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Roger James Adams
Iowa State University

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ACID HYDROLYSIS AND ISOTOPIC EXCHANGE OF THE

CHLORIDE LIGANDS FOR TRANS-DICHLORODIAMMINEPLATINUM(II)

by

Roger James Adams

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:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean/ of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

1961

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I. INTRODUCTION

The purpose of this research has been to investigate the kinetics of the acid hydrolysis and isotopic exchange of chloride ion with the chloride ligands of trans-dichloro-diammineplatinum(II). This work was a continuation of the studies of the chloroammineplatinum(II) series previously begun in this laboratory (1, 2, 3, 4, 5, 6). It was hoped that these studies would clarify the mechanism of substitution reactions involving square planar platinum(II) complexes.

Platinum(II) complexes normally exist in a square planar configuration rather than in the familiar tetrahedral arrangement. This structure permits the investigation of cis- and trans-effects on the kinetic behavior of various isomers. The results of this work with the trans-[Pt(NH$_3$)$_2$Cl$_2$] complex are contrasted with the behavior of the cis-[Pt(NH$_3$)$_2$Cl$_2$] isomer as well as the other chloroammineplatinum(II) complexes in section V.

The trans-dichlorodiammineplatinum(II) complex was first prepared by Reiset (7) in 1840 and is sometimes referred to as "Reiset's Salt." Five years later the cis-dichlorodiammine-platinum(II) complex was synthesized by Peyrone (8). About fifty years passed, however before Werner (9) was able to correctly ascertain that these two compounds were the cis and trans isomers of a square planar configuration about the central metal atom. His postulation was based entirely on
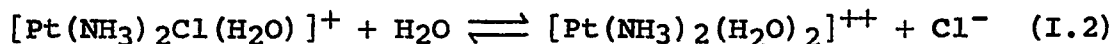
chemical evidence and other workers, Reihlen et al. (10),
refuted this conclusion as late as 1926, claiming that the
trans-isomer was really a dimeric form of the cis compound.
Their conclusion was based on molecular weight determinations
using liquid ammonia as a solvent. Werner's postulation, how-
ever, was ultimately proven to be correct by structural
studies (11).

Among the early workers studying platinum(II) compounds
was Jorgenson (12). He investigated substitution reactions of
$[Pt(NH_3)_4]^{\ddagger}$ and $[PtCl_4]^{=}$ and observed the formation of dif-
ferent isomers of the general formula $[Pt(NH_3)_2Cl_2]$. He found
the properties of these isomers to be similar to the products
obtained earlier by Reiset (7) and Peyrone (8).

A year after Werner's postulation, a test for distin-
guishing the cis and trans isomers was discovered by Kurnakow
(13). He noted that cis-$[Pt(NH_3)_2Cl_2]$ reacted with thiourea
(tu) to yield $[Pt(tu)_4]Cl_2$, whereas under the same conditions,
the trans isomer gave $[Pt(tu)_2Cl_2]$.

The behavior of aqueous solutions of chlorcammineplati-
num(II) complexes was first studied by Werner and Miolati (14)
who observed conductivity evidence of a reaction occurring.
Later, in a more extensive study, Drew et al. (15) studied the
extent of reaction using conductivity measurements and found
that both cis- and trans-$[Pt(NH_3)_2Cl_2]$ attained an appreciable
conductivity after several hours in solution.

Jensen (16) interpreted this behavior in terms of hydrolysis reactions of the type:

$$[Pt(NH_3)_2Cl_2] + H_2O \rightleftharpoons [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^- \qquad (I.1)$$

$$[Pt(NH_3)_2Cl(H_2O)]^+ + H_2O \rightleftharpoons [Pt(NH_3)_2(H_2O)_2]^{++} + Cl^- \quad (I.2)$$
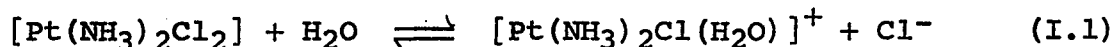
Later, King (17, 18) investigated compounds of the type $[Pt(NH_3)_2X_2]$ and $[Pt(NH_3)_3X]X$. This work showed that compounds in which X was Cl^-, Br^- or NO_2^- behaved as non-electrolytes in the diammine case and as salts of univalent cations in the triammine case. When X was NO_3^-, $SO_4^=$ or picrate the compounds hydrolyzed either completely or substantially into the aquo di- and triammines.

The aquation rates of cis- and trans-dithiosulfato-platinate(II) were measured by Vakhtin (19) using conductivity. He found the cis isomer hydrolyzed much more readily than the trans form of the salt.

The effects of ultraviolet radiation on the stability of aqueous solutions of cis-$[Pt(NH_3)_2Cl_2]$ was studied by Babaevo and Mosyagina (20). They found that under intense radiation a black precipitate containing polymerized $Pt(OH)_6^=$ groups was formed.

Grantham et al. (2) observed that $[PtCl_4]^=$ undergoes an acid hydrolysis and that the observed exchange of chloride ion with complexed chloride could be explained by this aquation reaction plus an additional first order reaction with the monoaquo complex. The suggested possibility of a second

hydrolysis forming the diaquo species was later investigated quantitatively by Sanders and Martin (5). An extensive study of the acid hydrolysis of $K[Pt(NH_3)Cl_3]$ was carried out by Elleman et al. (3) in which it was demonstrated that a second aquation following the initial hydrolysis provided pathways to explain all of the observed exchange. The non-equivalent chlorides in the complex were observed to undergo separate hydrolyses. The hydrolysis rates and equilibrium of cis-$[Pt(NH_3)_2Cl_2]$ were studied by Reishus and Martin (6). Again the observed exchange could be explained by a two step acid hydrolysis system. The hydrolysis of $[Pt(NH_3)_3Cl]^+$ has recently been studied by Aprile and Martin[1] who found that a second order direct chloride exchange term was necessary in addition to the hydrolysis process to completely characterize the observed exchange. Grinberg et al. (21, 22) also studied the hydrolysis kinetics of $K[Pt(NH_3)Cl_3]$, $K_2[PtCl_4]$, $[Pt(NH_3)_3Cl]Cl$, cis- and trans-$[Pt(NH_3)_2Cl_2]$.

Leden and Chatt (23) reported a very rapid aquation for the $[Pt(C_2H_4)Cl_3]^-$ complex, the equilibrium being attained in two minutes.

Complexes have been classified by Taube (24) as labile or inert, based on their substitution and exchange behavior. Taube proposed that if the central metal atom has unutilized

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[1]Aprile, F. and Martin, D. S., Jr., Ames, Iowa. Exchange and hydrolysis data. Private communication. 1961.

inner orbitals, the ligands will usually be labile; whereas if all sub-shells are filled, the complex will exhibit inert behavior. He explained these observations in terms of an exchange transition state which was stabilized by the donation of an electron pair from the entering ligand to an empty metal orbital. Platinum(II), then, would be classified as an inert complex according to Taube's definition. Indeed the exchange rates of the chloroammineplatinum(II) series have been slow enough to conveniently measure, the trans-[Pt(NH$_3$)$_2$Cl$_2$] complex having the fastest rate.

Banerjea et al. (25) studied the hydrolysis and substitution reactions of some chloroammineplatinum(II) complexes with a variety of nucleophilic reagents. They observed no acid hydrolysis for trans-[Pt(NH$_3$)$_2$Cl$_2$] although the complex did undergo a measurable chloride exchange. The reactions studied fell into two categories: (1) those that were first order in complex but zero order in reactant and all of nearly the same rate; (2) those that were first order in both the complex and the reactant with faster rates than those of the first category. In general the reactants of category 1 were low in the trans-directing series whereas reactants of category 2 had high trans-directing properties. They proposed a "dissociation" mechanism for the substitution reactions of square planar complexes which was later discussed in more generalized form by Basolo and Pearson (26, pp. 188-189).

The well known <u>trans</u>-effect will not be discussed in detail here as the subject has been reviewed by others (27). In essence, the <u>trans</u>-effect, originally designated by Chernyaev (28), refers to the observation that substitution of ligands into the inner coordination sphere of Pt(II) complexes was not statistical in nature, but rather was governed by a directional effect. Certain ligands present in the square planar configuration induced substitution into the position <u>trans</u> to the ligand rather than into the <u>cis</u> position. The use of this theory in preparing various isomeric Pt(II) complexes was discussed by Quagliano and Schubert (29). Several theories have been proposed to explain this effect, however two proposals seem to satisfy the largest number of experimental observations. For ligands unable to form π-bonds with the metal atom, Grinberg (30) suggested that induced dipoles, directed away from the ligand <u>trans</u> to the labilizing ligand, weakened the bond to the <u>trans</u>-ligand rather than the two <u>cis</u>-ligands. The magnitude of this weakening depended on the polarizability of the electron cloud of the labilizing ligand. For ligands which may form π-bonds with the metal atom by utilizing the d electrons of Pt(II) and vacant p or d orbitals on the ligands, the theory of Chatt <u>et al</u>. (31) and Orgel (32) seems to suffice well. They proposed that the $p\pi$ - $d\pi$ or the $d\pi$ - $d\pi$ bond reduces the electron density near the ligand <u>trans</u> to the labilizing ligand, thereby lowering the energy

of the transition state for an S_n2 attack by another potential ligand at this position. These theories substantially predict the following observed order of decreasing trans-effect: $CN^- \sim C_2H_4 \sim CO \sim NO \sim SC(NH_2) \sim R_2S \sim R_3P \sim NO_2^- \sim I^- \sim CNS^- > Br^- > Cl^- >$ pyridine $> NH_3 > OH^- > H_2O$.

Substitution reactions in which OH^-, NH_3 and pyridine replaced the chlorides in $K_2[PtCl_4]$, $K[Pt(NH_3)Cl_3]$, $[Pt(NH3)_3Cl]Cl$ and $K_2[PtBr_4]$ have been studied by Grinberg (33). He found first order kinetics for alkaline hydrolysis in each case and second order reactions for the NH_3 substitution. Accordingly, an aquation step followed by neutralization of the acidic proton on the water ligand was proposed as the mechanism of alkaline hydrolysis. Grinberg also discussed the trans-effect and noted that the order of trans directing ligands changes, depending on the type and valence state of the central metal atom and the temperature. He also cited evidence for a cis-effect: the rate of NH_3 substitution of $[Pt(NH_3)Cl_3]^-$, in which the NH_3 substitutes in the cis position, was greater than the rate for $[PtCl_4]^=$; also bromide exchanged more rapidly with $[Pt(NH_3)Br_3]^-$ than with $[PtBr_4]^=$. This cis-effect was stronger in Br-Pt-Br systems than in Cl-Pt-Cl and quite weak in NH_3-Pt-Cl compounds.

Basolo et al. (34) studied the relative reactivities of replaceable ligands in planar Pt(II) complexes of the type $[Pt(dien)X]^+$, where dien = diethylenetriamine. They found

the following order of replaceability: $NO_3^- > Cl^- > Br^- >$ $I^- > SCN^- > NO_2^-$. This paralleled the _trans_-effect series and inferred that strongly _trans_ directing ligands are more difficult to dislodge.

Chatt and co-workers (35) have recently reported an extraordinary series of compounds of the type _trans_- $[Pt(R_3M)_2XH]$, where M = P or As; X = NO_3, Cl, Br, I, NO_2, SCN, CN and R = alkyl or aryl radical. The hydride is directly bound to platinum and it was found to have a large _trans_- directing effect.

Rather complete proposals on the possible mechanisms of substitution of square planar complexes have been made by Basolo and Pearson (26, pp. 188-189). If one of the ligands (L) is capable of forming $p\pi - d\pi$ or $d\pi - d\pi$ bonds with the platinum atom, the authors propose a trigonal bipyramid transition state for reactions of the type:

$$\underline{trans}\text{-}[PtA_2LX] + Y \longrightarrow \underline{trans}\text{-}[PtA_2LY] + X \qquad (I.3)$$

The transition state may be represented as follows:

$$L = Pt \overset{\displaystyle A}{\underset{\displaystyle A}{\overset{\displaystyle |}{\underset{\displaystyle |}{\big|}}}} \overset{\nearrow Y}{\searrow X}$$
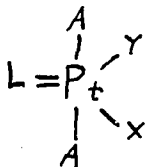
Since the d_{xz} orbital electrons of Pt(II) have a maximum concentration along the Pt-X and Pt-Y directions, the π-bond formed between Pt and L reduces this electron density and hence lowers the transition state energy. By the same

reasoning proposed by Chatt and Orgel in explaining the <u>trans</u>-effect, the greater the π-bonding tendency of L, the greater its <u>trans</u>-effect on the ligand X.

The mechanism for complexes containing π-bonding ligands involving this intermediate proposed by Basolo and Pearson is given below.

(I.4)
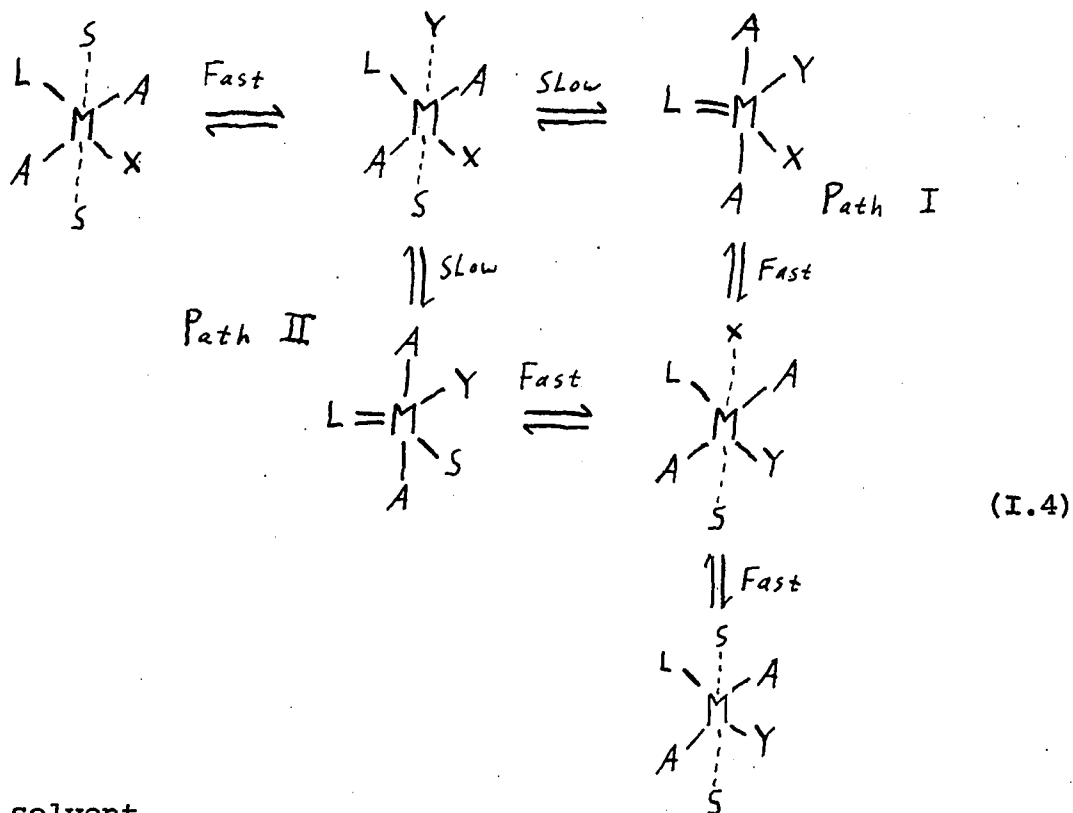
S - solvent
--- weak bond

Path II includes the possibility that X may be lost initially in forming the trigonal bipyramid intermediate. According to this scheme, the rate of reaction will generally be first order in Y, however, in some cases the solvent (S) may take the place of Y as a reagent and the overall rate may be

independent of the concentration of the reagent which
eventually replaces the solvent.

Another "dissociation" mechanism in which a five-coordinate intermediate forms from the dissociation of a ligand from the tetragonal structure about the Pt(II) ion has also been proposed by Basolo and Pearson:

(I.5)
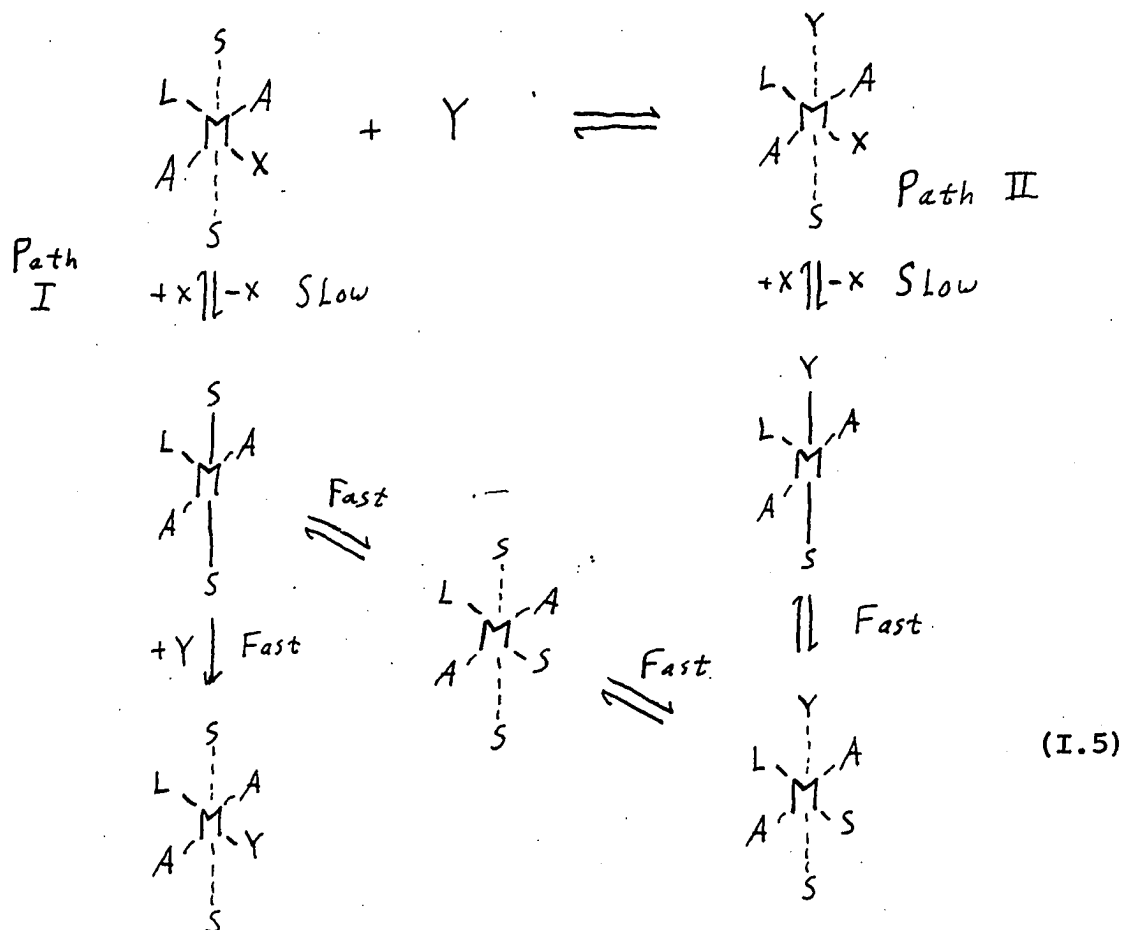
The five-coordinate intermediates above were designated as having a tetragonal pyramid structure similar to the intermediate proposed for substitutions in the regular octahedron

of cobalt(III). This mechanism is consistent with the ob-
servation that substitution reactions of Pt(II) complexes
follow either first or second order kinetics. If the reaction
proceeds by Path I, it should show a zero order dependence on
the concentration of Y, whereas if it involves Path II there
will be a first order dependence on the concentration of Y.
Which of the two paths predominates will depend upon the
complex, the nature of Y and of the solvent. If both Paths
I and II are involved, the rate will be made up of two terms,
one zero order in Y and one first order in Y. Because of the
dissociation step, the reaction rates of either Path I or II
should exhibit a strong dependence on the ionic strength of
the solution.

II. EXPERIMENTAL

A. Materials

1. Platinum

Platinum was obtained from either the Fisher Scientific Company in the form of $K_2[PtCl_6]$ or from the Mallinckrodt Chemical Works, Bram Chemical Company and Allied Chemical Company in the form of $H_2[PtCl_6] \cdot n\ H_2O$.

To avoid the catalytic effects on exchange reactions due to $[IrCl_6]^=$ (1), all platinum was treated as follows. A slurry of slightly soluble $K_2[PtCl_6]$ was made basic with NaOH and the $[PtCl_6]^=$ was reduced to Pt° by a slight excess of hydrazine. The platinum metal was then washed with water, hot concentrated HCl, more water to remove the Cl^-, hot concentrated HNO_3 and finally water to yield the Pt free of the less noble metals. The platinum was then converted to $H_2[PtCl_6]$ by addition of hot aqua regia, according to the method described by Vezes (36). Heating to dryness several times with concentrated HBr converted the $H_2[PtCl_6]$ to $H_2[PtBr_6]$. Addition of excess KBr yielded the moderately soluble $K_2[PtBr_6]$ and subsequent recrystallization of this violet salt effectively eliminated the iridium contamination.

The iridium-free $K_2[PtBr_6]$ was then reduced to Pt° by hydrazine in basic solution.

All solutions containing platinum were saved after

experimentation was complete and this platinum was periodically reclaimed by the procedure outlined above.

2. Potassium tetrachloroplatinate(II)

The preparation of $K_2[PtCl_4]$ was essentially identical to that previously described by Vezes (36). $H_2[PtCl_6]$ was prepared by treatment of platinum metal with hot aqua regia and excess KCl was added to convert it to insoluble $K_2[PtCl_6]$. This compound was then refluxed for one-half hour with stoichiometric amounts of $K_2C_2O_4$ and a small amount of $Pt°$ to form $K_2[PtCl_4]$.

$$K_2[PtCl_6] + K_2C_2O_4 \longrightarrow K_2[PtCl_4] + 2CO_2 + 2KCl \qquad (II.1)$$
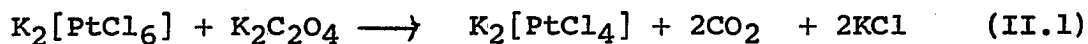
Grinberg's investigation (37) indicated that the mechanism of the reduction involved an intermediate of platinum metal and that trace amounts of $Pt°$ accelerated the reaction.

The reddish crystals of $K_2[PtCl_4]$ were recrystallized from hot water by cooling and evaporation to obtain maximum yields of the very soluble salt.

3. Tetrammineplatinum(II) chloride

The method of preparation of $[Pt(NH_3)_4]Cl_2$ was a modification of that described by Reiset (7) and by Gildengershel (38). A large excess of NH_3 was added to solutions of $K_2[PtCl_4]$ and refluxed until complete conversion to $[Pt(NH_3)_4]Cl_2$ was obtained as indicated by complete re-dis-

solution of the initially formed green precipitate
($[Pt(NH_3)_4][PtCl_4]$). The compound was then crystallized by
reducing the solution volume to 50 ml. and adding 500 ml. of
a 45% acetone, 45% ether, 10% alcohol solution. The white
crystals were then recrystallized from hot water and stored
in tightly stoppered darkened containers in an ammonia
desiccator to minimize decomposition.

4. Trans-dichlorodiammineplatinum(II)

One of the methods for preparing trans-$[Pt(NH_3)_2Cl_2]$
outlined by Drew et al. (15) was used in this work. Quanti-
ties of solid $[Pt(NH_3)_4]Cl_2$ were heated to 250° C. for one-
half hour in a shallow container. It was necessary to control
the temperature fairly accurately ($\pm$ 5° C.) because of low
reaction rates below 250° C. and considerable decomposition
above 250° C. A "Wood's metal" bath was used with a Meeker
burner heat source to achieve reliable temperature control.
The trans-$[Pt(NH_3)_2Cl_2]$ was then extracted from the residue
with hot 0.5 N HCl. After filtering the hot solution and
crystallizing the trans-salt, the compound was recrystallized
twice more from hot 0.5 N HCl and then twice from hot water,
filtered, washed with water, alcohol and ether, and dried in
air. This multi-recrystallization process with the last two
recrystallizations in water was required to attain acceptable
purity as indicated by platinum and chloride analyses and by

u.v. absorption spectra. The crystals could be stored indefinitely in a desiccator with no decomposition. This process gave a 60% yield of <u>trans</u>-[Pt(NH$_3$)$_2$Cl$_2$].

The other method proposed by Drew <u>et al</u>. (15) involved reacting solid [Pt(NH$_3$)$_4$]Cl$_2$ with hot concentrated HCl. Banerjea <u>et al</u>. (25) found, however, that it was very difficult to obtain pure <u>trans</u>-[Pt(NH$_3$)$_2$Cl$_2$] in good yield from the product mixture. Consequently, this method was not used in this work.

5. Additional reagents

Reagents such as Na$_2$SO$_4$, used to adjust the ionic strength; NaOH, used in potentiometric titrations; KCl, NaNO$_3$, K$_2$C$_2$O$_4$, NH$_3$ etc. required a definite knowledge of purity and were purchased as reagent grade chemicals from the Baker Chemical Company, Fisher Scientific Company or Allied Chemical Company. When carbonate free NaOH was desired, the method described by Allen and Low (39) was used to purify the NaOH.

6. Chlorine-36

Chlorine-36 was obtained in the form of approximately 2 N HCl from the Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee. This isotope decays by emission of a 0.71 Mev beta particle with a half-life of

3.5×10^5 years (40).

7. Water

All experiments were done using tap distilled water which was redistilled from alkaline permanganate solutions. Water used in conductivity studies was ion-exchange purified tap water which was distilled from alkaline permanganate solutions.

B. Equipment

1. Ion exchange columns and resin

Two sizes of ion-exchange columns were used, depending on the aliquot volume used; 50 cm. long, 11 mm. inside diameter and 50 cm. long, 23 mm. inside diameter. The column sizes were determined by investigating the resin capacity for chloride using blank solutions of KCl and Na_2SO_4. The columns were fitted with coarse sintered glass filters for rapid flow and packed with 20 mesh resin.

The anion resin used was strongly basic Amberlite IRA-400 purchased from the Rohm and Haas Company. The resin was shipped in the chloride form and was converted to the nitrate form using concentrated $NaNO_3$.

2. Geiger-Muller counter

A Tracerlab Inc. TCG-1 end window, self-quenching Geiger-Muller counter tube was used to measure activities in all of

the samples. The mica window thickness was 2.5 mg./cm.^{2} and the tube deadtime was found to be 200 microseconds by the matched sample technique (41, p. 266). The sample rack was mounted 7 mm. below the end window inside a lead housing. A Berkeley decimal scalar, model 100, was used to record the pulses from the tube.

3. Filtering equipment

Exchange rate studies by radioactive tracer techniques require smooth, reproducible samples. This was achieved by directly filtering well coagulated slurries of the radioactive AgCl samples onto round pieces of fine (Red Ribbon) filter paper. A glass chimney of inside diameter 2.8 cm. was fastened by rubber bands to a round sintered glass disk of the same diameter, fused into the top of a small funnel. A slight vacuum created by an aspirator was used to control the rate of filtration.

4. Constant temperature bath

A Sargent constant temperature bath was used for maintaining all solutions within 0.1° C. of the desired temperature. The 25° C. bath was cooled by tap water running through a cooling coil and a series of intermittant heaters balanced the cooling effect. The 35° C. bath required no auxiliary cooling other than the atmosphere. The 15° C. bath

was cooled by a portable refrigeration coil manufactured by
the Blue M. Electric Company, Blue Island, Illinois. Precise
temperatures were maintained by balancing with the inter-
mittant, thermo-regulated heaters.

5. Additional equipment

A Machlett Auto-Burette, self-filling burette, cali-
brated to hundredths of a milliliter, was used in the
potentiometric titrations of aquated complexes with NaOH.
A Beckman model "G" pH meter, standardized against a pH 7
buffer, was used to follow pH changes. In order to allow pH
determinations outside the shielded cabinet, shielded
electrodes, model 1190-80 (standard calomel and glass), were
used. Immediate mixing of the NaOH with the reaction solution
was achieved with a magnetic stirrer.

Potentiometric titrations of chloride were made with the
same pH meter used as a potentiometer. Potential differences
between a Ag-AgCl electrode and a standard calomel electrode
were measured as $AgNO_3$ was added to the reaction solution.
The Ag-AgCl electrode was constructed according to the method
outlined by Bates (42, pp. 204-206).

Conductivity measurements were made using an Industrial
Instruments, Inc. conductivity bridge, model RC 16. A Freas
type conductance cell with freshly platinized electrodes was
used for all conductivity experiments.

A Cary Recording Spectrophotometer, model 12, manu-
factured by Applied Physics Corporation, Pasadena, California,
was used for characterization of compounds and kinetics
studies. The experimental solutions were contained in 10 cm.,
glass stoppered silica cells.

For the analysis of platinum in trans-[Pt(NH$_3$)$_2$Cl$_2$]
by thermal decomposition, a muffle furnace of 700° C. maxi-
mum temperature manufactured by Schaar and Company, Chicago,
Illinois, was used. An alternate procedure for platinum
analysis involved electrodeposition of the metal onto a
platinum electrode using a Sargent-Slomin Electrolytic
Analyzer.

C. Procedures

1. Analysis of trans-dichlorodiammineplatinum(II)

Characterization of uniformity of purity for each
preparation of trans-[Pt(NH$_3$)$_2$Cl$_2$] consisted of platinum and
chloride analyses and the u.v. absorption spectrum taken be-
tween 220 mu and 400 mu. Originally, the platinum analysis
was done electrolytically by weighing a known amount of
trans-salt into a solution containing 0.5 N sulfuric acid and
a drop of nitric acid which acts as a cathodic depolarizer to
prevent excessive hydrogen evolution. The platinum was then
deposited on weighed platinum electrodes using currents of

0.2 amp. for 2 hours. Subsequently, the chloride analysis
was done gravimetrically on the same sample by addition of
excess $AgNO_3$ to precipitate AgCl. Precautions were taken to
avoid errors in this determination by keeping the AgCl in
darkened areas and the supernatant solution slightly acidic.
Later, platinum analyses by thermal decomposition proved to be
somewhat more precise than the electrodeposition procedure.
Weighed quantities of trans-[Pt(NH$_3$)$_2$Cl$_2$] were slowly heated
to 500° C. in a muffle furnace, converting the sample quanti-
tatively to platinum black. The chloride analysis was then
done on a separate sample by reacting a known amount of trans-
compound dissolved in water with excess NH_3 to strip the com-
plexed chloride from the compound. Then the solution was
acidified, excess $AgNO_3$ was added and the AgCl precipitate
was weighed.

In general, the crystals of trans-salt were considered
to be of acceptable purity when the observed analysis deviated
from the calculated values by less than 0.1%.

Comparison of the u.v. absorption spectra of trans-
[Pt(NH$_3$)$_2$Cl$_2$] with that published by Chatt et al. (43) was
found to be a sensitive criterion of purity. The valley
absorbance at 252 mu was particularly sensitive to impurities
and, in general, if the optical density of this valley was
95% or less of the optical density of the valley at 295 mu,
acceptable purity was indicated. A typical spectrum of

trans-[Pt(NH$_3$)$_2$Cl$_2$] showing the changes produced by acid
hydrolysis appears in Figure 1.

2. Determination of first acid hydrolysis equilibrium

Because of low solubility [0.00122 M at 25° C., cf. Drew
et al. (15)] and slow rates of dissolution, the concentration
range studied in this research was very much limited. A
known amount of trans-compound was dissolved in the desired
amount of water by shaking the mixture for about 6 hours at
35° C. The proper amount of Na$_2$SO$_4$ was added to yield an
ionic strength of 0.318 neglecting contributions from the
hydrolysis products ([Pt(NH$_3$)$_2$Cl(H$_2$O)]$^+$ and Cl$^-$ contribute
less than 0.1% of the total ionic strength at equilibrium).
The flask was then diluted to the mark and allowed to reach
equilibrium at the desired temperature for at least 48 hours.
The flasks were usually covered with black tape to minimize
photo-induced decomposition, however, exposure to room lights
in a few instances did not seem to alter the results. Ali-
quots were then titrated with approximately 0.1 N. NaOH using
the microburette, stirrer and pH meter previously described.
All NaOH solutions used were standardized with reagent grade
sulfamic acid using phenolphthalein as an indicator. The
first aliquot was titrated rather deliberately to ascertain
the titration curve in general, subsequent titrations being
carried out rapidly with more points concentrated near the

Figure 1.   Ultraviolet absorption spectrum of trans-$[Pt(NH_3)_2Cl_2]$.
Spectrum obtained with a solution: 7.59×10^{-4} M.
trans-$[Pt(NH3)_2Cl_2]$, 0.010 M. KCl (to suppress hydrolysis)
in a 10 cm. silica cell. Dotted line shows spectrum of a
solution with no KCl taken 24 hours after dissolution to
illustrate spectral changes due to acid hydrolysis

0

Trans - $[Pt(NH_3)_2Cl_2]$

7.59×10^{-4} M

—— KCl = 0.01 M.

- - - AGED SOLUTION

ϵ

WAVE LENGTH - mμ

23
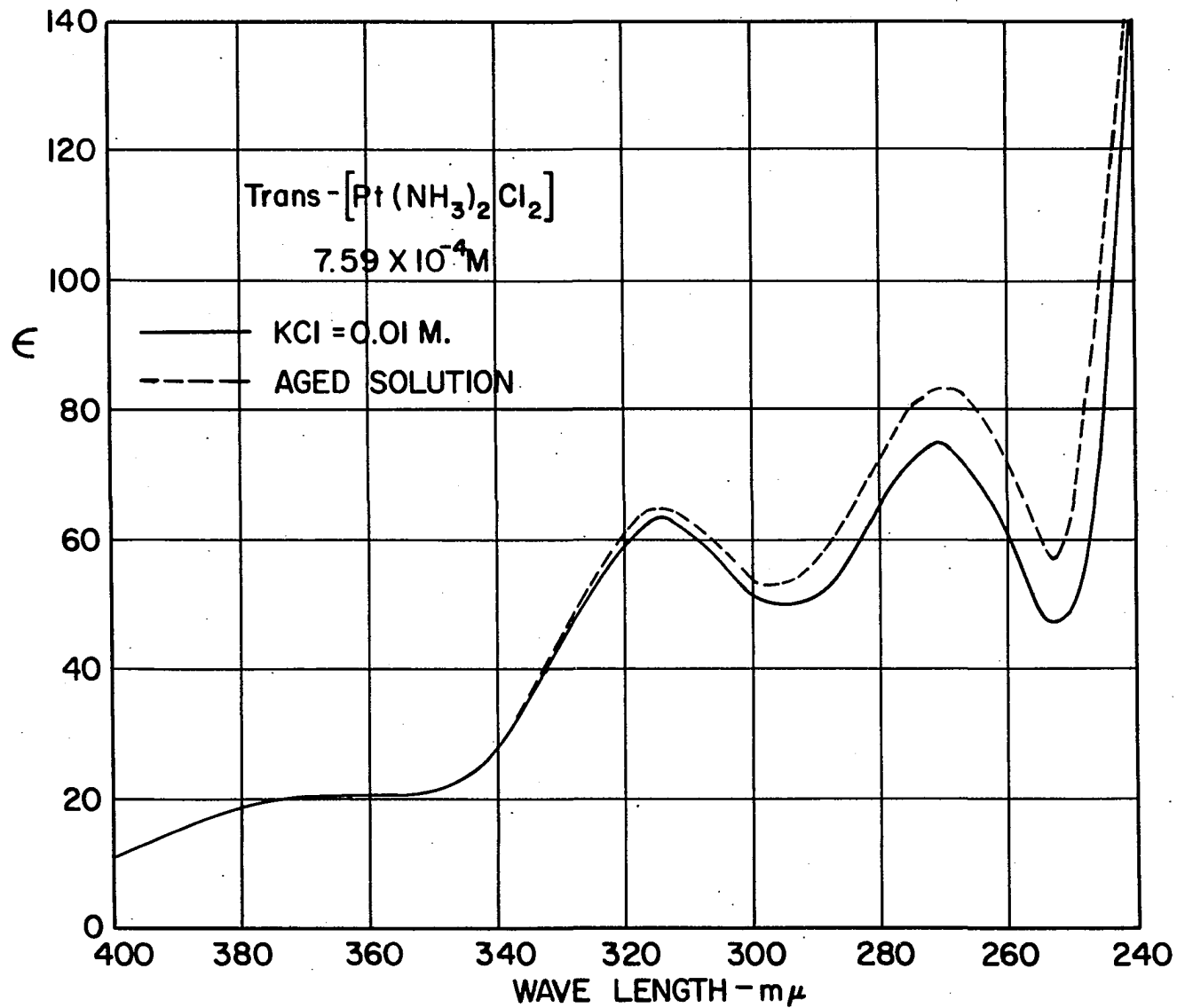
endpoint. Aliquots quenched by cooling to 5° C. exhibited considerable reversal of the hydrolysis equilibrium as significantly lower titres (25%) were obtained. Single point titrations were also carried out, in which the pH measured after addition of nearly the exact amount of base required to reach the endpoint could be used to indicate the amount of base-induced aquation occurring during the titration. This latter titre was used as the most accurate measure of the endpoint and averages of several such titres were used to obtain the first acid hydrolysis equilibrium constant by means of the equations in section III A. A typical titration curve is shown in Figure 2.

Occasional drift of the pH reading just prior to attainment of the endpoint was observed, especially in the experiments done at low ionic strength. This was probably due to a combination of incomplete rinsing of the electrodes between aliquots, CO_2 absorption and base-induced hydrolysis.

3. Determination of first hydrolysis rate constant

In the evaluation of kinetics of reversible reactions by potentiometric titration methods one must have fresh solutions and half-times of reaction long enough to obtain several points before equilibrium is reached. The rate constant for the formation of the acidic trans-$[Pt(NH_3)_2Cl(H_2O)]^+$ species was determined by following the acid titre during the first

Figure 2. Potentiometric titration curve used to determine the first acid hydrolysis equilibrium constant for trans-$[Pt(NH_3)_2Cl_2]$. Initial trans-salt concentration was 7.53×10^{-4} M., 50 ml. aliquot, $\mu = 0.318$, $25°$ C.

SINGLE POINT
TITRATION

ML. NaOH ADDED
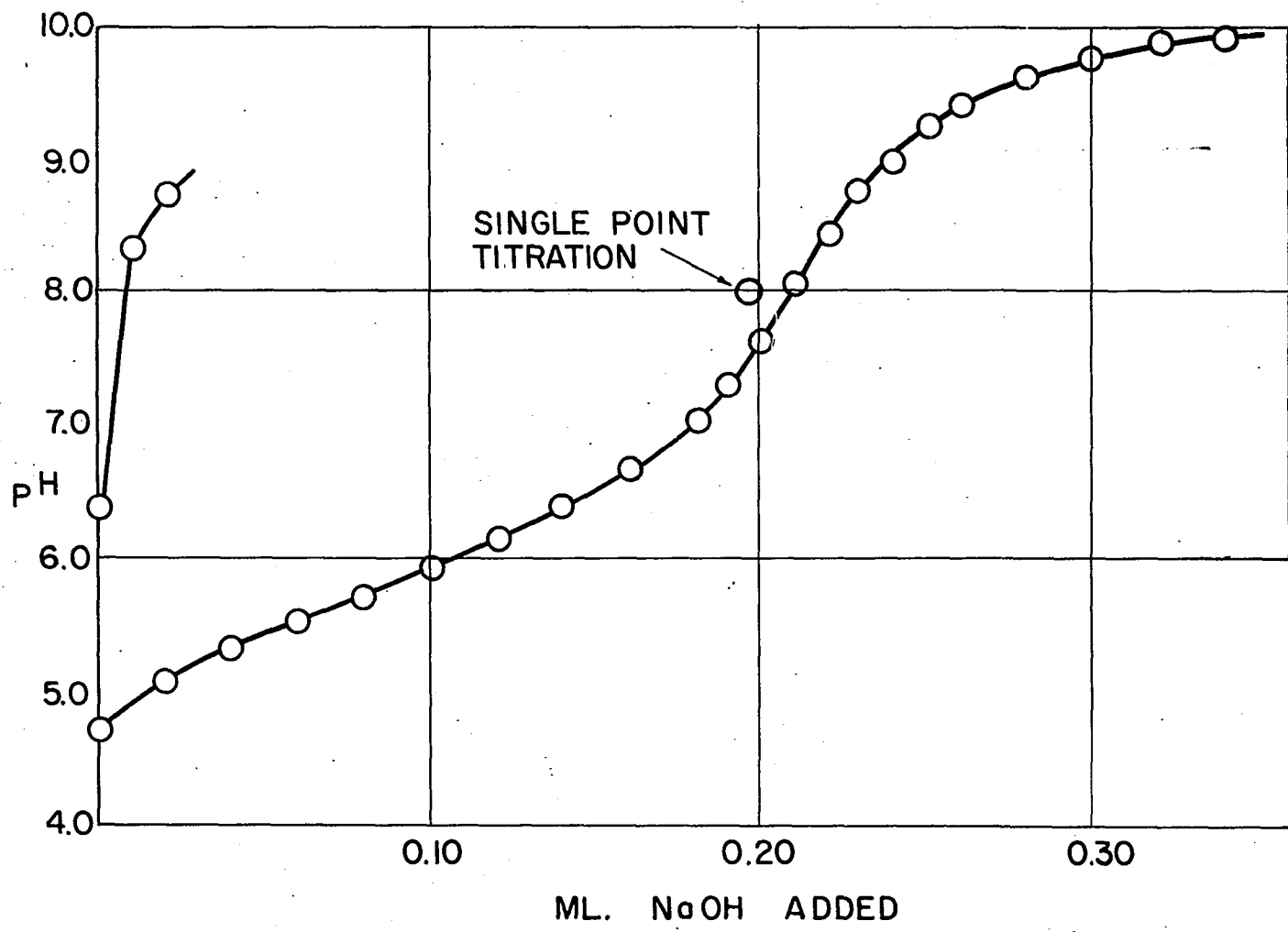
three half-times of reaction. A weighed quantity of trans-[Pt(NH$_3$)$_2$Cl$_2$] was shaken for 10 minutes in an aqueous solution of the proper volume, temperature and ionic strength (μ = 0.318 by addition of Na$_2$SO$_4$) The undissolved crystals were then filtered off and aliquots were withdrawn for titration. The zero time was taken to be 5 minutes after the slurry was started shaking. In each run a 100 ml. aliquot of the solution was reserved to be analyzed for platinum content by the methods described in Section II C. The trans-salt concentration was also checked by using the equilibrium titre and the known equilibrium constant. The titrations were carried out as rapidly as possible to minimize any base-induced hydrolysis. In some of the runs the aliquots were quenched by cooling to 5° C., however the rate constant obtained differed insignificantly from that obtained in the unquenched runs. In general the rate constants could be reproduced to within about 15%, however, if the crystals had dissolved any more slowly or if the hydrolysis rate had been much faster, this method could not have been used. By plotting G(x), which is the function of the observed titres and equilibrium constant given by Equation III.9, versus time, the rate constants were determined from the half-time. A typical set of titration curves is given in Figure 3.

4. Isotopic exchange experiments

The purpose of the exchange experiments was to follow the rate of introduction of chlorine-36 into the complex species;

Figure 3. Titration curves used to determine the acid hydrolysis rate
constant for trans-[Pt(NH$_3$)$_2$Cl$_2$]. Initial trans-salt con-
centration was 2.68 x 10^{-4} M., 50 ml. aliquots, 15° C.,
μ = 0.318

TITRATION CURVES FOR Trans $-\left[Pt(NH_3)_2 Cl_2\right]$

2.68×10^{-4} M.   15° $\mu = 0.318$

BLANK

27   107   204   394   2d

m.   3d

pH

ml. NaOH , 0.1071 N.

29
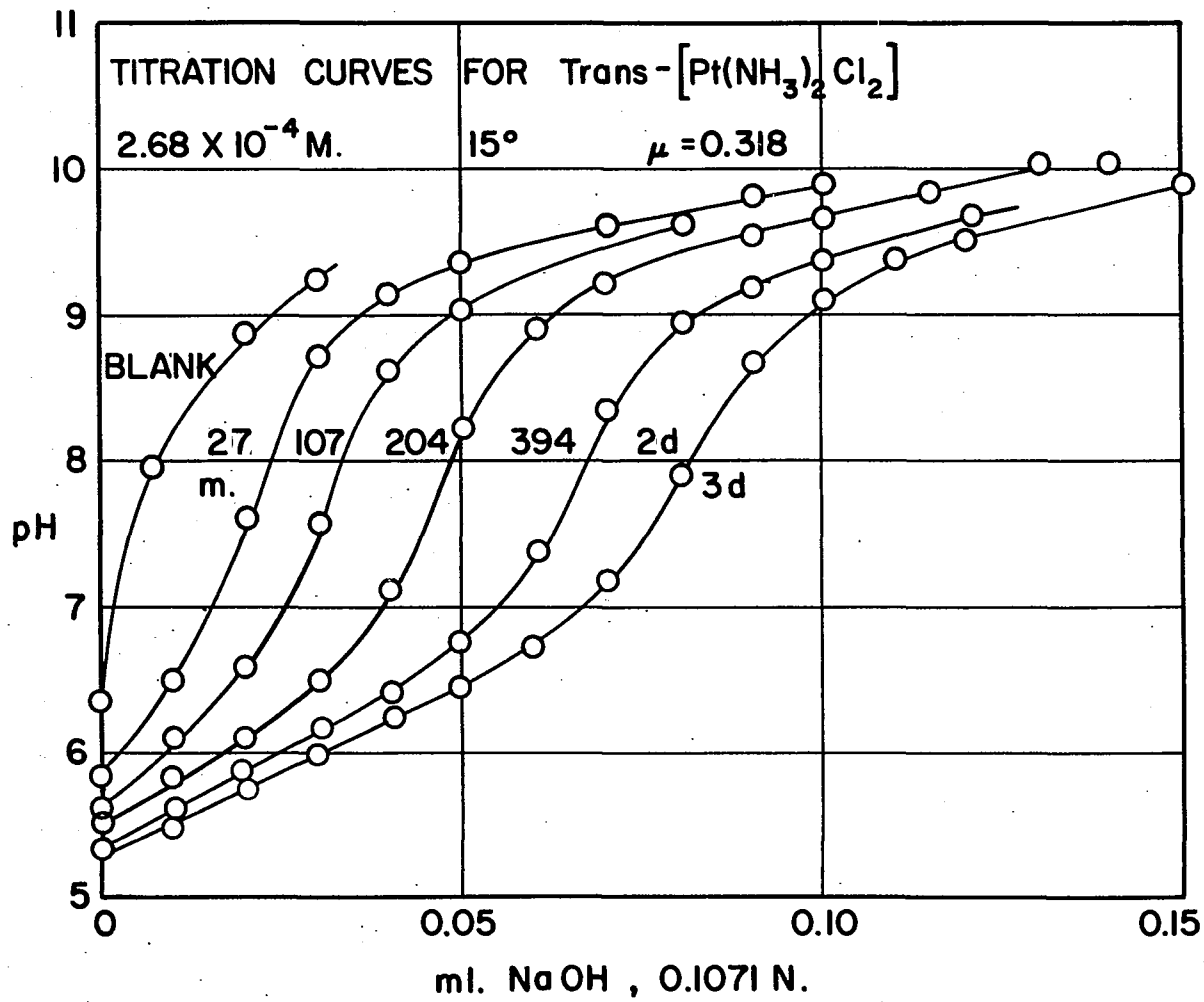
i.e. trans-[Pt(NH$_3$)$_2$Cl$_2$] and trans-[Pt(NH$_3$)$_2$Cl(H$_2$O)]$^+$. Such experiments yield information concerning chloride lability and extent of a second acid hydrolysis.

All of the exchange experiments in this work were performed with "aged" solutions. In these solutions the trans-[Pt(NH$_3$)$_2$Cl$_2$] was allowed to reach equilibrium with its hydrolysis species before the exchange was initiated by the addition of chlorine-36. All of the solutions were kept at a constant ionic strength of 0.318 by simultaneous adjustment of KCl and Na$_2$SO$_4$ concentrations. The experiments were carried out at different chloride and trans-salt concentrations. In each experiment the rate of introduction of chlorine-36 into both the neutral and positively charged complex species (i.e. trans-[Pt(NH$_3$)$_2$Cl$_2$] and trans-[Pt(NH$_3$)$_2$Cl(H$_2$O)]$^+$) was obtained. It was not feasible to measure the active chloride in the separate species.

The exchange experiments required a clean separation of the platinum complexes from the ionic chloride, and then the measurement of the specific activity of the complexed chloride. The obvious method of adding AgNO$_3$ and filtering off the ionic chloride as AgCl failed completely. Apparently, a rapid exchange, induced by the precipitation process, was occurring. Also, inefficient separations of the Ag Cl precipitate from the filtrate and stripping chloride from the complex species by addition of excess AgNO$_3$ introduced

difficulties. Because of the success found by Reishus (6) using an ion exchange separation technique, this method was tried and found to serve well in the characterization of the exchange reactions.

The exchange experiments employed Amberlite IRA-400 anion resin in the NO_3^- cycle. Weighed quantities of trans-$[Pt(NH_3)_2Cl_2]$ were dissolved by shaking at 35° C. for several hours in water of the proper volume containing the desired amount of KCl and Na_2SO_4. Any possible errors due to the presence of KCl and Na_2SO_4 during the dissolution (i.e. chloride substitution of NH_3 etc.) were not detected by other exchange experiments in which the KCl and Na_2SO_4 were added after completely dissolving the trans-salt in water. The flask was then wrapped with black tape and allowed to equilibrate at the desired temperature for at least 3 days but no longer than a week. Then the exchange was initiated by addition of 5 to 50 microliters of approximately 2 N. HCl[36], this moment being taken as the zero time of exchange. The amount of 2 N. HCl[36] added was in all cases negligible compared to the chloride already present in the system. Aliquots, appropriately sized to yield the desired amount of final AgCl precipitate, were then pipetted into the anion exchange column at various times covering from 3 minutes to three half-times of exchange. The exchange resin very effectively removed all of the ionic chloride, quenching the

exchange reaction, and permitted the _trans_-compound and any

aquo species to pass through the bed. All aliquots were

eluted from the resin by a 4-fold excess of water. The ef-

fluent solution was then boiled to reduce the volume to 50

ml. Then the solutions were boiled with excess aqueous NH_3

for 30 minutes to substitute NH_3 for all chloride ligands,

forming $[Pt(NH_3)_4]^{++}$ and ionic chloride. After acidification

with H_2SO_4, excess $AgNO_3$ was added to precipitate the

chloride. The precipitate was coagulated by heating for 20

minutes and carefully filtered on weighed filter papers as

described in section II B. After drying in the open air and

weighing, the AgCl samples were mounted on cardboard squares

using wide Scotch tape, counted, and the specific activity

(cts./min. mg. Cl) was determined for each sample. Several

blank filter papers were weighed with the samples to determine

the correction for weight changes due to humidity differences.

The fact that the specific activities of several exchanging

species are identically the same at exchange equilibrium and

are equal to the original ratio of radioactive chloride to

total chloride in the system permitted sampling the infinity

aliquots, _i.e._ equilibrium samples, at any time after exchange

was initiated. These aliquots were treated directly with NH_3

and the total chloride was precipitated and treated in like

manner to the other aliquots. All aliquot sizes were cal-

culated to yield at least 10 mg. of final AgCl precipitate so

as to minimize self-absorption errors by working on the plateau
of the self-absorption curve (2). Generally, about 90% of the
theoretically calculated complexed chloride was obtained in
the final precipitates. The fraction of exchange, F(F =
S_t/S_∞ where S_t and S_∞ denote specific activities at time t
and at equilibrium), for each sample was calculated and plots
of log (1 - F) versus time were made to obtain the half-time
of exchange. A typical exchange reaction plot appears in
Figure 4. The exchange resin was regenerated after each
sample by running concentrated $NaNO_3$ through the column.

5. Conductivity experiments

All conductivity experiments were done using electrodes
coated with platinum black and 1000 c.p.s. currents to
minimize polarization effects. The cell constant was deter-
mined by measuring the resistance of a standard 0.0200 N KCl
solution. The electrodes were thoroughly rinsed with
conductivity water of at least 1.5×10^{-7} ohm^{-1} cm.$^{-1}$
specific conductance between each experimental sample. The
Freas type conductance cell was thermostated at 25° C. for
all experiments. Some of the solutions were prepared by
completely dissolving weighed quantities of trans-$[Pt(NH_3)_2Cl_2]$
in water. Others were prepared by shaking a slurry of trans-
salt crystals in water for a few minutes, filtering off the un-
dissolved crystals and later analyzing for platinum con-

Figure 4. Typical exchange plot of $\log(1-F)$ versus time for the iso-
topic chloride exchange of trans-$[Pt(NH_3)_2Cl_2]$. Trans-salt
concentration = 7.59×10^{-4} M., chloride concentration =
3.0×10^{-3} M., $\mu = 0.318$, $25°$ C.

trans-$[Pt(NH_3)_2Cl]_2$
$a = 7.59 \times 10^{-4}$
$b = 3.0 \times 10^{-3}$
$\mu = .318$, $25°$

$T_{\frac{1}{2}} = 160$ MIN.

1-F

TIME (MIN.)

35
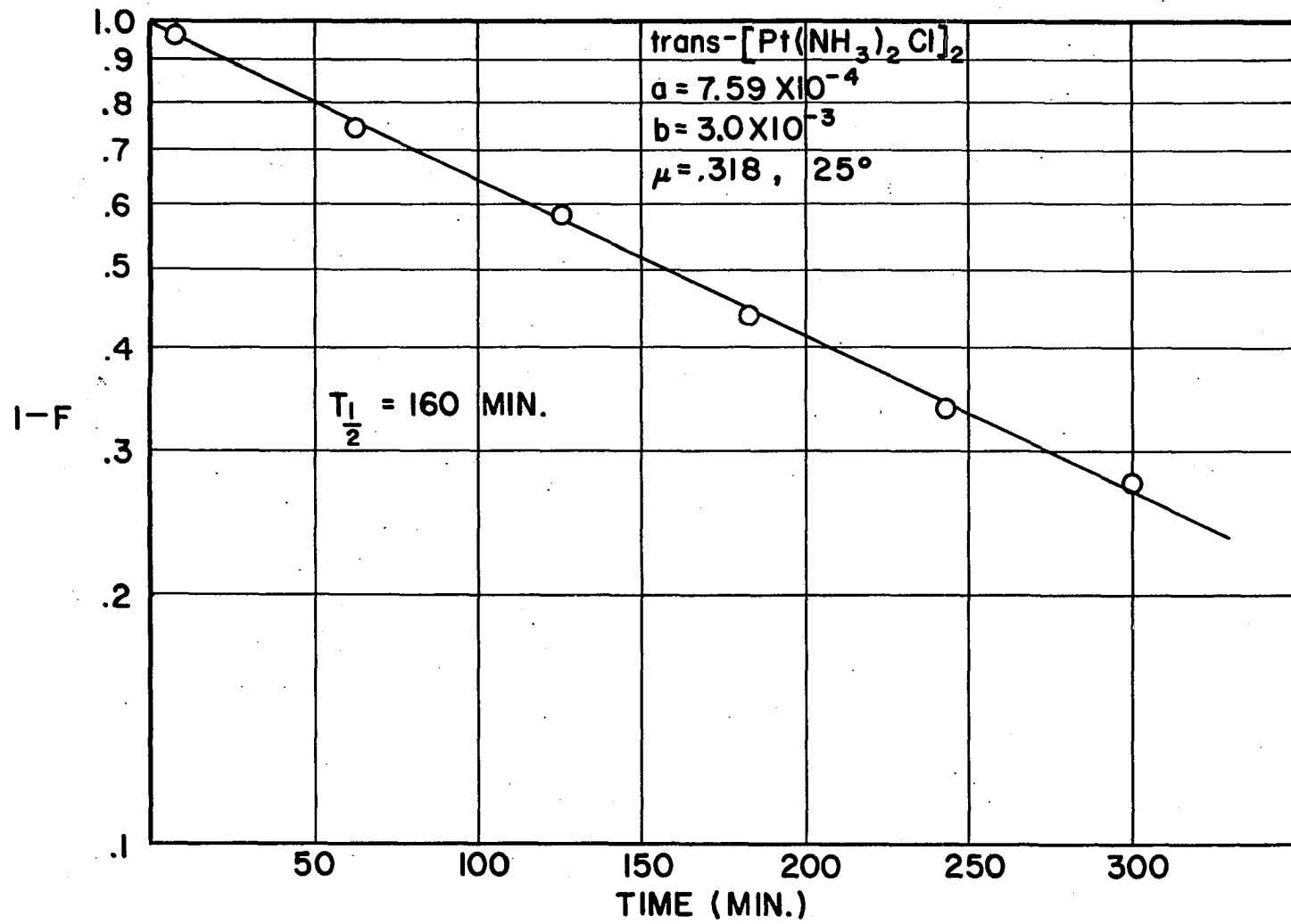
centration by the methods described in Chapter II-C. Also, conductivity measurements were made on effluent solutions from a column containing two types of ion exchange resins, one in the H^+ cycle and the other in the OH^- cycle. Conductivity readings were taken until a steady state had attained for each of the experiments and the equivalent conductances were calculated from the measured resistance (R), known concentration (C) and cell constant (k) using the classical expression relating these parameters:

$$\Lambda = 1000k/CR \qquad\qquad (II.2)$$

III. MATHEMATICAL TREATMENT OF DATA

A. First Acid Hydrolysis Equilibrium

Jensen (16) has indicated that trans-$[Pt(NH_3)_2Cl_2]$ under-goes acid hydrolysis when dissolved in water. In general, this hydrolysis may be described by the following equations:

$$trans\text{-}[Pt(NH_3)_2Cl_2] + H_2O \underset{R_{-1}}{\overset{R_1}{\rightleftharpoons}} [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^- \quad (III.1)$$

$$\quad (a-x-y) \qquad\qquad\qquad\qquad (x) \qquad\qquad (b+x+2y)$$

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

$$\quad (x) \qquad\qquad\qquad\qquad (y) \qquad\qquad (b+x+2y)$$
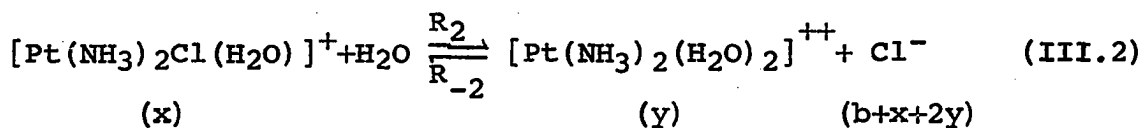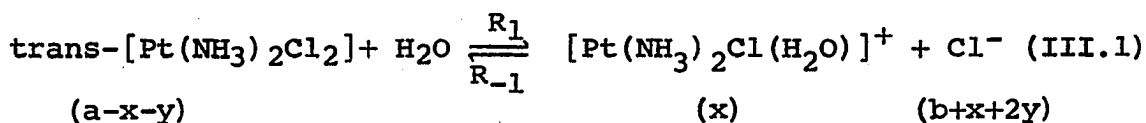
where a = initial concn. of t-$[Pt(NH_3)_2Cl_2]$, moles/l.

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 t-$[Pt(NH_3)_2Cl_2]$, 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

R_1 = rate of first acid hydrolysis, moles/l. sec.

R_{-1} = rate of reverse first acid hydrolysis, moles/l. sec.

R_2 = rate of second acid hydrolysis, moles/l. sec.

R_{-2} = rate of reverse second acid hydrolysis, moles/l. sec.

If the extent of hydrolysis of a second chloride (Reac-

tion III.2) were negligible, the equilibrium constant describing the system would be given by:

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

(III.3)

where the infinity subscripts refer to the concentrations at equilibrium or infinite time, and the γ's are the indicated activity coefficients. The measured acid titre is represented by T (equiv. acid/l.). Then x = T and Equation III.3 becomes:

$$K_1 = T_\infty(b+T_\infty)\gamma_\pm^2/(a-T_\infty)\gamma_o$$

(III.4)

For solutions of low ionic strength (i.e. no added salt so the ionic strength just equals x_∞ or T_∞), γ_o may be taken to be 1, and the activity coefficient of HCl in a solution of KCl (44, p. 575) with an ionic strength just equal to T_∞ may be used for $\gamma_\pm$. For solutions in which Na_2SO_4 is added to establish the ionic strength at 0.318 M., the concentration quotient, K_1', is defined by:

$$K_1' = K_1\gamma_o/\gamma_\pm^2 = T_\infty(b+T_\infty)/(a-T_\infty)$$

(III.5)

Under these conditions of a constant high ionic strength, all activity coefficients are expected to be constant and accordingly the concentration ratio, K_1', will also be constant with changes in concentration.

B. Rate Constant for First Acid Hydrolysis

In accord with the stoichiometry of Reaction III.1, the
first hydrolysis reaction is expected to be first order in
<u>trans</u>-$[Pt(NH_3)_2Cl_2]$ while the reverse reaction is first order
in $[Pt(NH_3)_2Cl(H_2O)]^+$ and first order in Cl^-. If, in addi-
tion, the second hydrolysis is assumed to be negligible, the
expression for the time rate of change of x in Reaction
III.1 becomes:

$$dx/dt = R_1 - R_{-1} = k_1(a-x) - k_{-1}(x)(b+x) \qquad (III.6)$$

where k_1 = rate constant for hydrolysis, sec.$^{-1}$

k_{-1} = rate constant for reverse hydrolysis, l./mole
sec.

Since $K_1' = k_1/k_{-1}$, Equation III.6 rearranges to:

$$dx/[x^2 + (b+K_1')(x) - K_1'a] = -k_{-1}dt \qquad (III.7)$$

which can be integrated with the limits x = 0 when t = 0, x =
x when t = t and the expression for x_∞ obtained from
Equation III.5 ($x_\infty = T_\infty$) to yield the solution:

$$-k_{-1}t = G(x)/\sqrt{4K_1'a + (b+K_1')^2} \qquad (III.8)$$

where $G(x) = \ln \dfrac{[(x_\infty-x)(-x_\infty+\sqrt{4K_1'a + (b+K_1')^2})]}{[x_\infty(x-x_\infty + \sqrt{4K_1'a + (b+K_1')^2})]}$ (III.9)

The measured acid titres may be substituted for the x's.
According to Equation III.8, plots of G(x) will be linear in
t. The half-time of hydrolysis, $t_{\frac{1}{2}}$, obtained from these

plots, is then used in the following expression to calculate the rate constant k_{-1}.

$$k_{-1} = \ln 2 / [(t_{\frac{1}{2}})(\sqrt{4K_1'a + (b+K_1')^2})]$$

(III.10)

Finally, k_1 can be calculated from the expression:

$$k_1 = k_{-1} K_1'$$

(III.11)

C.   Isotopic Exchange Equations

1.   General treatment of three component exchange systems

There may be several possible mechanisms whereby radioactive chloride is introduced into the trans-$[Pt(NH_3)_2Cl_2]$ or the $[Pt(NH_3)_2Cl(H_2O)]^+$ species. Two of these paths are by the acid hydrolyses illustrated in Reactions III.1 and III.2. Also, a direct exchange might occur in which ionic chloride replaces complexed chloride directly.

Including the possibility of a second acid hydrolysis, the chloride exchange scheme at chemical equilibrium may be represented by the following reactions:

$$\text{trans-}[Pt(NH_3)_2Cl_2] + H_2O \underset{R_{-1}=R_1}{\overset{R_1}{\rightleftharpoons}} [Pt(NH_3)_2Cl(H_2O)]^+ + Cl^-$$

$(a-x_\infty-y_\infty)$ $\qquad\qquad$ (x_∞) $\qquad$ $(b+x_\infty+2y_\infty)$
u, S_u $\qquad\qquad\qquad\qquad$ v, S_v $\qquad\quad$ s, S_s

(III.12)

$$\text{trans-}[Pt(NH_3)_2Cl_2] + Cl^{-*} \xrightarrow{R'} \text{trans-}[Pt(NH_3)_2ClCl^*] + Cl^-$$

(III.13)

$$[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})]^+ + \text{H}_2\text{O} \underset{R_{-2}=R_2}{\overset{R_2}{\rightleftharpoons}} [\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{++} + \text{Cl}^-$$

$$\quad (x_\infty) \qquad\qquad\qquad\qquad (y_\infty) \qquad\qquad (b+x_\infty+2y_\infty)$$

$$\quad v,\ S_v \qquad\qquad\qquad\qquad\qquad\qquad\qquad s,\ S_s$$

$$(\text{III.14})$$

$$[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})]^+ + \text{Cl}^{-*} \overset{R''}{\longrightarrow} [\text{Pt}(\text{NH}_3)_2\text{Cl}^*(\text{H}_2\text{O})]^+ + \text{Cl}^-$$

$$\quad (x_\infty) \qquad\qquad\qquad\qquad (x_\infty) \qquad\qquad (b+x_\infty+2y_\infty)$$

$$\quad v,\ S_v \qquad\qquad\qquad\qquad\qquad\qquad s,\ S_s$$

$$(\text{III.15}$$
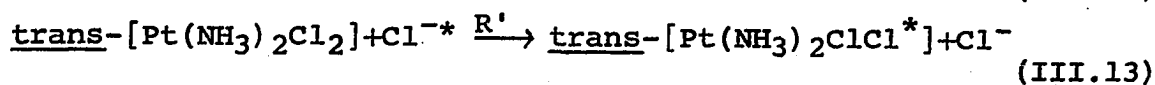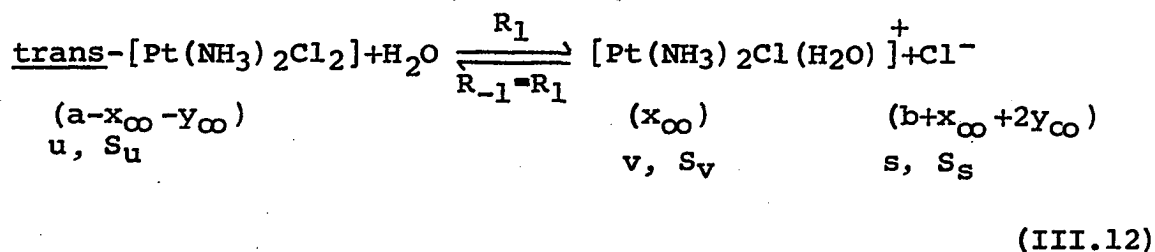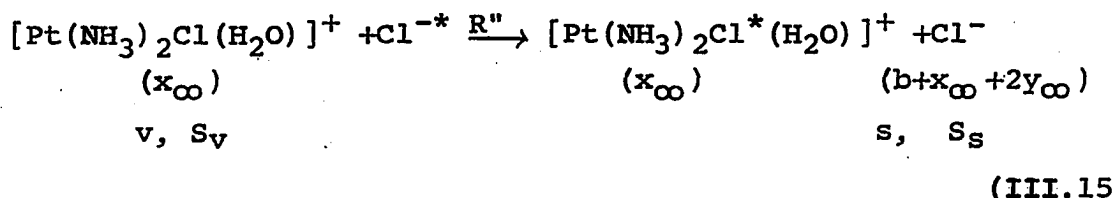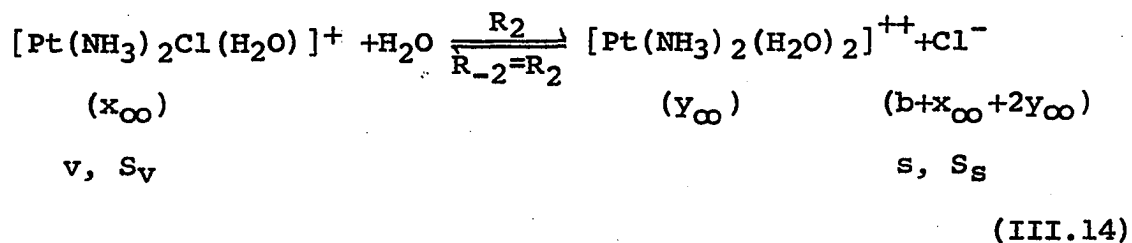
where u = Cl^{36} concn., Cl^*, atoms/ml. in $\underline{t}$-$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

S_u = $u/2(a-x_\infty-y_\infty)$, specific activity of the chloride

in $\underline{t}$-$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ at time t

s = Cl^{-*} concn., atoms/ml., in ionic chloride

S_s = $s/(b+x_\infty+2y_\infty)$, specific activity of the ionic

chloride at time t

R' = rate of direct chloride exchange process for

$\underline{\text{trans}}$-$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

v = Cl^{36} concn., atoms/ml., in $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})]^+$

S_v = v/x_∞, specific activity of the chloride in

$[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})]^+$ at time t

R'' = rate of direct chloride exchange for $[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{H}_2\text{O})]^+$

moles/l. min.

Other symbols have been previously defined. In this system,

the total concentration of chlorine-36 is defined by

$$I = u + v + s.$$

The time rate of increase of u is given by

$$du/dt = R_1(S_s + S_v - 2S_u) + R'(S_s - S_u) \qquad \text{(III.16)}$$

If a parameter, γ, is defined by

$$\gamma = R'/R_1 \qquad \text{(III.17)}$$

and S_s, S_v and S_u are put in terms of I, u, v, a, b, x_∞ and y_∞ in Equation III.16, the following equation is obtained:

$$\frac{1}{R_{\pm 1}} \frac{du}{dt} + u \left[\frac{(1+\gamma)}{(b+x_\infty+2y_\infty)} + \frac{(1+\gamma/2)}{(a-x_\infty-y_\infty)} \right] +$$

$$v \left[\frac{1+\gamma}{(b+x_\infty+2y_\infty)} - \frac{1}{x_\infty} \right] = \left[\frac{(1+\gamma)}{(b+x_\infty+2y_\infty)} \right] I \qquad \text{(III.18)}$$

where $R_{\pm 1} = R_1 = R_{-1}$, the rate of the first acid hydrolysis

at chemical equilibrium.

Similarly, the time rate of increase of v is given by

$$dv/dt = R_1(S_u - S_v) + R''(S_s - S_v) + R_2(S_s - S_v) \qquad \text{(III.19)}$$

With the definition of another parameter, β, by

$$\beta = (R'' + R_2)/R_1 \qquad \text{(III.20)}$$

and substitution of S_u, S_s and S_v in terms of I, u, v, a, b, x_∞ and y_∞ in Equation III.19, the following equation is obtained:

$$\frac{1}{R_{\pm 1}} \frac{dv}{dt} + v \left[\frac{(1 + \beta)}{(x_\infty)} + \frac{\beta}{(b + x_\infty + 2y_\infty)} \right] +$$

$$u \left[\frac{\beta}{(b+x_\infty+2y_\infty)} - \frac{1}{2(a - x_\infty - y_\infty)} \right] = \left[\frac{\beta}{(b+x_\infty+2y_\infty)} \right] I \qquad \text{(III.21)}$$

Equations III.18 and III.21 are linear first order differential equations and their solutions for the condition that

u = v = 0 at t = 0 are of the form

$$1 - u/u_\infty = 1 - S_u/S_{u\infty} = A_1 e^{-\alpha_1 t} + A_2 e^{-\alpha_2 t}$$

$$1 - v/v_\infty = 1 - S_v/S_{v\infty} = B_1 e^{-\alpha_1 t} + B_2 e^{-\alpha_2 t}$$

where the infinity subscripts refer to infinite time or equilibrium. These two solutions may be combined to yield the following expression:

$$1 - (u + v)/(u_\infty + v_\infty) = C_1 e^{-\alpha_1 t} + C_2 e^{-\alpha_2 t} \qquad \text{(III.22)}$$

The total fraction of exchange for all complexed chloride is given by $F_{u+v} = (u + v)/(u_\infty + v_\infty)$.

The parameters C_1, C_2, α_1 and α_2 are determined by a, b, K_1', k_1, β and γ. Expressions for evaluating the above parameters (C's and α's) are obtained by substitution of the above solutions into Equations III.18 and III.21. Therefore, the time of half-exchange for all complexed chloride (i.e., time for $(u + v)/(u_\infty + v_\infty) = \frac{1}{2}$) can be calculated from Equation III.22 for a given set of concentration conditions from the values of C_1, C_2, α_1 and α_2. This calculation requires that both β and γ be known. In general, the calculation involves trial and error adjustment of β and γ until the calculated time of half-exchange matches the experimental value. It is impossible to determine both β and γ if a single fraction of exchange, i.e., F_{u+v}, is measured. This problem can be resolved, however, if the concentration conditions can be adjusted so as to make one of these parameters very small.

The form of the other parameter (i.e., the rate laws and values of rate constants involved in the R's in the expression assumed for the parameter; Equations III.17 and III.20 are examples) can then be determined at these concentration conditions. Thus one of these parameters is known at concentration conditions in which both β and γ must be considered and the other parameter can be determined as follows. Calculated curves of $1 - F_{u+v}$ versus time are prepared for various values of the unknown parameter (for example β) and a known value of γ. A value of β for each experiment is then selected for which the calculated time of half-exchange matches the experimental values.

It should be pointed out that if the value of the fraction of exchange in t-[Pt(NH$_3$)$_2$Cl$_2$] only, viz. u/u_∞, is known at some instant of time, this knowledge yields no information concerning the value of the fraction of exchange in [Pt(NH$_3$)$_2$Cl(H$_2$O)]$^+$, vis. v/v_∞, or the value of F_{u+v}. This is true because there are three exchanging species: trans-[Pt(NH$_3$)$_2$Cl$_2$], [Pt(NH$_3$)$_2$Cl(H$_2$O)]$^+$ 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_{u+v} but rather any two of the three.

2. Treatment of two component exchange system

If the initial concentration of ionic chloride is much larger than the concentration quotient, i.e., b $\gg$ K$_1'$, then

the equilibrium concentration of $[Pt(NH_3)_2Cl(H_2O)]^+$ will be much less than the total platinum concentration, i.e., $x_\infty \ll a$. Consequently, v will be much less than u and it follows that dv/dt will be much less than du/dt. If dv/dt in Equation III.19 is set equal to zero, there obtains the following expression for β:

$$\beta = (S_v - S_u)/(S_s - S_v) \qquad (III.23)$$

If β is replaced by $(R" + R_2)/R_1$, Equation III.23 is solved for the product $R_1 S_v$, this product is substituted into the equation for du/dt (Equation III.16) and finally $(R" + R_2)$ is replaced by βR_1, the following expression is obtained:

$$du/dt = [\frac{(1 + 2\beta)R_1}{(1 + \beta)} + R'] (S_s - S_u) \qquad (III.24)$$

The exchange system is now a "two component" one in which exchange is taking place between trans-$[Pt(NH_3)_2Cl_2]$ and Cl^- only. This system is characterized by Reactions III.12 and III.13. The total rate of exchange in this system is designated as R which is given by

$$R = (1 + 2\beta)R_1/(1 + \beta) + R' \qquad (III.25)$$

Since x_∞ and y_∞ are much smaller than a in this system (see the discussion on page 44) they may be omitted in the expressions for S_s and S_u; i.e., $S_s = s/b$ and $S_u = u/2a$. Under these conditions, I, the total number of radioactive chloride atoms per milliliter, becomes $I = u + s$ since a negligible number of Cl^{-*} atoms are in the mono-aquo complex.

Substitution for the quantities of S_S and S_u in terms of I, u, a, and b in Equation III.24 and incorporation of R from Equation III.25 yields

$$du/dt + R(b + 2a)u/2ab = RI/b \qquad (III.26)$$

This expression is easily integrated to yield a single exponential solution for u. The following expression for R/a is readily obtained from this solution.

$$R/a = \ln 2 \ (2b)/T_{\frac{1}{2}} \ (b + 2a) \qquad (III.27)$$

where $T_{\frac{1}{2}}$ = the half-time of exchange at high chloride concentrations, i.e., in a two component system.

In accord with the stoichiometry of Reactions III.12, III.13, III.14 and III.15 the rates are expected to have the following forms:

$$R_1 = k_1 (a - x_\infty - y_\infty)$$

$$R' = k' (a - x_\infty - y_\infty)(b + x_\infty + 2y_\infty)$$

$$R_2 = k_2 (x_\infty)$$

$$R'' = k'' (x_\infty)(b + x_\infty + 2y_\infty)$$

where k_1, k', k_2 and k'' are the rate constants for the indicated reactions.

As the initial concentration of ionic chloride (b) becomes high, keeping the initial concentration of trans-salt ("a") constant, x_∞ and y_∞ will become smaller. In the limit at very high chloride concentrations, R_2 will go to zero and R'' will become constant since $(x_\infty)(b + x_\infty + 2y_\infty)$ =

$K_1'(a - x_\infty - y_\infty)$ at chemical equilibrium. Also, R_1 will be-
come constant and R' will be proportional to b.

From the measured half-times of exchange at high chloride
concentrations, calculations of R/a at various values of b can
be made using Equation III.27. Thus a plot of R/a versus b
can be made to determine the dependence of R/a on b. From
the considerations of the exchange rate behavior at high
chloride concentrations discussed on page 46, this plot might
be expected to be a straight line with zero or a finite slope
depending on the value of k'. By extrapolation of this plot
to obtain the ordinate value at zero chloride concentration,
information concerning the magnitudes of k_2 and k", or R_2 and
R" can be obtained if the value of k_1 is known. If k_2 and k"
are very small, this ordinate value should be just k_1. If k_2
and k" are appreciable, the ordinate value will be higher than
k_1. If R_2 and R" are small, then β is small and from
Equation III.24, the expression for the rate of exchange at
high chloride concentrations becomes:

$$R = R_1 + R' \qquad\qquad \text{(III.28)}$$

IV. RESULTS

## A. First Acid Hydrolysis Equilibrium

The existence of an acid hydrolysis reaction of
trans-[Pt(NH$_3$)$_2$Cl$_2$] in aqueous solutions was demonstrated
by several experimental observations.

First, the absorption spectrum of the complex changed on
aging aqueous solutions as shown in Figure 1. The equilibrium
spectrum reverted back to the initial spectrum on adding ex-
cess chloride. Observations with other chloroammineplatinum(II)
complexes have revealed that substitution of an H$_2$O group for
chloride in the coordination sphere causes the transition
peaks to shift to lower wavelengths in general. Conclusions
based on ligand field theory (45) indicate that H$_2$O has a
higher ligand field strength than chloride. The spectral
changes occurring for trans-[Pt(NH$_3$)$_2$Cl$_2$] indicate a shift
of peaks to lower wavelengths.

Second, the initial molar conductance of freshly pre-
pared solutions of the trans-salt was found to be about
7 l./ohm mole cm. However, the conductivity changed quite
rapidly, reaching an equilibrium value of about 35 l./ohm mole
cm. after 3 hours at 25° C. Several solutions were run through
cation and anion exchange columns in the H$^+$ and OH$^-$ cycles
to completely remove any ionic impurity; however, the ef-
fluent solutions always exhibited the same conductivity

behavior.

Third, the solution pH decreased on aging due to the acid dissociation of the aquo complex

$$[Pt(NH_3)_2Cl(H_2O)]^+ \rightleftharpoons [Pt(NH_3)_2Cl(OH)] + H^+ \qquad (IV.1)$$
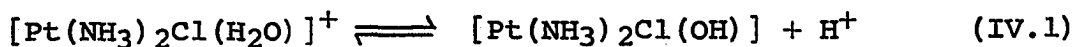
Fourth, potentiometric titrations of the system with standard NaOH indicated the formation of a weak acid, the rate of formation of which reached an equilibrium value. A typical set of titration curves is shown in Figure 3.

Also, some potentiometric titrations of chloride using a Ag-AgCl electrode, standard AgNO$_3$ and acidified acetone solvent indicated a general increase in chloride concentration on aging freshly prepared aqueous solutions of trans-compound. No quantitative data were obtained using this technique, however, due to inconsistent blank determinations.

Because of the results of Banerjea et al. (25), who were unable to detect a significant acid hydrolysis for trans-[Pt(NH$_3$)$_2$Cl$_2$], great care was taken to insure the purity of the compound and the consistency of the above mentioned observations. The compound was re-synthesized several times and as many as eight successive fractional crystallizations were carried out without altering the behavior or the ultra-violet absorption spectrum. It is believed that Banerjea et al. found no change in conductivity because the hydrolysis had probably already reached equilibrium during their lengthy dissolution period.

The NH_3 ligands could not have been replaced as this substitution would have increased the pH as the reaction proceeded whereas a decrease was observed.

The results obtained from equilibrium potentiometric titrations at 15°, 25° and 35° C. are given in Table 1. The equilibrium quotients were calculated from the measured titres using Equations III.4 (low ionic strength) and III.5 (high ionic strength). The titres shown represent averages of two to four titrations and the equilibrium quotients were averaged over all such sets of titrations. A typical titration curve with a single point titration is shown in Figure 2.

If there were an appreciable second acid hydrolysis, Equations III.4 and III.5 would not satisfactorily describe the equilibrium and one would observe changes in an equilibrium constant calculated from these equations as the initial trans-[Pt(NH_3)_2Cl_2] concentration is changed. As can be seen in Table 1, the calculated equilibrium constants were substantially unchanged over the approximately 2.5 fold concentration range. Therefore, this system appeared to be very well characterized by the single equilibrium shown in Reaction III.1. A value of 2×10^{-5} M. at 25° C. was set as an upper limit for a second hydrolysis equilibrium quotient, K_2', from the indicated variations for K_1'. The estimated uncertainty in K_1' is about 10%.

The acid, trans-[Pt(NH_3)_2Cl(H_2O)]$^+$, was indicated from

Table 1. Equilibrium quotients for the acid hydrolysis of trans-$[Pt(NH_3)_2Cl_2]$

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[a] "b" (M. x 10^4)	Equilibrium quotient K_1' or K_1 (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

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

the titration curves to have a pK of approximately 6. This
is slightly lower than the pK indicated for cis-
$[Pt(NH_3)_2Cl(H_2O)]^+$ which was about 6.7 (6).

From the temperature dependence of K_1', shown in Figure 5,
$\Delta H°$ for Reaction III.1 was found to be approximately 5.5
kcal./mole.

B. Rate Constant for First Acid Hydrolysis

The mathematical treatment of the kinetics of acid
hydrolysis were discussed in Chapter III. Graphs of G(x)
versus time, where G(x) is defined in Equation III.9, ob-
tained from the titration of fresh solutions of trans-
$[Pt(NH_3)_2Cl_2]$ at 25 ° C., zero and 0.318 ionic strength, are
shown in Figure 6. The straight lines in Figure 6 do not go
through 1 because of the uncertainty in zero time due to the
slow dissolution of the crystals of trans-salt. A typical set
of titration curves illustrating the hydrolysis proceeding to
equilibrium is shown in Figure 3. From the slopes of the
graphs in Figure 6, the values of k_{-1} and k_1 were calculated
by the procedure discussed in Chapter III. The results show-
ing k_1 and k_{-1} are tabulated in Table 2.

The reactions could be followed satisfactorily for about
two half-times and rate constants could generally be dupli-
cated to within about 15%. The exchange experiments described
in the next section probably provided better values for the

Figure 5. Temperature dependence of the acid hydrolysis equilibrium
quotient, K_1', for <u>trans</u>-$[Pt(NH_3)_2Cl_2]$. $\Delta H^\circ = 5.5$ kcal./mole

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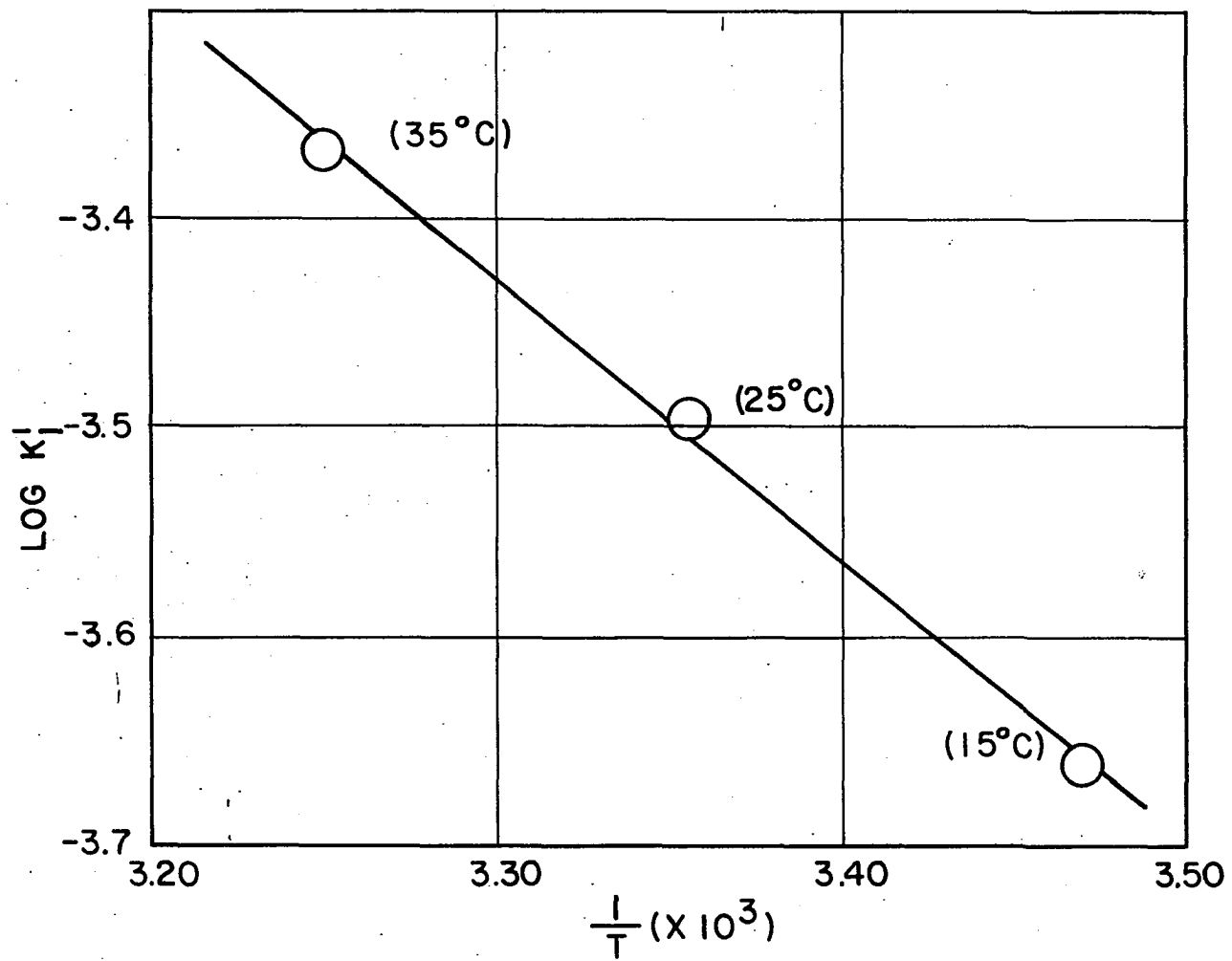
Figure 6. Plots of G(x) versus time for the first acid hydrolysis kinetics of trans-$[Pt(NH_3)_2Cl_2]$ at 25° C., zero and 0.318 ionic strengths. Initial trans-compound concentrations were 5.23 x 10^{-4} M. and 3.25 x 10^{-4} M. at zero and 0.318 ionic strengths respectively

trans−$[Pt(NH_3)_2Cl_2]$ −25°

$\mu = 0.318$
$a = 3.25 \times 10^{-4} M$

$k_1 = 8.9 \times 10^{-5} SEC.^{-1}$

$\mu = 0$

$a = 5.23 \times 10^{-4} M$
$k_1 = 10. \times 10^{-5} SEC^{-1}$

y-axis: $\dfrac{(T_\infty - T)(-T_\infty + \sqrt{K_1^2 + 4K_1 a})}{T_\infty (T - T_\infty + \sqrt{K_1^2 + 4K_1 a})}$

x-axis: TIME (MIN.)
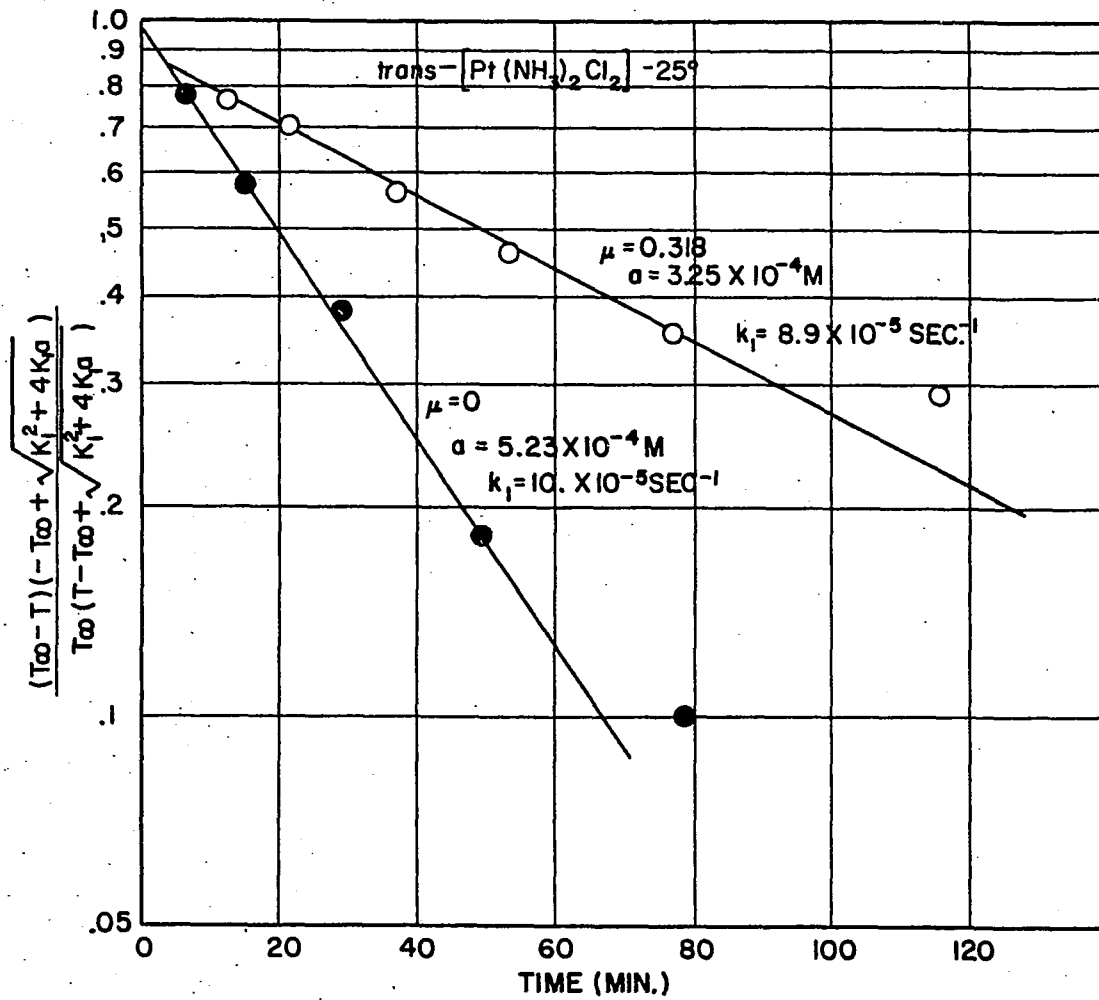
Table 2. Rate constants for the reversible acid hydrolysis of _trans_-$[Pt(NH_3)_2Cl_2]$

Temp. °C.	Initial $[Pt(NH_3)_2Cl_2]$ "a" M. x 10^4	Initial ionic strength "μ" M.	Equilibrium $[Pt(NH_3)_2Cl(H_2O)^+]$ "T_∞"	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

acid hydrolysis rate constants. One of the sources of error
in the potentiometric titration experiments was the low titre
due to very small amounts of $[Pt(NH_3)_2Cl(H_2O)]^+$ formed during
the early stages of hydrolysis. Also, drift in the pH
readings, base-induced hydrolysis and inaccurate values of
the total platinum concentration found by analysis introduced
additional error.

It is interesting to note that the markedly different
slopes in Figure 6 for zero ionic strength and 0.318 ionic
strength correspond to nearly the same value of k_1 as is
indicated in Table 2. Thus all of the ionic strength in-
fluence on K_1' is reflected in k_{-1}. The implications of this
feature on the mechanism of hydrolysis are discussed in
Chapter V.

Figure 7 shows the temperature dependence of k_1 and k_{-1}
graphically. The enthalpy of activation, $\Delta H^{\ddagger}$, was cal-
culated to be 19.6 kcal./mole for k_1 and 13 kcal./mole for
k_{-1}. The entropy of activation, $\Delta S^{\ddagger}$, was -11 e.u. for k_1
and -19 e.u. for k_{-1}.

C. Exchange of Chloride with <u>Trans</u>-dichlorodiammine-
platinum(II) and <u>Trans</u>-chloroaquodiammineplatinum(II)

The experimental procedures and mathematical treatment of
the kinetics of exchange reactions were discussed in Chapters
II and III. In each exchange experiment the total fraction of

Figure 7. Temperature dependence of the acid hydrolysis rate constants, k_1 and k_{-1}, for <u>trans</u>-$[Pt(NH_3)_2Cl_2]$. $\Delta H^{\ddagger} = 19.6$ kcal./mole for k_1 and 13 kcal./mole for k_{-1}. $\Delta S^{\ddagger} = -11$ e.u. for k_1 and -19 e.u. for k_{-1}
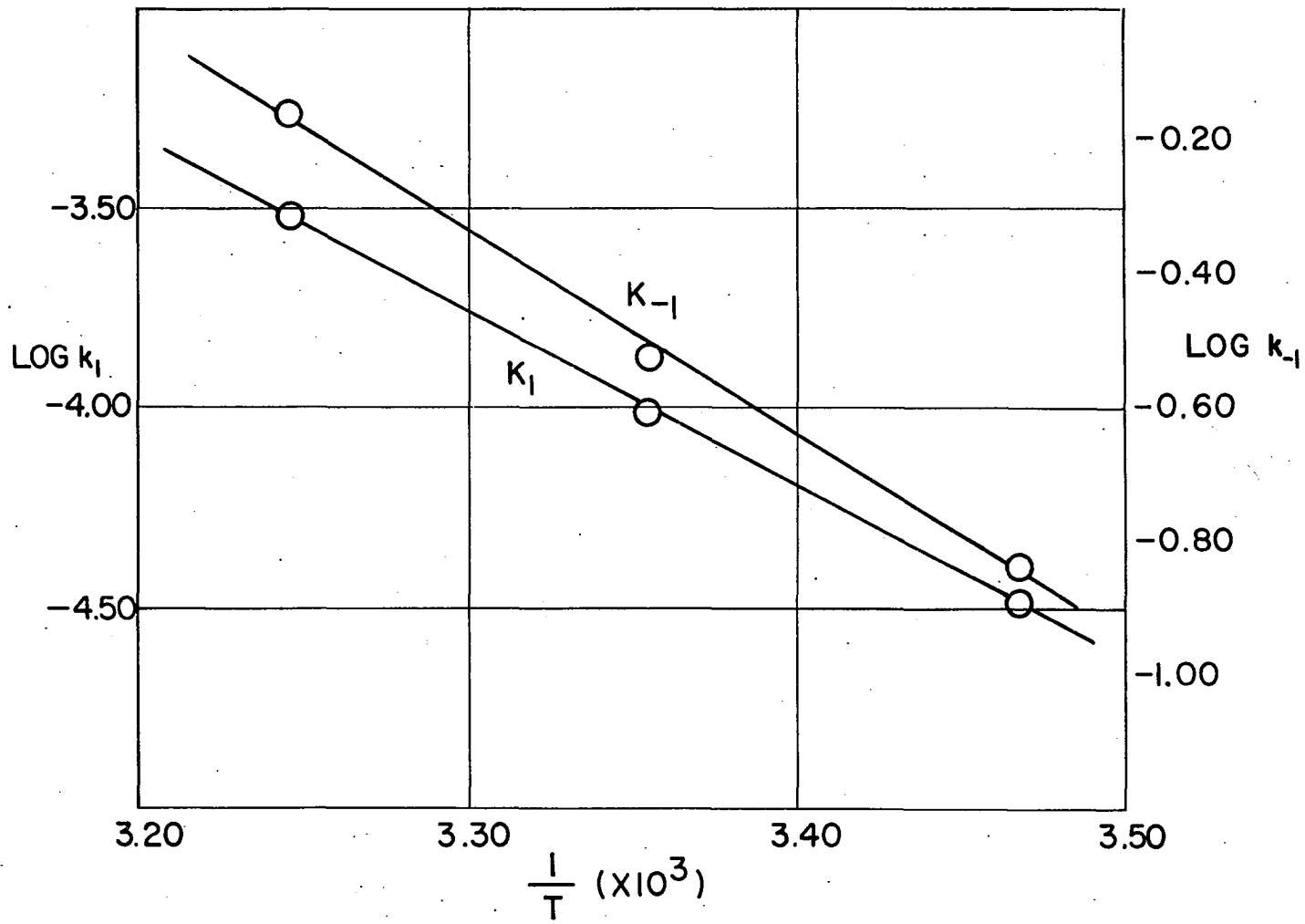
exchange, F_{u+v}, was measured since both trans-[Pt(NH$_3$)$_2$Cl$_2$] and [Pt(NH$_3$)$_2$Cl(H$_2$O)]$^+$ came through the ion exchange column. A typical exchange plot of ln(1-F_{u+v}) versus time is shown in Figure 4. Normally, these plots appeared linear over a period of at least twice the times of half-exchange. The rates of exchange were calculated from the observed times of half-exchange using Equation III.27, which was derived under the assumption that the amount of [Pt(NH$_3$)$_2$Cl(H$_2$O)]$^+$ present was very small so that the exchange system was a "two component" system. This assumption is valid at all chloride concentrations above 0.01 N. because the amount of mono-aquo compound present at equilibrium is negligible under these conditions. The conditions and the results of the exchange experiments at 15°, 25° and 35° C. are tabulated in Table 3.

Exchange of chloride with the two platinum species present must take place through the acid hydrolysis reactions. In addition to acid hydrolysis, exchange might also take place through some other pathway such as a direct chloride exchange which may or may not be chloride dependent.

It was observed that the times of half-exchange initially increased with increasing chloride concentration, then reached a maximum at about 0.01 N. KCl and then decreased as the chloride concentration increased further. This strongly suggested that a second process, such as direct chloride exchange, was competing with the hydrolysis reaction

Table 3. Exchange of the chloride ligands of <u>trans</u>-$[Pt(NH_3)_2Cl_2]$

Temp. ($^\circ$C.)	Initial $[Pt(NH_3)_2Cl_2]$ "a" (M. x 10^4)	Initial added $[Cl^-]$[a] "b" (M.)	Equilibrium $[Pt(NH_3)_2(H_2O)Cl^+]$ "T_∞" (M. x 10^6)	Time of half-exchange (min.)	Rate of exchange[b] R (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.

[a]Ionic strength was adjusted to $\mu = 0.318$ by addition of Na_2SO_4.

[b]R calculated with assumption that R" = 0 and that x $\ll$ a.

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in the total observed exchange. The quantity R/a (recall R is the total rate of exchange and a is the initial trans-compound concentration), calculated from Equation III.27 for each of the experiments, was then plotted as a function of chloride ion concentration for 15°, 25° and 35° C. These graphs are shown in Figure 8. For all of the experiments with $[Cl^-] > 0.003$ M. the points for each temperature fell closely along straight lines. The straight lines all had finite positive slopes. This, then was graphic evidence for the existence of direct exchange by a chloride dependent process. The straight lines extrapolated back to zero chloride concentration gave values of the ordinate which agreed quite closely with the values of k_1 determined by the potentiometric titration method. Thus, the values of k_1, the first acid hydrolysis rate constant, and k' the direct exchange rate constant, were determined from the intercept and slope of the straight line function. The values of k_1 and k' obtained from the exchange plots are given in Table 4 along with the values of k_1 obtained by titration procedures. The fact that k_1, obtained from the exchange plot intercept, and k_1, obtained by titration, agreed quite well with each other indicated that $(R'' + R_2)$ was not very large in the linear portion of the curve. The reasoning behind this conclusion was discussed in Chapter III, page 47.

So, for all chloride concentrations greater than

Figure 8. Plots of R/a versus chloride concentration at
15°, 25° and 35° C. for the chloride exchange
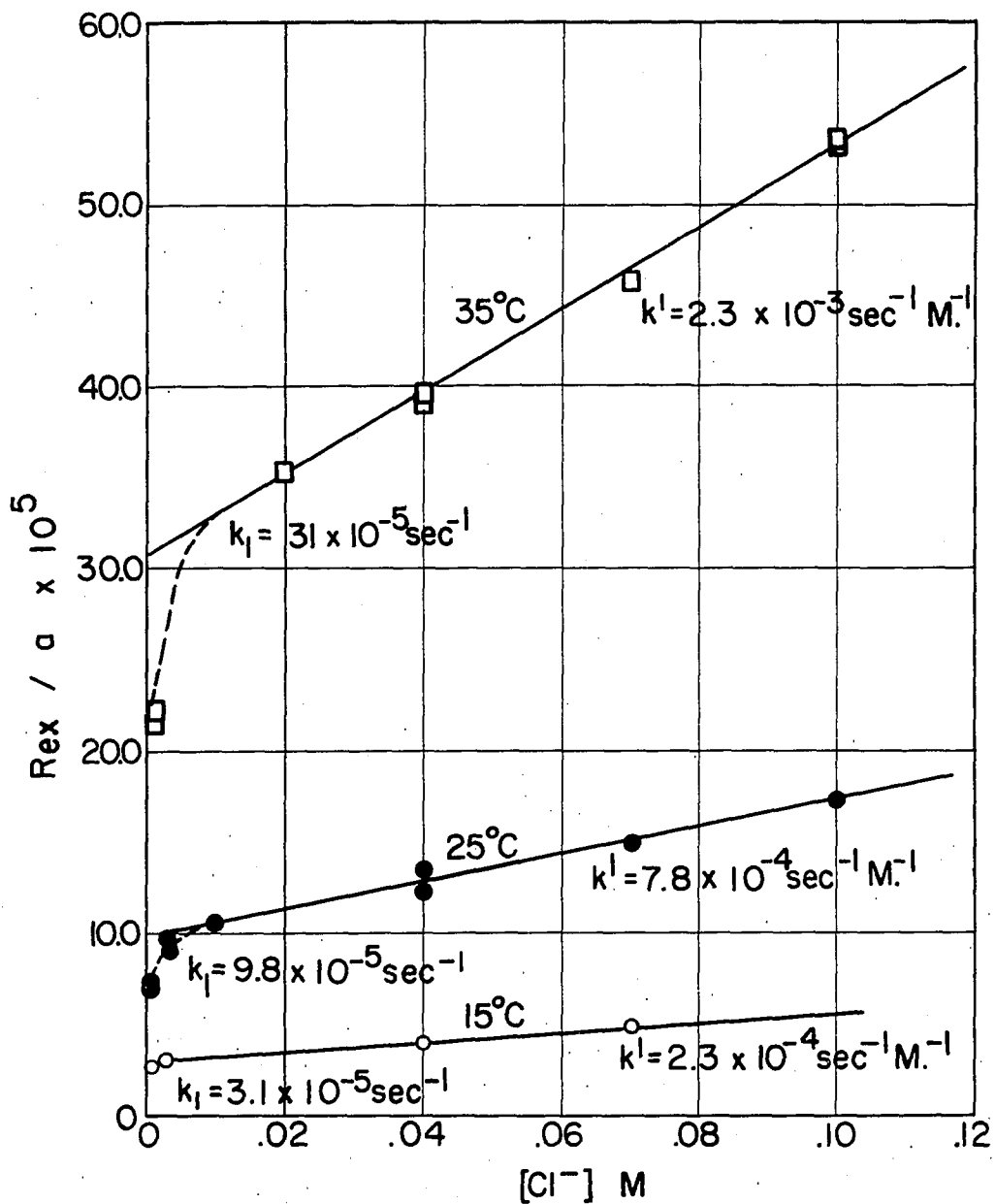of trans-[Pt(NH$_3$)$_2$Cl$_2$]. Ionic strength = 0.318

Table 4. Comparison of first hydrolysis rate constants from
exchange data and titration data and values of
direct chloride exchange rate constant at 15°, 25°
and 35° C. for _trans_-[Pt(NH$_3$)$_2$Cl$_2$]. (μ = 0.318)

| Temp. (°C.)	k_1 (x10^5 sec.$^{-1}$) by exchange	k_1 (x10^5 sec.$^{-1}$) by titration	k' (x10^4 M.$^{-1}$ sec.$^{-1}$)
15.0	3.1	3.2	2.3
25.0	9.8	8.9	7.8
35.0	31.0	28.0	23.0

0.003 M., the expression for the total rate of exchange was:

$$R = R_1 + R' = k_1[\underline{t}\text{-Pt(NH}_3)_2\text{Cl}_2] + k'[\underline{t}\text{-Pt(NH}_3)_2\text{Cl}_2][\text{Cl}^-] \qquad (IV.2)$$

Because of the smaller experimental error, it is pro-
posed that the values of k_1 obtained from the isotopic ex-
change data are more accurate than those found by titration.
The temperature dependence of k' is shown graphically in
Figure 9. The enthalpy of activation for k', $\Delta H^{\ddagger}$, was
calculated to be 19.6 kcal./mole and the entropy of activation,
$\Delta S^{\ddagger}$, was -7 e.u.

The _trans_-[Pt(NH$_3$)$_2$Cl$_2$] complex and the [Pt(NH$_3$)$_3$Cl]$^+$
complex are the only members of the series of chloroammine
platinum(II) complexes which have a measurable, second order,
direct chloride exchange process in addition to the expected
acid hydrolysis. The possible reasons for this are dis-
cussed in Chapter V. For the _trans_-[Pt(NH$_3$)$_2$Cl$_2$] complex,
the two processes, _i.e._, acid hydrolysis and direct exchange,

Figure 9. Temperature dependence of the direct chloride exchange rate constant, k', for trans-[Pt(NH$_3$)$_2$Cl$_2$]. $\Delta H^{\ddagger}$ = 19.6 kcal./mole, $\Delta S^{\ddagger}$ = -7 e.u.
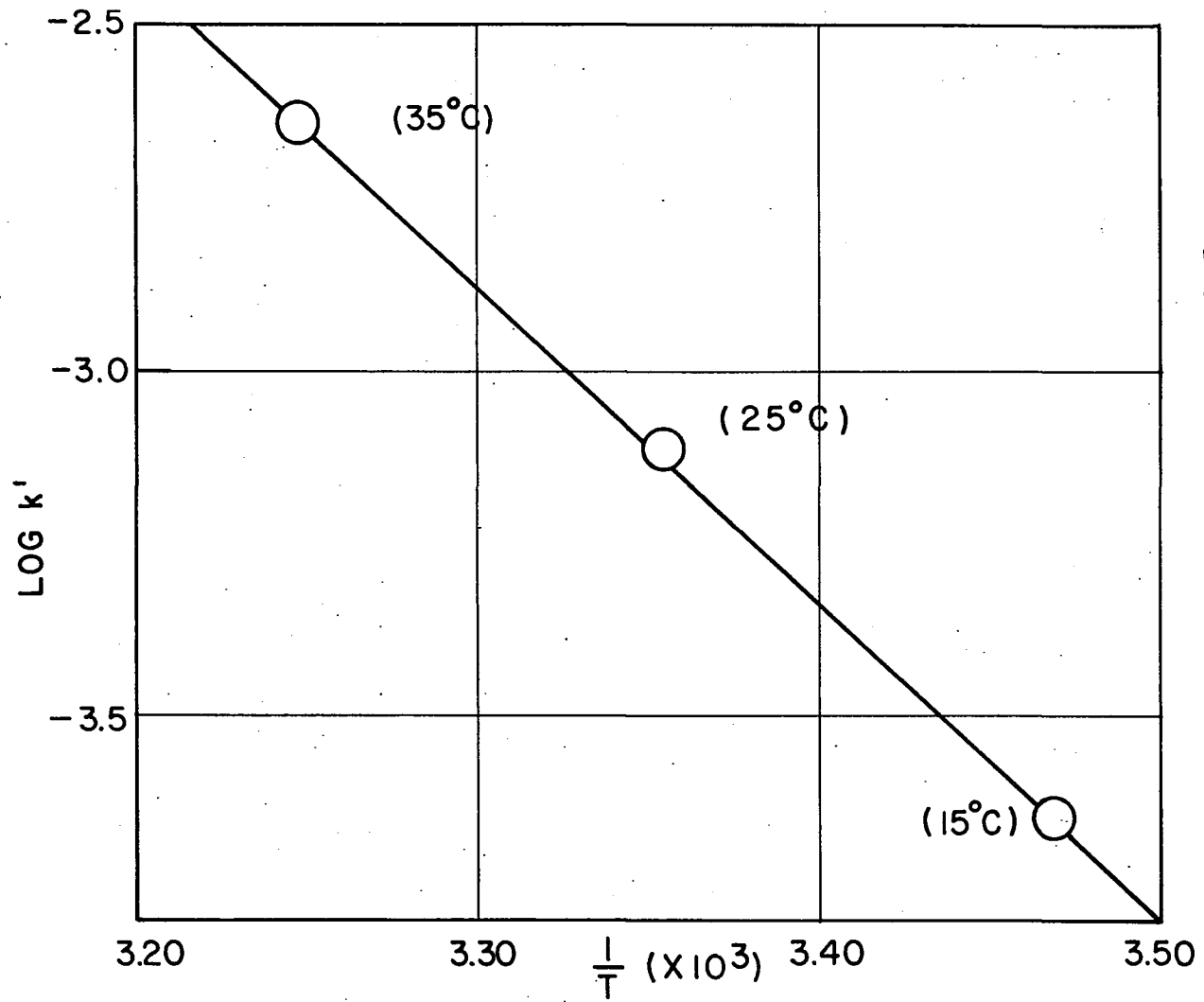
contribute about equally to the total exchange at $[Cl^-] =$ 0.1 M.

At very low chloride concentrations ($<$ 0.003 M.) the points in Figure 8 deviate quite severely from the straight line function. This is due to the fact that the assumption that $[Pt(NH_3)_2Cl_2] \gg [Pt(NH_3)_2Cl(H_2O)]^+$ is no longer valid at low chloride concentrations and therefore Equation III.27 does not hold in this region. The amount of direct chloride exchange becomes negligible at low chloride concentrations, however, exchange with the $[Pt(NH_3)_2Cl(H_2O)]^+$ species must be taken into account. The mathematical treatment of the exchange kinetics of "three component" systems is discussed in Chapter III-C. The values of γ, defined by

$$\gamma = R'/R_1 = k'(a-x)(b+x)/k_1(a-x) \qquad\qquad (IV.3)$$

and used in the calculation of a time of half-exchange, were fixed by the known parameters a, b, K_1' (to obtain x), k_1 and k' (obtained from high chloride exchange). By adjusting $\beta = (R'' + R_2)/R_1$ until the calculated time of half-exchange agreed to within 10% of the observed value, the best value of β explaining the observed exchange was found for 15°, 25° and 35° C. The times of half-exchange were also calculated assuming that $\beta = 0$, i.e., no exchange with the $[Pt(NH_3)_2Cl(H_2O)]^+$ species takes place. The results of these calculations are given in Table 5.

It is apparent that times of half-exchange calculated

Table 5. Chloride exchange experiments for $\underline{\text{trans}}$-$[Pt(NH_3)_2Cl_2]$ at low chloride concentrations (added KCl = 0.001 M., μ = 0.318 M.)

Temp. °C.	Initial $[Pt(NH_3)_2Cl_2]$ "a" M. x 10^4	Equilibrium $[Pt(NH_3)_2Cl(H_2O)^+]$ "T" M. x 10^4	Time of Half-exchange hrs. obsd.	Calc. for $(R''+R_2)/R_1=0$	Indicated $(R''+R_2)/R_1$
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

for $(R'' + R_2)/R_1 = 0$ did not differ greatly from the observed quantities. Therefore $(R'' + R_2)$ was not large and was not indicated accurately by these experiments. It was impossible to separate the acid hydrolysis rate (R_2) and the direct exchange rate (R'') whereas these were easily separated for $R = R_1 + R'$. From the value of $(R'' + R_2)/R_1$ which will account for the observed time of half-exchange, an upper limit of $0.5\ k_1$ can be set for a first order rate constant k_2.

V. DISCUSSION

The rate constants for the reversible acid hydrolysis of trans-[Pt(NH$_3$)$_2$Cl$_2$] are shown in Table 2, Chapter IV. The value found for k$_1$, the initial hydrolysis rate constant, was almost three times larger than the value which Banerjea et al. (25) reported for the isotopic chloride exchange rate constant. However, the first order rate constants which they found for substitution reactions of the trans-salt with glycine, analine, pyridine and hydroxide were all approximately equal to the value of k$_1$ found in this work. It therefore appears likely that the first order dependence of these substitutions can be attributed to a rate-determining acid hydrolysis followed by a rapid replacement of H$_2$O by the substituting group or neutralization in the case of OH$^-$. Grinberg (33) has also proposed this process to account for hydroxide substitution rates evaluated in his laboratory. However, preliminary experiments in this laboratory have indicated that a process which is first order in hydroxide occurs also. It appears possible in view of the measurable direct chloride exchange, that a process first order in hydroxide may also contribute to this reaction.

As is shown in Table 2, the rate constant, k$_1$, is substantially independent of ionic strength, whereas the rate constant for the reverse reaction, k$_{-1}$, is strongly affected. Indeed, an ionic strength of 0.318 increases the equilibrium

quotient, K_1', which is given by k_1/k_{-1}, to about four times K_1, the equilibrium quotient at zero ionic strength. Since the reverse of acid hydrolysis involves a reaction between two ions whereas the acid hydrolysis reaction takes place between two neutral molecules, this ionic strength effect is not surprising. The Debye-Huckel Theory leads to the prediction that the rate of a reaction between ions of charge Z_A and Z_B should vary with the ionic strength, μ, of a solution as shown in the following equation (46, p. 102):

$$\log k_\mu = \log k_o + 2AZ_AZ_B \sqrt{\mu} \qquad (V.1)$$

where k_μ and k_o are the rate constants at ionic strengths μ and 0, and A is a constant which depends on the solvent.

This ionic strength feature argues against a simple "dissociative" mechanism such as that suggested by Basolo and Pearson (26, pp. 188-189) which is discussed on page 10, Chapter I. It also supports the hypothesis that the transition state for the hydrolysis has zero charge. A possible mechanism, which is an adaptation of the mechanism discussed on page 9, Chapter I, is shown in Figure 10.

In this mechanism the initial coordination figure is a distorted octahedral arrangement in which the complex with its four square planar ligands forms weaker bonds to solvent molecules along the normal to the plane. These solvent ligands are quite labile and can undergo substitution reactions by other potential ligands in solution such as ionic chloride

Figure 10. Mechanism for the acid hydrolysis and direct chloride exchange reactions for trans-[Pt(NH$_3$)$_2$Cl$_2$] .
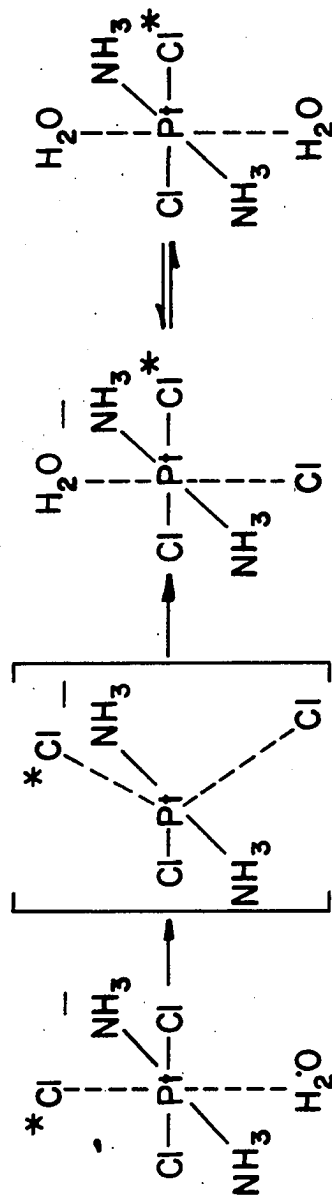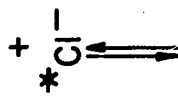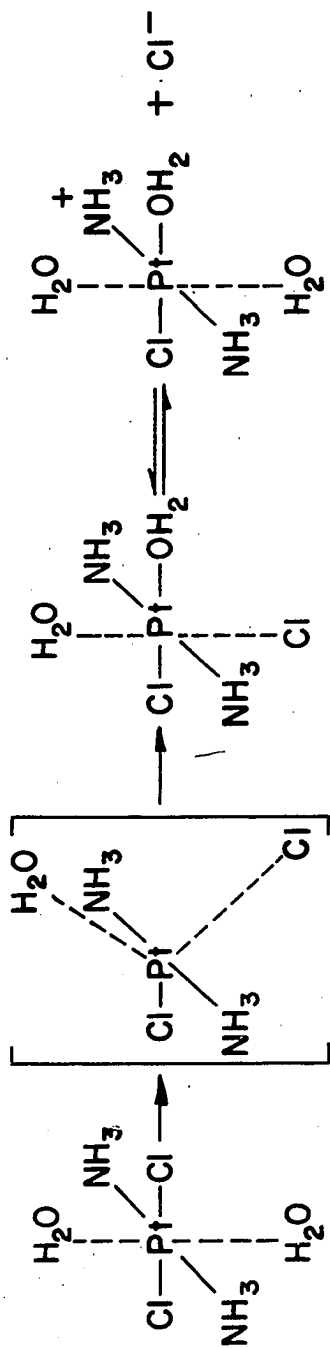
with rapidly established equilibria. The transition state
is formed when one of these axial H_2O groups moves in, dis-
placing the chloride, to yield approximately a trigonal
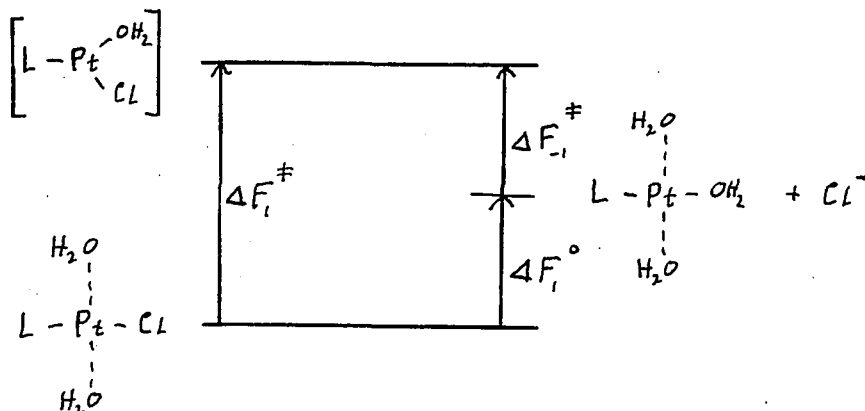bipyramid arrangement. If the ligand <u>trans</u> to the group being
replaced by H_2O is capable of forming π-bonds in which
platinum donates the electrons, then the transition state is
stabilized as was discussed on page 8, Chapter I. The
availability of the five orbitals ($5d_{x^2-y^2}$, 6s and $6p_{x,y,z}$) to
form bonds also adds favor to this transition state. The
transition state then collapses to the tetragonal configura-
tion with a H_2O group in the square and a chloride in a
labile axial position. This chloride is rapidly replaced by
H_2O, which is present in large excess, to form the products.
This same mechanism also seems quite feasible to explain the
direct chloride exchange process, also shown in Figure 10.

The remainder of this chapter is devoted to comparisons
of acid hydrolysis and chloride exchange reactions for the
series of chloroammineplatinum(II) complexes. It may be in-
structive for consideration of reactions of the following type:

$$
L - \underset{\substack{H_2O \\ | \\ H_2O}}{Pt} - Cl \xrightarrow{\Delta F_1^{\ddagger}} \left[L - Pt \overset{OH_2}{\underset{Cl}{\diagdown}} \right]^{\ddagger} \xrightarrow{-\Delta F_{-1}^{\ddagger}} L - \underset{\substack{H_2O \\ | \\ H_2O}}{Pt} - OH_2 \qquad (V.2)
$$

$$\Delta F_1^{\circ}$$
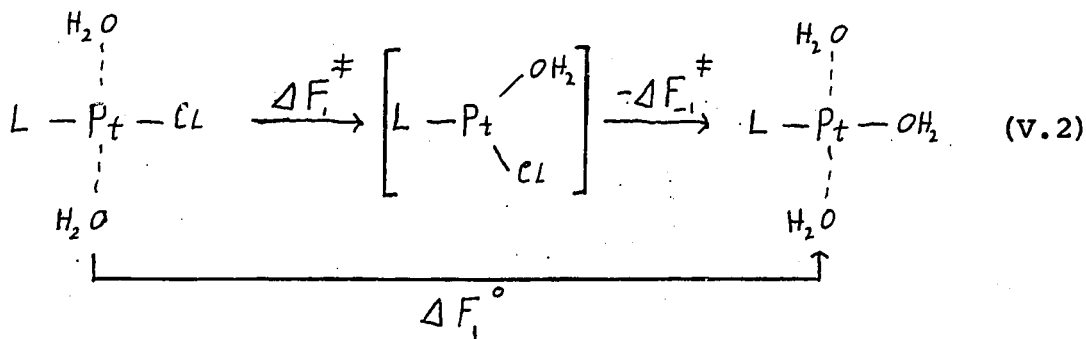
where L = NH₃ or Cl and the groups in the square <u>cis</u> to the

substated groups have been omitted for clarity,

to consider the following free energy diagram:

$$\left[L - Pt \underset{\diagdown Cl}{\overset{\diagup OH_2}{}} \right]$$

$$\Delta F_{-1}^{\ddagger} \quad H_2O$$

$$\Delta F_1^{\ddagger} \qquad \qquad L - Pt - OH_2 \quad + \quad Cl^-$$

$$\Delta F_1^{\circ} \quad H_2O$$

$$H_2O$$

$$L - Pt - Cl$$

$$H_2O$$

where $\Delta F_1^{\ddagger}$ = free energy of activation for acid hydrolysis

$\Delta F_{-1}^{\ddagger}$ = free energy of activation for reverse acid

   hydrolysis

ΔF_1° = standard free energy change for acid hydrolysis.

The equilibrium quotients for acid hydrolysis and the

rate constants for acid hydrolysis and direct chloride ex-

change for the entire series of the chloroammine complexes of

platinum(II) are shown in Table 6. The values in parentheses

are for zero ionic strength, all the others being for 0.318

ionic strength.

In order to make a rational comparison of the equilibrium

quotients and rate constants for the first acid hydrolysis,

each should be divided by a statistical factor n, the number

of equivalent chloride ligands in the complex. A plot of log

K_1'/n versus the complex species in order of increasing charge

Table 6. Acid hydrolysis equilibrium constants, first aquation rate constants, and direct chloride exchange rate constants for the chloroammine-platinum(II) complex series at 25.0° C.[a]

	$[PtCl_4]^=$ [b]	$[Pt(NH_3)Cl_3]^-$ [c]	c-$[Pt(NH_3)_2Cl_2]$ [d]	$t[Pt(NH_3)_2Cl_2]$	$[Pt(NH_3)_3Cl]^+$ [e]	
K_1'	1500 (3000)	c - 1400 t - $<$200	330 (84) [f]	32 (8.2)	27 (8.4)	M.
K_1'/n	375 (750)	c - 700	165 (42) [f]	16 (4.1)	27 (8.4)	M.
K_2'	50 (100)	4	40	$<$2	–	M.
k_1	3.9	c - 3.6 t - 2.3	3.3	9.8	2.6 sec.$^{-1}$	
k_1/n	.98	c - 1.8	1.6	4.9	2.6 sec.$^{-1}$	
k_{Cl}	$<$3	$<$ 3	~3	78	7 M.$^{-1}$sec.$^{-1}$	

[a]All values listed have been multiplied by 10^5. Values listed in parentheses are for zero ionic strength, all others are for ionic strength 0.318. Values listed without additional values for zero ionic strength are the same at both zero and 0.318 ionic strength.

[b](2,5).

[c](3,4).

[d](6).

[e]Aprile, F. and D. S. Martin, Ames, Iowa. Acid hydrolysis and chloride exchange of $[Pt(NH_3)_3Cl]$. Private communication. 1961.

[f]Estimated values.

is shown in Figure 11. In this plot a line of negative slope has been drawn through points for cis-[Pt(NH$_3$)$_2$Cl$_2$] and [Pt(NH$_3$)$_3$Cl]$^+$. The slope of this line can be explained by considering the coulombic interaction between the chloride and the complex. The acid hydrolysis involves separating a negative species, Cl$^-$, from the complex and one would expect this process to become easier, giving a larger value of K_1'/n, as the charge on the complex becomes more negative. For these two complexes the chloride replaced must be trans to an NH$_3$.

Another line drawn through the points for PtCl$_4^=$ and trans-[Pt(NH$_3$)$_2$Cl$_2$], for which the replaced Cl$^-$ is trans to a Cl$^-$, lies approximately parallel to the first line. Values of K_1'/n in this line are roughly a factor of 10 below the first line. This indicates that ΔF_1^o is less positive for NH$_3$-Pt-Cl $\longrightarrow$ NH$_3$-Pt-OH$_2$ than for Cl-Pt-Cl $\longrightarrow$ Cl-Pt-OH$_2$. If π-bonding was contributing significantly to the stability of the Pt-Cl bond, then a Cl$^-$ trans to a Cl$^-$ is expected to destabilize the system since the two π-bonds must compete for the same platinum d orbital. Instead, the opposite effect is observed. Therefore, it appears likely that π-bonding is not significant in this system.

The [Pt(NH$_3$)Cl$_3$]$^-$ complex was purposely omitted from the above discussion as it requires special consideration. The acid hydrolysis reactions for this complex were studied by Elleman et al. (3, 4). Their assignment of the acid hydroly-

Figure 11. Plot of log K_1'/n for the entire series of
            chloroammineplatinum(II) complexes comparing
            the acid hydrolysis equilibria
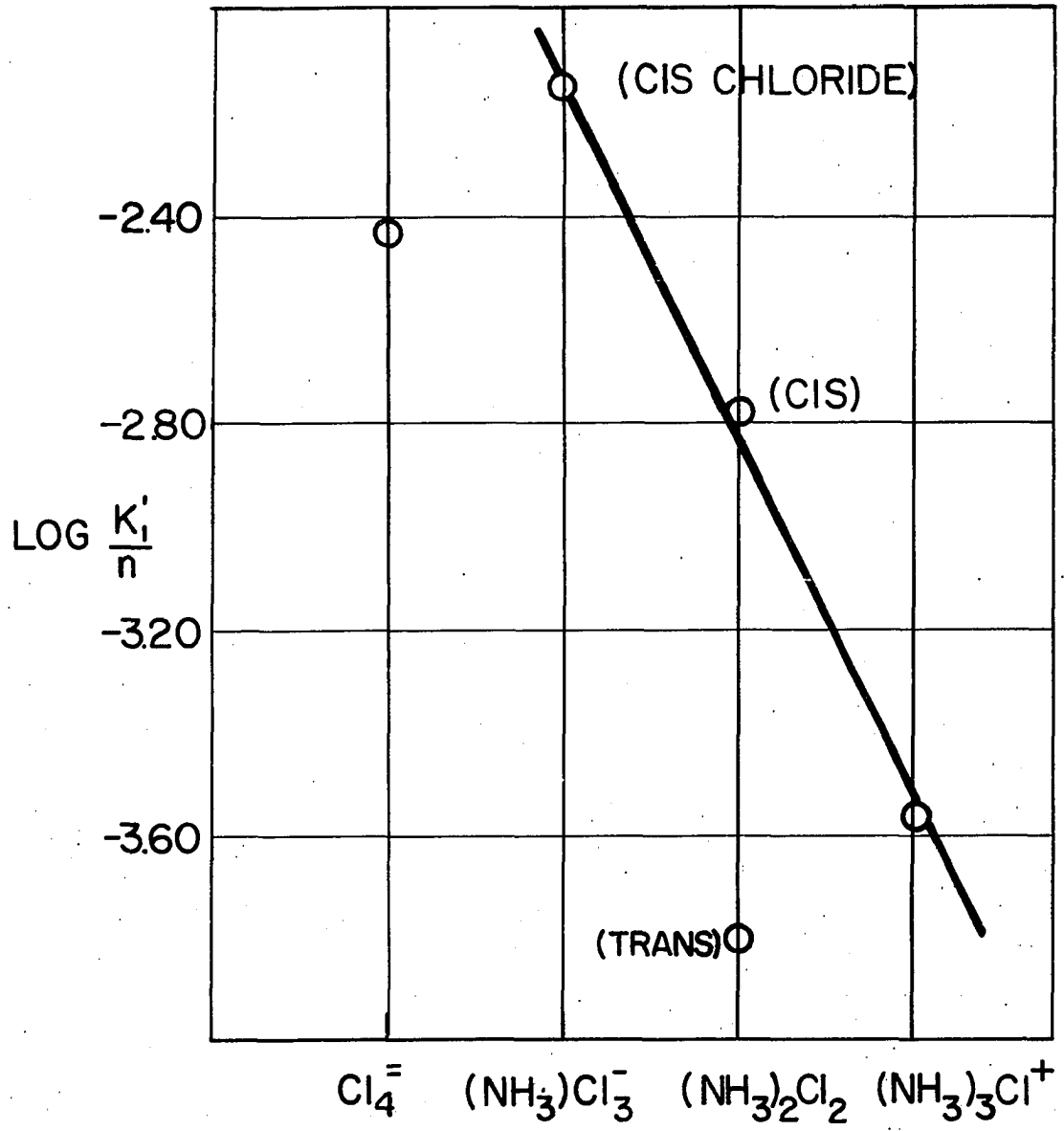
sis predominantly to the chloride <u>cis</u> to an ammonia ligand was made from tracer studies of substitution reactions which could possibly be subject to misinterpretation, especially if significant amounts of both <u>cis</u>- and <u>trans</u>-$[Pt(NH_3)Cl_2(H_2O)]$ were present. If this assignment were reversed to indicate hydrolysis of the <u>trans</u>-chloride, then the value of log K_1'/n measured for this complex would fit nicely with the curve for the replacement of <u>trans</u>-chloride. From Table 6 it can be seen that K_2', the second acid hydrolysis equilibrium quotient, is very low for the $[Pt(NH_3)Cl_3]^-$ complex and out of line with the values found for $PtCl_4^=$ and <u>cis</u>-$[Pt(NH_3)_2Cl_2]$. If hydrolysis of the <u>trans</u>-chloride is assumed, then the second hydrolysis involves the reaction $Cl-Pt-Cl \longrightarrow Cl-Pt-OH_2$. Thus, the low value of K_2' would be in agreement with the previously discussed stability of $Cl-Pt-Cl$, compared to $NH_3-Pt-Cl$.

The effect of increasing ionic strength on the equilibrium quotient for $PtCl_4^=$ is to cause a significant decrease. The equilibrium quotient for $[Pt(NH_3)Cl_3]^-$ remains unchanged with increasing ionic strength and the value for $[Pt(NH_3)_3Cl]^+$ increases considerably. The equilibrium quotient for <u>cis</u>-$[Pt(NH_3)_2Cl_2]$ was not measured at varying ionic strength. These observations are expected since, from Equation V.1, the product $z_A z_B$ will be positive, zero and negative for the reverse acid hydrolyses of $PtCl_4^=$, $[Pt(NH_3)Cl_3]^-$, and $[Pt(NH_3)_3Cl]^+$ respectively. Thus an increase in μ will increase k_{-1} for $PtCl_4^=$, cause no change in k_{-1} for $[Pt(NH_3)Cl_3]^-$ and decrease k_{-1} for $[Pt(NH_3)_3Cl]^+$. Therefore,

since k_1 is essentially independent of ionic strength for all of these complexes, the equilibrium quotients, given by $K_1' = k_1/k_{-1}$, are expected to vary inversely with k_{-1}.

The enthalpies and entropies of activation for the acid hydrolysis and direct chloride exchange reactions together with the standard free energy change of hydrolysis are given in Table 7.

Table 7. Enthalpies, entropies and standard free energy change of acid hydrolysis for hydrolysis and direct chloride exchange reactions of the chloroammine-platinum(II) complexes

Complex	K_1'	k_1		k_{-1}		k'	
$\mu = 0.318$	ΔF° kcal.	$\Delta H^{\ddagger}$ kcal.	$\Delta S^{\ddagger}$ eu.	$\Delta H^{\ddagger}$ kcal.	$\Delta S^{\ddagger}$ eu.	$\Delta H^{\ddagger}$ kcal.	$\Delta S^{\ddagger}$ eu.
$[PtCl_4]^=$	2.48	21	-8	15	-18	$-$	$-$
$[Pt(NH_3)Cl_3]^-$	2.52	19	-15	17	-14	$-$	$-$
$\underline{c}$-$[Pt(NH_3)_2Cl_2]$	3.38	19.5	-14	17	-14	$-$	$-$
$\underline{t}$-$[Pt(NH_3)_2Cl_2]$	4.78	19.5	-11	13	-19	19.5	-7
$[Pt(NH_3)_3Cl]^+$	4.86	18	-18	19	-4	29	19

The most striking feature in these quantities is the similarity in $\Delta H^{\ddagger}$ for k_1, all of the values being within 2 kcal. of 19 kcal./mole. This remarkable similarity in the hydrolysis rate constants despite the wide variation in the charge of the complex is also revealed in a plot of log k_1/n which appears in Figure 12. Furthermore, it can be seen from

Figure 12. Plot of log k_1/n for the entire series of chloroammineplatinum(II) complexes comparing the acid hydrolysis rates
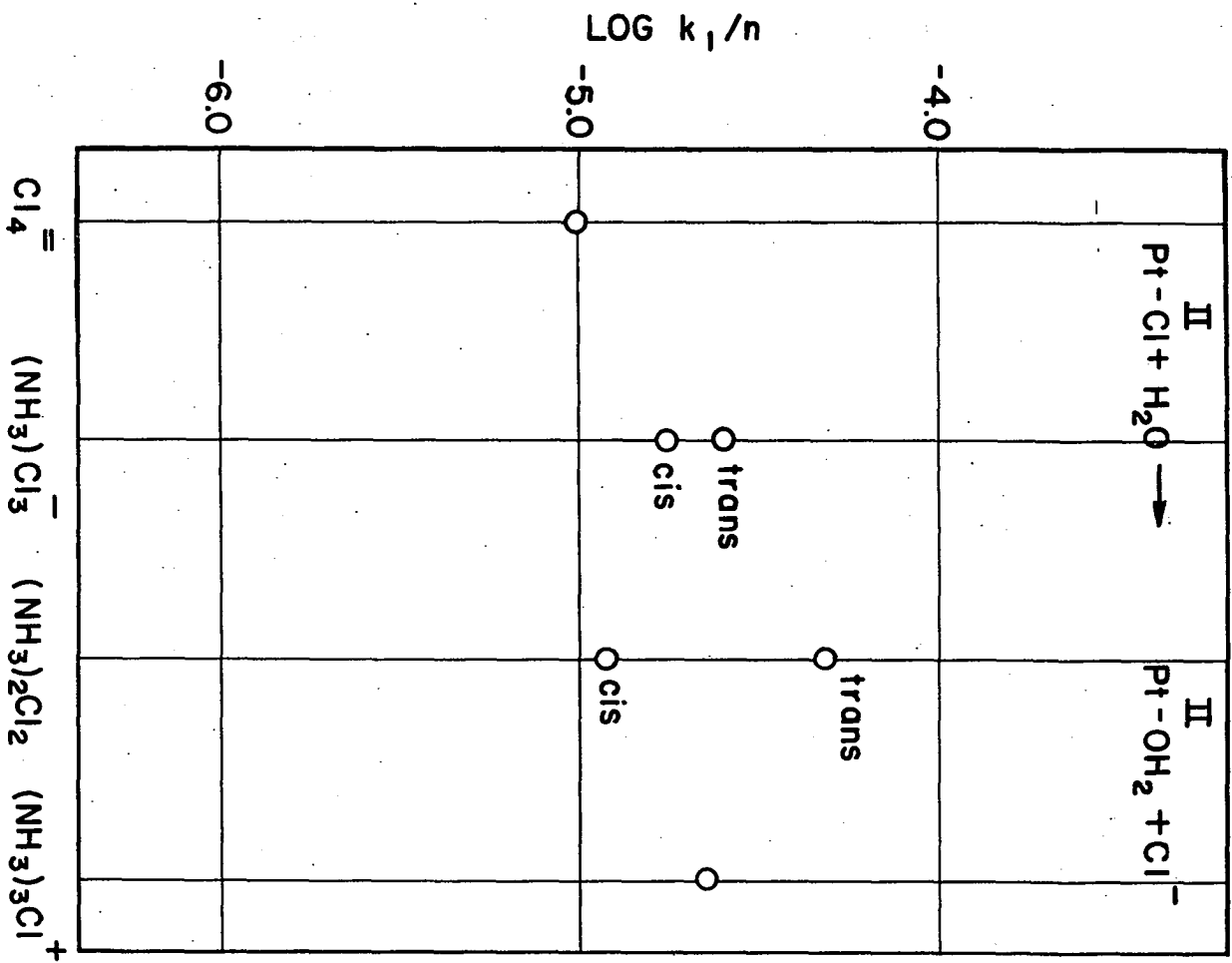
Table 6 that k_1 for each complex remains unchanged despite large changes in the ionic strength of the solution. These observations could not be explained by a "dissociation" mechanism to yield a coordination number of three for the transition state, as such a process is expected to show large ionic strength effects and probably would exhibit widely different rate constants. These facts are consistent, however, with the mechanism shown in Figure 10 in which the trigonal bipyramid transition state is formed by a similar intra-molecular rearrangement for each of the complexes with little dependence upon ionic charge.

A wide variation in $\Delta S^{\ddagger}$ for both k_1 and k_{-1} is observed, as shown in Table 7. However, this is not too surprising since the 2 kcal. variation in $\Delta H^{\ddagger}$ is equivalent to an entropy effect of $\pm$ 6 e.u. The values of $\Delta H^{\ddagger}$ can scarcely be determined with greater accuracy. Therefore, it is rather difficult to speculate any significant trend in the values of $\Delta S^{\ddagger}$. One would expect the largest change in $\Delta S^{\ddagger}$ for k_{-1} from complex to complex since this reaction involves ionic species uniting to form a transition state with a different charge from the original complex. Except for the trans-[Pt(NH$_3$)$_2$Cl$_2$] complex, a trend is observed towards more negative values of $\Delta S^{\ddagger}_{k_{-1}}$ as the complex charge becomes more negative.

The values of $\Delta F^{\ddagger}_1$ for acid hydrolysis are relatively independent of the complex. The acid hydrolysis rate for

trans-[Pt(NH$_3$)$_2$Cl$_2$] is the fastest, but only by a factor of four over the slowest rate. This reactivity possibly reflects the absence of a permanent dipole in the complex reactant.

The effectiveness of the trans-effect in NH$_3$ substitution by Cl for the preparation of cis-[Pt(NH$_3$)$_2$Cl$_2$] is surprising in view of the lability of both the cis- and trans-chlorides toward acid hydrolysis. A factor of only five in the rate constants might account for the high yield of cis-compound since any trans-[Pt(NH$_3$)$_2$Cl$_2$] formed would react much faster with NH$_3$ and be removed from the products.

The values of log k_{-1} are plotted in Figure 13. This plot reveals two sets of points with larger values of k_{-1} as the complex charge becomes more positive. This general trend is consistent with the coulombic attraction of chloride to the complex. The set containing [PtCl$_4$]$^=$ and trans-[Pt(NH$_3$)$_2$Cl$_2$] lies above the set of points containing cis-[Pt(NH$_3$)$_2$Cl$_2$] and [Pt(NH$_3$)$_3$Cl]$^+$. Again if the assignment of cis- and trans- chlorides for [Pt(NH$_3$)Cl$_3$] were reversed, then the members of the top series would be characterized by having the H$_2$O group trans to a chloride, whereas each complex in the lower sequence would have H$_2$O trans to an NH$_3$ ligand. Thus, Figure 13 indicates that $\Delta F^{\ddagger}_{-1}$ is lower if the H$_2$O being replaced is trans to Cl, in agreement with the classical trans-effect.

The chloride dependent exchange reaction found for

Figure 13. Plot of log k_{-1} for the entire series of chloroammineplatinum(II) complexes comparing the reverse hydrolysis rates
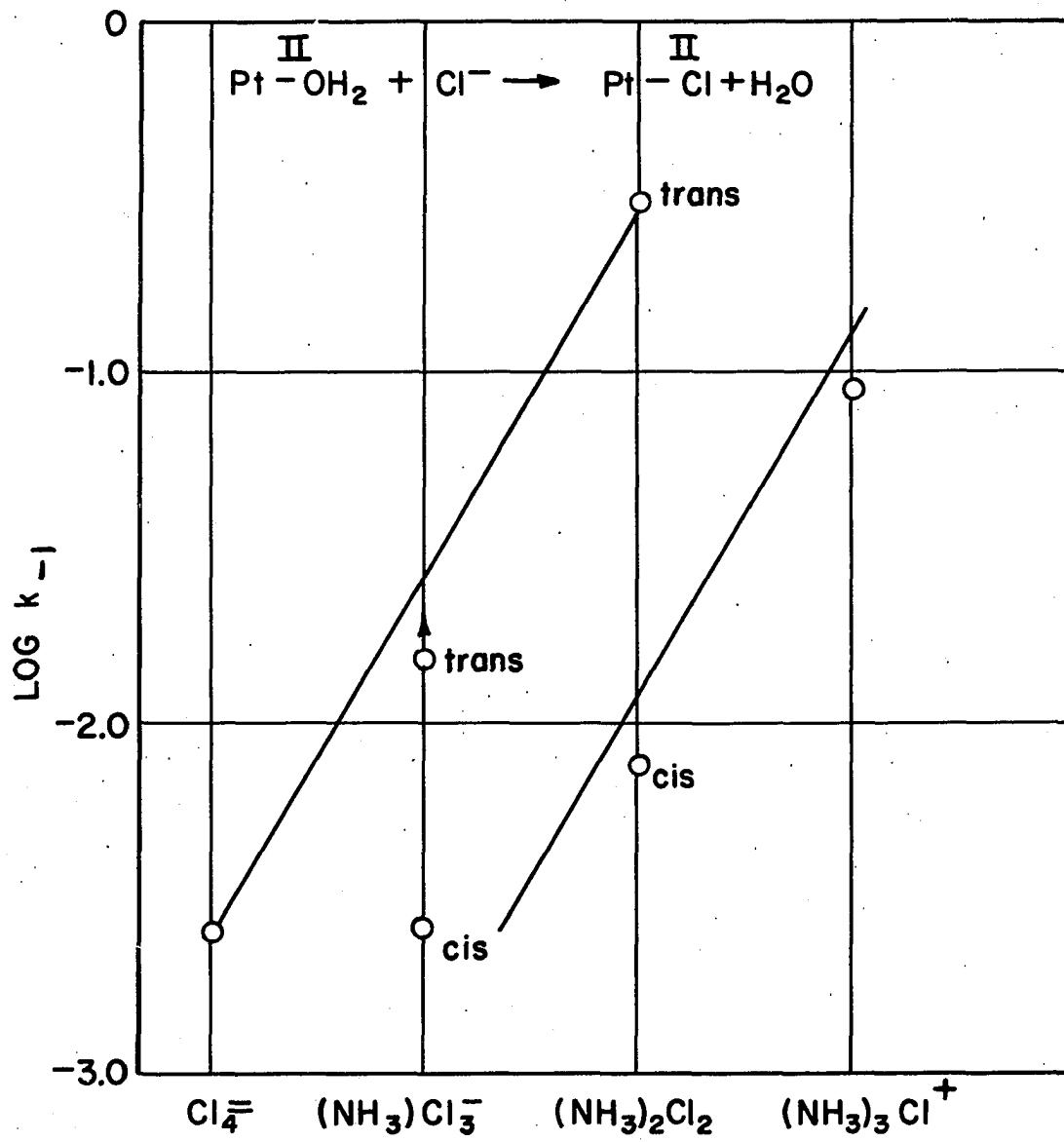
trans-[Pt(NH$_3$)$_2$Cl$_2$] and [Pt(NH$_3$)$_3$Cl]$^+$ is the only such measurable process found with any of the chloroammine complexes of platinum(II). Examples of chloride competing with the solvent, which is present in large excess, for displacing a chloride are quite rare. Such a process has been found, however, in the exchange of Cl$^-$ with the square planar [AuCl$_4$]$^-$ (47). It appears likely that the replacement of chloride ligands by ionic chloride is enhanced as the ionic charge on the complex becomes more positive. This, again, is consistent with the coulombic attraction between chloride and the complex. The rate constant, k', for trans-[Pt(NH$_3$)$_2$Cl$_2$] must be at least 25 times that for cis-[Pt(NH$_3$)$_2$Cl$_2$] which was too small to be measured in the presence of the acid hydrolysis. This indicates that $\Delta F'^{\ddagger}$, the free energy of activation for direct chloride exchange, is less positive when the transition state involves three chlorides in the trigonal plane, i.e.,

$$\left[Cl - Pt \underset{Cl}{\overset{Cl}{<}} \right]$$
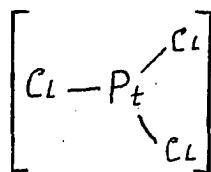
Indeed, the lability of the chloride in the trans-[Pt(NH$_3$)$_2$Cl$_2$] complex is quite exceptional.

VI. SUMMARY

The equilibrium and kinetics of acid hydrolysis for trans-[Pt(NH$_3$)$_2$Cl$_2$] were measured. The equilibrium quotient at high ionic strength, K_1', for this reaction was determined to be 2.2, 3.2, and 4.4 x 10^{-4} moles/l. at 15°, 25° and 35° C. respectively. The equilibrium quotients at zero ionic strength were 0.82 and 1.1 x 10^{-4} moles/l. at 25° and 35° C. respectively. The equilibrium was satisfactorily described by a single chloride hydrolysis. The extent of a second hydrolysis was so small that only an upper limit of 2 x 10^{-5} moles/l. can be set for a second acid hydrolysis equilibrium constant, K_2'. The rate constant for the single acid hydrolysis, k_1, was found to be 3.2, 9.8 and 32 x 10^{-5} sec.$^{-1}$ at 15°, 25° and 35° C. respectively. This rate constant was independent of ionic strength and values of 19.6 kcal./mole and -11 e.u. were found for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ respectively. An upper limit of 0.5 k_1 was set for the second acid hydrolysis rate constant, k_2.

The rate law for exchange of Cl$^-$ with trans-[Pt(NH$_3$)$_2$Cl$_2$] was found to be:

$$R = k_1[Pt(NH_3)_2Cl_2] + k'[Pt(NH_3)_2Cl_2][Cl^-] \qquad (VI.1)$$

The value of k_1 found by exchange experiments agreed with that found by titration procedures. The second order direct exchange rate constant, k', was 7.8 x 10^{-4} M.$^{-1}$ sec.$^{-1}$ and $\Delta H_k^{\ddagger}$, = 19.6 kcal./mole and $\Delta S_k^{\ddagger}$, = -7 e.u.

The behavior of <u>trans</u>-[Pt(NH$_3$)$_2$Cl$_2$] with respect to acid hydrolysis and chloride exchange was contrasted with the behavior of the other chloroammineplatinum(II) complexes.

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VIII. ACKNOWLEDGMENTS