 25.0° C. was approximately .35 x 10^{-4} sec^{-1}.

The exchange of Cl^- with <u>cis</u>-$[Pt(NH_3)_2Cl_2]$ was found to follow first order kinetics in the complex, zeroth order kinetics in chloride, and to proceed via the first aquation step shown above. The exchange of Cl^- with $[Pt(NH_3)_2Cl(H_2O)]^+$ was characterized by the same kinetics and was found to proceed by a chloride independent process which could be assigned to the second aquation step shown above.

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