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Base hydrolysis of trans-dichlorodiammineplatinum (II)

Ronald George Gunther
Iowa State University

D. S. Martin
Iowa State University

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BASE HYDROLYSIS OF TRANS-DICHLORODIAMMINEPLATINUM(II)

by

Ronald George Gunther and D. S. Martin
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BASE HYDROLYSIS OF TRANS-DICHLORODIAMMINEPLATINUM (II)*

Ronald George Gunther and D. S. Martin

ABSTRACT

The reactions

\[
\begin{align*}
    \text{t} - \left[ \text{Pt(NH}_3\text{)}_2\text{Cl}_2 \right] + \text{OH}^- & \rightarrow \text{t} - \left[ \text{Pt(NH}_3\text{)}_2\text{Cl(OH)} \right] + \text{Cl}^- \\
    \text{t} - \left[ \text{Pt(NH}_3\text{)}_2\text{Cl(OH)} \right] + \text{OH}^- & \rightarrow \text{t} - \left[ \text{Pt(NH}_3\text{)}_2\text{(OH)}_2 \right] + \text{Cl}^-
\end{align*}
\]

in aqueous solutions were studied by measuring the changes in specific conductivity and in ultraviolet absorption which occurred during the course of the reactions. The rates of reaction were determined from a plot of \( \ln L(t) \) vs time, where \( L(t) \) is either (optical density at infinite time) - (optical density at time \( t \)) for the spectrophotometric determinations or (conductivity at time \( t \)) - (conductivity at infinite time) for the conductometric experiments. The conductometric experiments also required correction for hydroxide attack upon the measuring vessel. Both reactions were found to be zero order in hydroxide, to be the only reactions occurring between the platinum complex and the hydroxide for times up to one day, and to involve the formation of an aquo intermediate. The rates for the first hydrolysis were \( 6.21 \times 10^{-5} \text{ sec}^{-1} \) at \( 20^\circ C \), \( 10.6 \times 10^{-5} \text{ sec}^{-1} \) at \( 25^\circ C \), and \( 29.3 \times 10^{-5} \text{ sec}^{-1} \) at \( 35^\circ C \), with an energy of activation of \( 18.0 \text{ kcal} \) and an entropy of activation of \( -16 \text{ cal/°K} \). The rates for the second hydrolysis were \( 0.17 \times 10^{-5} \text{ sec}^{-1} \) at \( 25^\circ C \) and \( 0.50 \times 10^{-5} \text{ sec}^{-1} \) at \( 35^\circ C \), with an energy activation of \( 19.1 \text{ kcal} \) and an entropy of activation of \( -21 \text{ cal/°K} \).

*This report is based on an M.S. thesis submitted by Ronald George Gunther, February, 1964, to Iowa State University, Ames, Iowa.
I. INTRODUCTION

The purpose of this research has been the study of the kinetics and mechanism of the reaction of trans-dichlorodiammineplatinum(II) with hydroxide. This study is a continuation of previous work at this laboratory on the chloroammineplatinum(II) complexes (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11).

Despite previous work done at this laboratory (8) and at others (12) on the system herein considered, several questions remained unanswered. The rate at which the complex reacts with a second equivalent of hydroxide was undetermined. Some question existed as to whether a previously undetected rapid reaction between the complex and the hydroxide was occurring during the initial minutes of the reaction. Finally, there was the question as to whether the reactions of this system are dependent upon the hydroxide concentration (8).

The trans-dichlorodiammineplatinum(II) complex was first prepared by Reiset (13) in 1840, and is sometimes referred to as Reiset's salt, particularly in the Russian literature. Synthesis of cis-dichlorodiammine-platinum(II) five years later by Peyrone (14) caused some controversy, because these two complexes have the same composition but different chemical and physical properties. It remained for Werner (15) to correctly define the difference between these complexes some fifty years later. He proposed that platinum(II) formed square planar complexes, and that these two complexes were the cis and trans isomers of the same complex. Werner based his conclusion solely on chemical evidence, and his conclusions have been confirmed by structural studies conducted in fairly recent times (16).
Jorgenson (17), another of the early workers on the chemistry of platinum(II), found in his studies of the substitution reactions of \([\text{Pt(NH}_3\text{)}_4]^{++}\) and \([\text{PtCl}_4]^{-}\) that two products were formed depending on the starting materials. When \([\text{Pt(NH}_3\text{)}_4]^{++}\) was treated with chloride, \(_t-[\text{Pt(NH}_3\text{)}_2\text{Cl}_2]\) was formed, whereas when \([\text{PtCl}_4]^{-}\) reacted with ammonia, \(_q-[\text{Pt(NH}_3\text{)}_2\text{Cl}_2]\) was formed. These reactions are classical examples of the trans-effect of Chernyaev (18). The trans-effect, coupled with the general inertness of ammine ligands in platinum(II) complexes, is the basis for Kurnakov's test for the cis and trans isomers of diammine-platinum(II) complexes (19). The trans isomer will react with thiourea (tu) to yield \(_t-[\text{PtA}_2(tu)_2]^{++}\), while the cis isomer under the same conditions will yield \([\text{Pt(tu)}_4]^{++}\), where A is either ammonia or an amine.

The aqueous solutions of the trans and cis isomers were subjected to investigation by conductometric methods by Werner and Miolati (20), and by Drew et al. (21), and were found to undergo conductivity changes indicative of some chemical reaction. These changes were interpreted by Grinberg and Ryabchikov (22, 23) and Jensen (24) to be the result of the acid hydrolysis reactions:

\[
[\text{Pt(NH}_3\text{)}_2\text{Cl}_2] + \text{H}_2\text{O} \rightleftharpoons [\text{Pt(NH}_3\text{)}_2\text{Cl(H}_2\text{O)}]^{++} + \text{Cl}^- \quad (1.1)
\]

\[
[\text{Pt(NH}_3\text{)}_2\text{Cl(H}_2\text{O)}]^{++} + \text{H}_2\text{O} \rightleftharpoons [\text{Pt(NH}_3\text{)}_2\text{Cl(H}_2\text{O})_2]^{++} + \text{Cl}^- \quad (1.2)
\]

The aqueous solutions of these complexes were titrated with sodium hydroxide, and the acid strengths of the species present in the solution were determined (22, 23, 25). The reaction was interpreted as being the neutralization of the aquo species formed by the reactions given in Eqs. 1.1 and 1.2. The hydrolysis reaction of Eq. 1.1 has been studied for both isomers (6, 8, 12, 26) with both the reaction rate and equilibrium quotient
having been determined. The reaction rate for the trans isomer has been found to be higher than that for the cis isomer; this difference has been attributed to differences in the trans labilizing influence of chloride compared to ammine and is a further example of the importance of the trans-effect in studies of platinum(II) complexes.

The trans-effect has been considered in several reviews (27, 28, 29), so no comprehensive treatment of all the experimental evidence for the nature of the trans-effect will be given here. Just a statement of a general definition of the trans-effect and the theory proffered to explain its existence will be presented. The trans-effect is exhibited by any group which affects the rate of substitution reactions of the ligand which is in the position trans to it in the square plane of the complex. The important idea in this presentation of the effect is that it is the rate of the substitution reaction which is concerned in the trans-effect. Thus, consider a complex in which a ligand, designated as $X$, on a complex, is replaced by group $Y$. If with comparable groups cis to $X$ the reaction for the complex with $L$ trans to $X$ is more rapid than that for the complex with $L'$ trans to $X$, then $L$ is considered to have a stronger trans-directing property than $L'$. If in the same complex, $L$ and $L'$ occupy cis positions, and each is trans to equivalent ligands, then substitution reactions will yield mostly the product in which the group trans to $L$ has been replaced. Since Cl$^-$ has a greater trans directing effect than NH$_3$, the kinetics for the replacement of a chloride by ammonia in the complex $[Pt(NH_3)Cl_3]^-$ leads to the cis-dichlorodiammineplatinum(II) which is thermodynamically less stable than the trans-isomer which is the alternative product.
An explanation of the trans-effect suggested by Grinberg (30) is that an induced dipole on the central metal atom weakens the bond of the ligand in the position trans to the labilizing group, thus enhancing the rate of the substitution reactions of the leaving group. The dipole is induced on the platinum when the primary charge of the platinum(II) polarizes the electron cloud of the trans-labilizing ligand. The dipole induced on this polarized ligand in turn interacts with the electron cloud of the platinum to yield an increment in the electron charge density in the region of the ligand which is in linear opposition to the polarized, labilizing ligand, as is seen in Fig. 1, where X is the leaving group and L is the labilizing group.

![Diagram](attachment://L-Pt-X.png)

Figure 1. Distribution of charge in induced dipoles in the L-Pt-X coordinates of trans-[PtALX]

This increment in electron density causes a weakening of the bond of the leaving group, with a resultant increase in the rate of reaction. According to this theory, the higher the polarizability of the trans labilizing group, the greater is its trans influence, which is in accord with experimental evidence. When stated in this bald fashion, however, this theory has some inadequacies which require further explanation and elaboration of the theory.
Another factor to be taken into account is that the highly polarizable groups which have a large trans influence have low electronegativities, and form covalent bonds with the platinum which involve extensive electron transfer to the platinum. This transferal to the platinum leaves the directional nature of the trans-effect unexplained, however, because a general decrease of the strength of all platinum-ligand bonds would be expected from a decrease in the net positive charge on the platinum, rather than a stereospecific effect. The directionality has been explained by Syrkin on the basis of the platinum orbitals which are used in forming the covalent bonds with the ligands (31), and the electron probability distribution which is found when one of the ligands is strongly covalent in its bonding. Considering that the \( d_{x^2-y^2} \) along with the \( g_{\pi} \), the \( p_x \), and \( p_y \) orbitals of the platinum are involved in the bonding, he has claimed that strong covalent bonding by one of the ligands causes an increase in the covalent character of the bonds to ligands which are cis to it and a decrease in covalency of the trans position, on the basis of resonance models for the system. This lessening of the covalent character of the trans ligand was taken to correspond to a weakening of the bond in that position, according to this treatment. Because the \( d \) orbital is of lower energy than the \( p \) orbital, if this orbital was more strongly involved in the bond of one of the ligands, then it could not be used by the ligand which is trans to that ligand, given the directional character of the \( d \) orbital involved.

Basolo and Pearson have proposed a different approach to this problem of polarizability as related to the trans-effect by the observation that
those ligands which are easily polarized have low lying excited states, and that polarization can be explained in terms of the wave functions of these low lying excited states mixing with the wave function of the ground state (32). Because the excited states of the ligand which are involved in the mixing are presumably orbitals with \( \pi \)-symmetry character, the resultant hybrid will cause the \( d \) orbital electrons of the platinum to be displaced towards the \textit{trans} position with, again, an increment in the electron probability in this region causing the bond to be weakened. When considered in this fashion, the Pauli exclusion principle is brought to bear, besides the purely electrostatic consideration.

Inasmuch as an electrostatic basis involving polarization of the ligands and covalent \( \pi \)-bonds is inadequate to explain the strong \textit{trans}-effect of such groups as \( R_3P \), \( C_2H_4 \), and \( CO \), an alternative theory for the \textit{trans}-effect was introduced by Chatt \textit{et al.} (33) and Orgel (34). Certain ligands which exhibit a strongly labilizing influence on the \textit{trans} ligand are definitely known to have no weakening effect on the bond of that ligand, and for these the increase in the rate of reaction of this \textit{trans} ligand is ascribed to stabilization of the transition state. In order that this may be more clearly seen, a digression to the possible transition states for the reactions of platinum(II) complexes is apt.

To start with, it has been found that a number of substitution reactions of platinum(II) complexes can have their rate of reaction expressed by the equation,

\[
\text{Rate} = k_1 [\text{complex}] + k_2 [\text{complex}] [Y] \quad (1.3)
\]

where \([Y]\) is the concentration of the incoming ligand (35). Furthermore, when aqueous solutions are being studied, \( k_1 \) turns out to be the acid
hydrolysis rate for the complex (9). Other observations of import in the assessment of the reactions of the platinum(II) complexes are the following (29). The rates of reaction are dependent both on the entering and leaving group; the reaction rates of the various complexes with the solvent are relatively insensitive to the charge of the complex (cf. Table 2, p. 49). When complexes contain ligands which sterically hinder the positions above and below the plane of the complex, both $k_1$ and $k_2$ of the reaction are decreased (36). Also, the rate of reaction with different solvents depends on the coordinating properties of the solvent, with the dielectric constant and the solvating properties of the solvent being immaterial (37). The ionic strength of the solution has no influence on the reaction rates of many of the complexes (8, 9).

These observations about the substitution reactions of platinum(II) complexes indicate that in general any reaction mechanism which involves bond breaking as the rate determining step is untenable, and that a mechanism involving bond formation as the rate determining step is followed in these reactions. Two such mechanisms are proposed (28, pp. 188-189), both of which start with the square planar complex in solution with the positions above and below the plane of the complex having solvent molecules coordinated to form a distorted octahedral configuration. Because the axial ligands are bound loosely, they can rapidly be replaced by solute molecules or ions. These axially bound ligands are used to form either a square pyramid intermediate, or a trigonal bipyramid intermediate, as shown in Fig. 2. For the square pyramid intermediate (cf. Fig. 2a), the axial ligands move in to displace the leaving group X. This square pyramid intermediate would then react either with the incoming group Z,
Figure 2a. Bimolecular reaction involving a square pyramid intermediate

Figure 2b. Bimolecular reaction involving a trigonal bipyramid intermediate
or with solvent molecules S. If it reacts with the solvent, the general lability of aquo complexes, when aqueous solutions are involved, will contribute to repeated formation of the intermediate until a more stable product is formed.

The other mechanism (cf. Fig. 2b) starts with one of the axial ligands moving in towards the platinum, the other axial ligand leaving, and the leaving group shifting towards the axial position thus vacated. At this point the intermediate is in the form of a trigonal bipyramid with the trans-labilizing group, the leaving group, and the group from the axial position forming the equator of the bipyramid. This intermediate can then go to the product by attaining the distorted octahedral configuration with the leaving group now located in the axial position, where it will be in labile equilibrium with the solution.

It is this trigonal bipyramid intermediate that is employed by Chatt et al. (33) and Orgel (34) to explain the trans-effect. The $d_{xz}$ orbital of the platinum has its highest electron density in the direction of the incoming $Y$ and the leaving $X$ groups of the trigonal bipyramid intermediate, so that any group which can shift the density away from these positions will enhance the stability of the intermediate by reducing the repulsion to the formation of this configuration. If the trans labilizing group $L$ is capable of forming a $\pi$-bond with the $d_{xz}$ orbital electrons of the platinum(II), just such a shifting will occur. Ligands which are capable of forming such a $\pi$-bond have been called bifililic (37) because they are nucleophilic in the formation of their primary bond to the platinum, and they are electrophilic in the formation of this $\pi$-bond with the platinum(II) $d_{xz}$ orbital electrons. With this as the intermediate,
both the mechanism of the substitution reactions of platinum(II), and the nature of the trans-effect for those ligands capable of $\pi$-bonding can be explained. Neither the polarization theory nor the $\pi$-bonding theory is adequate by itself to explain all cases of trans labilization, and, in fact, some cases require both to be applied for an adequate explanation.
II. EXPERIMENTAL

A. Materials

The platinum used in the experiments was recovered from compounds used in other experiments at this laboratory and was originally from many sources. Because of possible interference with kinetics studies, the platinum was freed of iridium impurities using the fractional crystallization of K$_2$PtBr$_6$ as recommended by Jowanovitz et al. (38). The $\text{-}\left[\text{Pt(NH}_3\text{)}_2\text{Cl}_2\right]$ was prepared by the thermal decomposition of $\left[\text{Pt(NH}_3\text{)}_4\text{Cl}_2\right]$ (39). All other chemicals used in the experiments were of analytical reagent grade meeting ACS specifications. Solutions were made from water which was first passed through ion exchange columns and then distilled from alkaline permanganate solution in order to remove any organic materials, with the resultant water having a specific conductivity of $0.54 \times 10^{-6}$ mhos/cm at 25°C. Sodium hydroxide solutions were prepared by reacting sodium metal with conductivity water under an argon atmosphere.

B. Equipment

A Cary Recording Spectrophotometer Model 14 with thermostated cell compartments was used for the spectrophotometric experiments. Thermoregulation of ± 0.1°C in the cell compartment was achieved by pumping water from a Sargent constant temperature bath through the thermostating jacket of the spectrophotometer. Matched quartz cells with a 100 mm path length were used in the experiments.

The conductometric studies were made with a type 716C capacitance bridge manufactured by the General Radio Company; this instrument has
resistance decades in the range 0.01 ohms to \(10^5\) ohms incorporated externally into its measurement system. A Hewlett-Packard 2000CD wide range oscillator and Tektronix type 122 low-level preamplifier were used with the capacitance bridge for the conductivity measurements. The conductivity cells were thermostated in a modified Sargent constant temperature bath. The sensitivity of the measuring device coupled with the relatively high variability of solution resistance with temperature changes necessitated the use of a thermistor controlled thermoregulator, constructed at this laboratory, which regulates the transformer oil thermobath to \(\pm 0.02^\circ\text{C}\). The conductivity cells used for the kinetics studies have cell constants of 6.3506 cm\(^{-1}\), 6.3344 cm\(^{-1}\), and 6.2786 cm\(^{-1}\), and are designed to conform with the recommendations of Jones and Bollinger (40). Transformer oil was used as the thermostatic medium because of its desirable electrical properties.

1. **Preparation of solutions**

For both the spectrophotometric and conductometric experiments, the \(\text{[Pt(NH}_3)_2\text{Cl}_2]^-\) solutions were prepared by first dissolving a known amount of KCl in a volumetric flask, then adding a known amount of the platinum complex and dissolving this by means of a shaker and a 35\(^\circ\text{C}\) constant temperature bath—this latter was because of the slow rate at which the complex dissolves, and its low solubility. The KCl served the twofold purpose of suppressing the aquation of the platinum complex before the introduction of hydroxide, and of providing an ionic medium to yield desirable resistances for the conductivity measurements. As was stated above, the NaOH solutions were prepared by reacting metallic sodium with conductivity water under an argon atmosphere; the hydroxide concen-
tration was determined by titrating potassium acid phthalate to a phenolphthalein endpoint. The NaOH solutions were prepared in this manner with a view to keeping carbonate concentrations as low as possible. Before the inception of the experiment proper, all of the solutions to be employed were brought to the temperature of the experiment by placing them in a constant temperature bath.

The experiments were timed from the moment of introduction by volumetric pipette of the NaOH. The reference solutions—solutions identical to the actual experimental solutions in all respects except that they contained no platinum complex—were started first, and then the experimental solutions. The initial minutes of the experiment were always somewhat unreliable because of the changes in the temperature of the solutions which occurred during the mixing of the reactants and the necessary rinsing out of the reaction vessels with the reaction solutions. The extreme temperature dependency of the conductivity revealed the room temperature to be the real determining factor in the conductivity measured during the early minutes of the experiment before the solutions reached the temperature of the constant temperature bath.

The platinum solutions were tested for stability in general and with respect to light. They were found to be relatively stable for long periods of time and completely stable with respect to light for the periods of time involved in the experiment (41). The reaction solutions upon being tested for stability with respect to light indicated either that the reaction rate was independent of light or if dependent, the change in rate constant was within the range of the experimental error and
could not be detected under the experimental conditions used. Light was, therefore, discounted as a factor in the present study. Ionic strength is a known factor in rates of reaction, but the present experiments were all conducted at low ionic strength (< 0.02), so this factor also could be disregarded; also, the hydrolysis reactions of platinum(II) are in general independent of ionic strength (9).

2. Spectrophotometric procedure

The ultraviolet absorption spectrum of the system being studied lends itself to kinetic determinations because an absorption valley for $t^- [\text{Pt(NH}_3)_2\text{Cl}_2]$ at 2950 Å grows into an absorption peak as the reaction with hydroxide proceeds. Furthermore, the changes in absorption at this point are quite large for the first hydrolysis reaction of the system, while any changes at this point due to any other reactions in the system are both small and occur at a rate which is quite slow in comparison to the reaction rate for the first hydrolysis reaction. The second hydrolysis reaction proceeds at such a slow rate that its measurement is difficult in the first place, and its measurement by spectrophotometric means is precluded by the steep slope of the absorption spectrum in the region where the most characteristic changes for this reaction occur. All of these features can be seen in Fig. 3.

The general procedure in these experiments was to follow the spectral changes in the 2500 to 4000 Å region, with the time elapsed since the introduction of the NaOH into the solution always being recorded as the spectral sweep passed 2950 Å. The cell compartment was completely dark between scannings.
Figure 3. Composite ultraviolet absorption spectra for a typical base hydrolysis experiment at 35°C. Spectra obtained with solution: 4.29 \times 10^{-4} \text{ M } \text{trans-Pt(NH}_3)_2\text{Cl}_2, 1.61 \times 10^{-2} \text{ M } \text{KCl}, 1.14 \times 10^{-3} \text{ M } \text{NaOH} \text{ in } 10 \text{ cm silica cell. The times indicated are the times after the inception of the experiment at which the absorption at 2950 Å was recorded.}
In order to ascertain whether other changes were occurring, throughout the course of some of the reactions concentrated HCl was added to an aliquot of the reaction solution. The high chloride and acid concentration reversed the course of the hydrolysis reaction so that the starting material should have been formed if no other reactions occurred in the system. If no such competing or subsequent reactions occurred, then the spectrum of the reaction solution which has been reversed would have approached that of the original solution, since the hydrolysis reaction is reversible.

3. **Conductometric procedure**

Conductometric measurements of the reaction were based upon the difference in conductance between hydroxide ions and chloride ions. The reaction under study was one in which hydroxide ions in solution were replaced by chloride ions, thus causing a change in the resistance of the solution. The chief difficulty was that hydroxide also had a proclivity to attack glass. This attack also resulted in a change in the resistance of the solution. The experimental procedure was designed in such a manner to take these facts into account.

Each experiment used at least two and sometimes three conductivity cells of approximately identical geometry. One cell contained a reference solution and the other one or two cells contained experimental solutions. The resistance of all the cells was measured over the period of the experiment, with the reference cell giving the amount of attack upon the glass by the hydroxide. All of the cells were constructed of the same material, were of the nearly same geometry, and contained the same concentration of ionic species. The platinum complexes involved were all
neutral and were at low concentrations, so that their influence on the activity of the ionic species was negligible. As a consequence the hydroxide attack on the glass of the reference cell was expected to closely replicate the attack in the reaction vessels.

The experiments were conducted at a low measuring voltage (approx. $3 \times 10^{-2}$ V), to avoid introducing extraneous electrochemical effects, through the use of a preamplifier and the highly sensitive null detector of the capacitance bridge. The measuring frequency used in all of the experiments was 1 Kc. Interfering phenomena were virtually eliminated through the use of properly designed conductivity cells, optimum platinization of the electrodes, low measuring voltage, and the use of transformer oil as the thermostating medium, so that a second measuring frequency was unnecessary.
III. TREATMENT OF DATA

A. Spectrophotometric Data

As was previously noted, the spectral changes at 2950 Å were fairly specific for the first hydrolysis reaction; the data at this wave length could therefore be treated as though this were the only reaction taking place in the system in accordance with the equation:

$$
\text{Pt(NH}_3\text{)}_2\text{Cl}_2 + \text{OH}^- \rightarrow \text{Pt(NH}_3\text{)}_2\text{Cl(OH)} + \text{Cl}^- \quad (\text{III.1})
$$

where $N_1$ and $N_2$ represent the molar concentration of the indicated species. If the hydroxide ion is present in a large excess so that the reaction can be considered pseudo-first order, or if the reaction is actually zero order in hydroxide, the rate expression is

$$
dN_1/\text{d}t = -k_1N_1 \quad (\text{III.2})
$$

where $k_1$ is the specific rate constant. The concentration $N_1$ at any time $t$ is given by,

$$
N_1(t) = N_1(0)e^{-k_1t} \quad (\text{III.3})
$$

If there were no further reaction of $\text{Pt(NH}_3\text{)}_2\text{Cl(OH)}$, then the concentration $N_2$ is given by,

$$
N_2(t) = N_1(0)(1 - e^{-k_1t}) \quad (\text{III.4})
$$

The concentrations of the Pt complexes are related to the optical density of the solution by the equation,

$$
D(t) = \varepsilon_1N_1(t) + \varepsilon_2N_2(t) \quad (\text{III.5})
$$
where

\[ D(t) = \text{optical density at time } t \]
\[ \varepsilon_1 = \text{extinction coefficient of } [\text{Pt(NH}_3)_2\text{Cl}_2] \]
\[ l = \text{length of optical path for spectrophotometric measurement} \]
\[ \varepsilon_2 = \text{extinction coefficient of } [\text{Pt(NH}_3)_2\text{Cl(OH)}] \]

Again, \( N_2(0) = 0 \), but also \( N_1(\infty) = 0 \) and, assuming there are no interfering reactions, \( N_2(\infty) = N_1(0) \), so Eq. III.5 assumes the forms,

\[ D(0) = \varepsilon_1 l N_1(0) \quad \text{(III.6)} \]

and,

\[ D(\infty) = \varepsilon_2 l N_2(\infty) = \varepsilon_2 l N_1(0) \quad \text{(III.7)} \]

Substitution of Eqs. III.3 and III.4 into Eq. III.5 yields

\[ D(t) = \varepsilon_1 l N_1(0) e^{-k_1 t} + \varepsilon_2 l N_1(0)(1 - e^{-k_1 t}) \quad \text{(III.8)} \]

The desired equation results when Eqs. III.6 and III.7 are substituted into Eq. III.8:

\[ D(t) = D(0) e^{-k_1 t} + D(\infty)(1 - e^{-k_1 t}) \quad \text{(III.9)} \]

or,

\[ e^{-k_1 t} = \frac{D(t) - D(\infty)}{D(0) - D(\infty)} \quad \text{(III.10)} \]

or,

\[ k_1 t = \ln \frac{D(\infty) - D(0)}{D(\infty) - D(t)} \quad \text{(III.11)} \]

By plotting \( \ln(D(\infty) - D(t)) \) vs \( t \), the rate constant \( k_1 \) will be the negative slope of the linear function, and \( \ln(D(\infty) - D(0)) \) will be the
intercept. Alternatively, the intercept can be used to find the half-time for the reaction, and $k_1$ can be calculated from the half-time. In the actual experimental results, however, only a $D_{\text{max}}$ was obtained because of the subsequent reactions which occurred in the system. Also, $e_2$ was not known, so that the concentrations could not be calculated directly. Since, however, the second reaction occurred at such a slow rate in comparison to the first, and the changes in the spectrum at 2950 Å due to the second hydrolysis reaction were very slight, the data could be treated by a method of successive reiterations. Approximate values for $D(\infty)$ were chosen until a plot of $\ln(D(\infty) - D(t))$ vs $t$ was obtained which was linear over a period of 2.5 half-times for the reaction.

B. Conductometric Data

Before giving an exposition of the method in which the conductometric data was treated, an explication and justification of the assumptions used in the treatment will facilitate the presentation. Central to the whole development was the assumption that the specific conductance of the solution could be represented by the sum of the specific conductances of the individual ionic species present. From the equation

$$L = \sum n L_n,$$

where $L$ is the specific conductance of the solution and $L_n$ is the specific conductance of the individual ions present in the solution, the next step was to relate the specific conductances to the concentrations of the conducting species present in the solution to yield

$$L = 10^{-3} \sum n c_n \lambda_n,$$

where $c_n$ is the normality of each compound present, and $\lambda_n$ is the equivalent conductance appropriate to each compound. This assumption
was justified by the fact that the measuring voltage and frequency were both low enough that they did not constitute a disturbing influence on the state of the ions in solution (42, p. 127). The transition from specific conductances to concentrations followed from the basic definition of equivalent conductance—it should be noted that actual values of the equivalent conductances did not enter into the treatment of data at any point so that it was unnecessary to consider what equivalent conductance value to use; the only requirement was that each compound which was taking part in conducting the current through the solution have some constant which when multiplied by the normality of that compound would yield the contribution of that compound to the overall conductivity of the solution.

While this is not an egregious requirement, some further remarks about it are required inasmuch as the composition of the solution changed as the reaction progressed, and equivalent conductances at finite concentrations are dependent upon the composition of the solution. The factors of importance are the following: the ions that are present, their valence and concentration, the ionic strength of the solution, the non-ionic species present, the viscosity of the solution, the solvent, and the temperature. Of these, the solvent and temperature can be ignored because these remained constant throughout the course of the reaction. Because the nature of the solution changed during the reaction, the remaining factors are a bit more complex. For convenience, remaining factors will first be considered as they appear in the reaction of the platinum complex and then with regard to extraneous reactions in the experimental system.
Unlike the spectrophotometric determinations, the conductometric experiments indicated changes associated with the second hydrolysis reaction, so the following are the reactions that have to be considered:

\[
\text{[Pt(NH}_3)_2\text{Cl}_2 \text{]} + \text{OH}^- \xrightarrow{k_1} \text{[Pt(NH}_3)_2\text{Cl(OH)}\text{]} + \text{Cl}^- \quad \text{(III.12)}
\]
\[
\text{(N}_1\text{)} \quad \text{(N}_2\text{)}
\]

\[
\text{[Pt(NH}_3)_2\text{Cl(OH)}\text{]} + \text{OH}^- \xrightarrow{k_2} \text{[Pt(NH}_3)_2\text{Cl(OH)}_2\text{]} + \text{Cl}^- \quad \text{(III.13)}
\]
\[
\text{(N}_2\text{)} \quad \text{(N}_3\text{)}
\]

where \(N_n\) is the concentration of the particular complex. The important features of this reaction with respect to the present consideration are that univalent ions were involved, and the ionic strength was unaffected by the reaction. Both of these would indicate that any changes which occurred in the solution properties would be regular and not very pronounced. Furthermore, with only one exception, the experimental solutions contained a large excess of hydroxide. Also, the nature of the complex with respect to its influence on the solution changed little, so that the viscosity of the solution was unchanged by the primary reaction. All of these taken together indicate that the equivalent conductances of the electrolytes in the solution were unaffected by the reaction of the Pt complex.

With respect to the extraneous reactions—the hydroxide attack on the glass, and changes which occurred in the Pt complex—a very important consideration is that these reactions were so slow that their influence should be negligible during the early portions of the reaction which were used in the determination of the rate constants. Here also, the presence
of the hydroxide in large excess in all the experiments except one has bearing on the solution being considered to remain at approximately constant composition with respect to the equivalent conductances of the electrolytes present in the solution. In Chap. IV of this thesis experimental evidence bearing on these contentions will be given.

While the above considerations on the equivalent conductances of the electrolytes will be of importance in the treatment of the experimental data, the difficulty still remains that these extraneous reactions contribute to the experimentally measured changes in the system, and some correction must therefore be made for these reactions before the rate constants for the Pt complex reactions can be ascertained. One of the extraneous reactions is the attack of the hydroxide on the glass of the reaction vessel; the manner of treating this problem will be considered first.

In the design of the conductometric experiments, many factors came into play: elimination of experimental errors such as the Parker effect, the necessity of having a high cell constant, the desirability of reproducibility and therefore of structural rigidity, .... Glass conductivity cells have the virtue of wide fabrication flexibility, but also a concomitant drawback of susceptibility to attack by hydroxide, which can be a limitation in sensitive conductivity measurements. Other materials from which the cells could be manufactured were ruled out either because of their lack of structural integrity and rigidity, or because of their adverse electrical properties. Dipping electrodes were ruled out for much the same reason, with the additional factor of the sealing off of
the system from the carbon dioxide of the atmosphere also being considered important. Glass seeming to possess only the drawback of reaction with hydroxide, efforts were made to correct this deficiency. Various methods of applying protective coatings to the glass walls without at the same time contaminating the platinized electrodes having failed, external correction was decided upon; another cell with similar materials and geometry was constructed, and this was used as a reference cell. The reference cell contained a solution which was identical to the solution of the experimental cell, with the exception of having no Pt complex present. The changes in the specific conductance of the reference solution were recorded and then a plot of the change in specific conductance with time was made using the relationship,

\[ \Delta L_R(t) = L_R(0) - L_R(t) \]  

(III.14)

where \( L_R(t) \) is the specific conductance of the reference solution at time \( t \). The value for \( L_R(t) \) at \( t = 0 \) (i.e. \( L_R(0) \)) was obtained by an extrapolation. Using the additivity of specific conductances, the experimental curve was then corrected by subtraction of the \( \Delta L_R(t) \) curve with the resultant difference curve being the changes in specific conductance due to the reaction of the Pt complex with hydroxide along with any other reactions of the Pt complex which changed the electrolytic composition of the solution. It was this corrected curve which was then used in calculating the rate constants for the Pt reactions. Chapter IV will also include experimental evidence for other reactions occurring in the system, but, again, these were so slow that they did not materially
influence the data used in the calculation of the rate constants. In the derivation which follows, all the extraneous reactions will be ignored on the basis of the arguments stated above.

For a system which initially contains only NaOH and KCl as electrolytes along with the Pt complex, and which reacts according to Eqs. III.12 and III.13, the specific conductivity $L$ at any time $t$ is given by the equation,

$$L(t) = 10^{-3}(c_{NaOH}(t) \wedge NaOH + c_{NaCl}(t) \wedge NaCl + c_{KCl} \wedge KCl)$$ (III.15)

where $c(t)$ is the normality of the designated electrolyte at times $t$, $\wedge$ is its equivalent conductance, and $c_{KCl}$ is not written as a function of time because it does not enter into the reaction. Inasmuch as the reaction entails the conversion of hydroxide into chloride through the reaction with Pt complexes, the following hold true:

$$c_{NaCl}(\infty) = 2N_1(0)$$ (III.16)
$$c_{NaOH}(\infty) = c_{NaOH}(0) - 2N_1(0)$$ (III.17)
$$c_{NaOH}(t) = c_{NaOH}(0) - c_{NaCl}(t)$$ (III.18)
$$c_{NaCl}(t) = N_2(t) + 2N_3(t)$$ (III.19)

where $N_n$ has the signification given in Eqs. III.12 and III.13, and the two reactions are assumed to be going to completion without any other reactions taking place in the system. As the time goes to infinity, the conductivity will approach an asymptotic value,

$$L(\infty) = 10^{-3}(c_{NaOH}(\infty) \wedge NaOH + c_{NaCl}(\infty) \wedge NaCl + c_{KCl} \wedge KCl)$$ (III.20)
Subtraction of the equalities of Eq. III.15 from Eq. III.10 and the appropriate substitutions from Eqs. III.16, III.17, III.18, and III.19 yields,

\[
(L(t) - L(\infty))10^3 = (c_{\text{NaOH}}(0) - N_2(t) - 2N_3(t)) \land_{\text{NaOH}}
\]

\[+ c_{\text{KCl}} \land_{\text{KCl}} + (N_2(t) + 2N_3(t)) \land_{\text{NaCl}}
\]

\[- (c_{\text{NaOH}}(0) - 2N_1(0)) \land_{\text{NaOH}}
\]

\[- c_{\text{KCl}} \land_{\text{KCl}} - 2N_1(0) \land_{\text{NaCl}} \quad (\text{III.21})
\]

\[
= (2N_1(0) + N_2(t) + 2N_3(t)) (\land_{\text{NaCl}} - \land_{\text{NaOH}}) \quad (\text{III.22})
\]

or,

\[
(L(t) - L(\infty))10^3/(\land_{\text{NaOH}} - \land_{\text{NaCl}})
\]

\[= 2N_1(0) + N_2(t) + 2N_3(t) \quad (\text{III.23})
\]

Again, through the use of high hydroxide concentrations in order to have the reaction pseudo-first order, or if the reaction is actually zero-order in hydroxide, the rate expressions are:

\[
\frac{dN_1}{dt} = -k_1N_1 
\]

\[
(\text{III.24})
\]

\[
\frac{dN_2(t)}{dt} = k_1N_1(t) - k_2N_2(t)
\]

\[
(\text{III.25})
\]

and,

\[
\frac{dN_3(t)}{dt} = k_2N_2(t).
\]

\[
(\text{III.26})
\]

The expressions for \(N_1(t)\), \(N_2(t)\), and \(N_3(t)\) resulting from these are:

\[
N_1(t) = N_1(0)e^{-k_1t}
\]

\[
(\text{III.27})
\]
Substitution of Eqs. III.28 and III.29 into Eq. III.23 results in the relationship,

\[
(L(t) - L(\infty)) = 2N_1(0) - \frac{k_1}{k_2 - k_1} N_1(0)(e^{-k_1 t} - e^{-k_2 t})
\]

\[
- \frac{2k_2}{k_1 - k_2} N_1(0)e^{-k_1 t} - \frac{2k_1}{k_2 - k_1} N_1(0)e^{-k_2 t} - 2N_1(0)
\]

\[
= \frac{k_1 - 2k_2}{k_1 - k_2} N_1(0)e^{-k_1 t} + \frac{k_1}{k_1 - k_2} N_1(0)e^{-k_2 t}
\] (III.30)

The observations to be made with regard to Eq. III.30 are the following. L(t) is an experimentally determined variable, and L(\infty) is a constant whose value is determined in the manner described below. (\textsuperscript{\wedge}NaOH - \textsuperscript{\wedge}NaCl) is a constant according to the arguments given previously. k_1 and k_2 are the rate constants to be determined. (L(t) - L(\infty)) is a function of the form Ae^{-k_1 t} + Be^{-k_2 t}, which is equivalent to saying that the changes in specific conductivity caused by the reactions of Eqs. III.12 and III.13 are expressed as two exponentials with periods characterized by the rate constant for the two hydrolysis reactions. The ratio of the contribution of these two exponentials, A/B, = 1/(2k_2/k_1).
In actual practice, $L(\infty)$ was indeterminable experimentally because the extraneous reactions in the system caused a continual change in the conductivity even after the termination of the principal hydrolysis reactions. This difficulty was surmounted by a method of successive approximations: a trial value for $L(\infty)$ was selected and $\log(L(t) - L(\infty))$ was plotted as a function of $t$, and a linear extrapolation to $t = 0$ was made of the portion of the curve which corresponded to the conductivity changes resulting from the second hydrolysis reaction. The experimental results had a sharp change in the slope of their logarithmic plot as a function of time. The portion of the curve which came after this change in slope and extended for approximately two and one-half half-times for the second hydrolysis reaction was used for the linear extrapolation, with the data for longer times being discarded because of the extraneous reactions which manifested themselves during the longer times. The linear component was then subtracted arithmetically from the original curve to yield the component at lower values of $t$. The intercepts of the two curves resulting from this resolution were then compared using the relationship in Eq. III.22, and a new value for $L(\infty)$ was chosen until the two resultant components had their respective intercepts in proper proportion. The two resultant components of this resolution corresponded to the periods for the reactions given by Eqs. III.12 and III.13, so the rates of reaction for these reactions could be determined by evaluating the slope for each component.
IV. RESULTS

The nature of the reacting system was shown from the changes observed in the spectrophotometric experiments and the conductometric experiments. The spectrophotometric experiments showed that the species present which had absorption in the ultraviolet region was undergoing changes in the presence of hydroxide, and these changes did not occur when hydroxide was absent. Also, addition of excess acid both as perchloric acid and as hydrochloric acid caused the spectrum of the solution to revert substantially to that of the starting Pt complex. The replacement of the ammine ligands was ruled out by this reversibility to the starting material, and by the general inertness of the ammine ligands in \( t \)-dichlorodiammineplatinum(II), which inertness was in part the basis for such reactions as Kurnakov's test. Grinberg and Ryabchikov (22, 23) and Jensen (25) both have studied the aqueous solutions of this complex, and have been able to measure an ionization quotient for the acid formed in the aqueous solution. Finally, the very basis of the conductometric experiments was the decrease in the conductivity of the solution with time upon the addition of hydroxide, which changes could be attributed to the replacement of hydroxide ions in solution by chloride ions—the experimentally measured changes in conductivity were closely approximated theoretically by using estimated values for the equivalent conductance of the individual ions present in Eqs. III.12 and III.13. The estimation of the equivalent conductances was necessitated by the paucity of such information to be found in the literature for systems of mixed electrolytes. The estimation of the values was made in the following manner,
based upon the Debye-Hueckel observation that electrolytic properties are a function of the square root of the ionic strength. Plots of the equivalent conductance as a function of the square root of the ionic strength were made for solutions of the pure electrolytes, and then the equivalent conductance of each electrolyte in a mixed solution was estimated from these plots using the square root of the total ionic strength of the mixed solution as the determining property. Such a procedure was justified by the low ionic strengths involved in the experiments, by the fact that all of the electrolytes were of univalent-univalent type, and because all of the ionic species present were regular in their electrolytic behavior.

Mention should be made of extraneous factors which entered into the system, because the above statements require modification when the reaction is considered at times in excess of approximately three half-times of the second hydrolysis reaction. Both the spectrophotometric and conductometric experiments gave indications that the Pt complex underwent reactions other than the primary reactions herein considered. After the hydroxide had been exhausted in a conductometric experiment which contained approximately one equivalent of hydroxide per equivalent of complex, the conductivity was observed to reverse itself and start to increase at a steady rate, thus indicating that either the ionic concentration of the solution was increasing, or that ions with higher conductance were replacing ions already present, or possibly both were occurring. One possible explanation is that the hydroxide attack upon the glass of the conductivity cells had caused a condition whereby ions
from the glass surface entered the solution even after the hydroxide of the solution was depleted. This was ruled out by an experiment in which a solution containing KCl and NaOH was allowed to sit in a cell for a day, at which time it was emptied out and replaced by a KCl solution. The conductivity of this KCl solution remained unchanged for the week during which measurements were made. It is possible that once the excess of hydroxide was removed, very slow hydrolysis reactions occurred, with the system subsequently reaching equilibrium. This explanation fails to account for the positive deviations from linearity which resulted when the experimental curves for experiments containing up to twentyfold excesses of hydroxide were resolved into their components using the method outlined in Chapter III. It also fails to account for the fact that excess chloride was added to the solutions to prevent hydrolysis reactions of the chloride ligands occurring to any appreciable extent. In experiments which contained excess hydroxide, the plots of ln(L(t) - L(\infty)) deviated positively from linearity after about two half-times for the second hydrolysis reaction. Further elucidation of this deviation from linearity arises from a consideration of the changes observed in the spectra obtained from the reversal of the reaction at long times. While the reaction was completely reversible during the times used in determining the rates of reaction (at least any lack of reversibility fell outside of the sensitivity of the spectrophotometer), after several days the reversed reaction yielded a spectrum which had a new peak which partially obliterated the valley for the trans-complex at 2500 Å. The unique aspect of this is that there is no possible simple complex of Pt(II) which could
cause such a change in spectrum under the experimental conditions which were obtained. The conclusion which follows from this is that there must be formation of Pt(IV) complexes. That such a conclusion be drawn is the consequence of the well known proclivity of Pt(II) complexes to undergo such reactions as decomposition, oxidation, and disproportionation under very mild conditions. The time involved for the formation of appreciable amounts of Pt(IV) was such that this cannot be regarded as invalidating the findings with regard to the base hydrolysis of the trans-dichlorodiammineplatinum(II), even though the greater sensitivity of the conductometric method detected this reaction much sooner than the spectrophotometer. Even in the case of the spectral detection, however, fairly low concentrations were detectable because all possible Pt(IV) complexes exhibit an extremely high extinction coefficient in this region. The general conclusion to be drawn is that despite this manifestation of the instability of Pt(II) complexes, the general experimental findings were in no way vitiated because of the time factors involved.

The experimental results are listed in Table 1 for both the conductometric and spectrophotometric determinations at 20, 25, and 35°C. No effort was made to determine the second rate constant at 20°C because the reaction in general was so slow that difficulty was encountered in its determination even at 25°C. Fig. 3 shows the spectral changes observed during the course of a typical reaction, while Fig. 4 shows a typical conductometric experiment both before and after the application of the corrective factor for the hydroxide attack on the walls of the cell. The resolution of this particular corrected curve into the component reactions
Table 1. Base hydrolysis of *trans*- [Pt(NH₃)₂Cl₂]

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Initial [Pt(NH₃)₂Cl₂] (M x 10⁻¹)</th>
<th>Initial NaOH (M x 10⁻³)</th>
<th>Added KCl (M x 10⁻²)</th>
<th>L(0)ᵃ (x 10⁻³ cm⁻¹ cm⁻¹)</th>
<th>L(0)ᵇ (x 10⁻³ cm⁻¹ cm⁻¹)</th>
<th>k₁ (x 10⁵ sec⁻¹)</th>
<th>k₂ (x 10⁵ sec⁻¹)</th>
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<tr>
<td>20</td>
<td>5.15</td>
<td>6.75</td>
<td>1.03</td>
<td>---</td>
<td>---</td>
<td>6.21</td>
<td>---</td>
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<tr>
<td></td>
<td>2.25</td>
<td>6.75</td>
<td>1.03</td>
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<td>4.81</td>
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ᵃExtrapolated value at t = 0 for specific conductivity of base hydrolysis experimental solutions.
ᵇExtrapolated value at t = 0 for specific conductivity of reference solutions.
ᶜSpectrophotometric determination of the reaction rate.
ᵈThe second hydrolysis specific rate constant unobtainable from spectrophotometric data.
ᵉReliable values unobtainable.
Figure 4. Experimental and corrected results from a typical conductometric study of the base hydrolysis reaction at 35°C. Initial concentrations were $[\text{Pt(NH}_3)_2\text{Cl}_2] = 3.80 \times 10^{-4} \text{ M}$, $\text{KCl} = 1.04 \times 10^{-2} \text{ M}$, $\text{NaOH} = 6.75 \times 10^{-3} \text{ M}$. The correction corresponds to the change in conductivity due to the attack of hydroxide on the glass of the conductivity cell. The time is the time after the inception of the reaction at which the conductivity was determined.
is shown in Fig. 5. The hydroxide attack on the glass was found to be independent of hydroxide concentration, although there was individual variation from experiment to experiment because of differences in the surface condition of the glass as is seen in Fig. 6, which is a composite of all the corrective factors applied to the various experiments. All of these curves indicate that there was an initial rapid attack upon the glass, which corresponds to the attack upon the hydroxide free surface, followed by a tapering off when the glass surface becomes saturated with hydroxide—the cells were filled with water between experiments, so that the surface conditions were changed upon the introduction of hydroxide. As is seen in Fig. 4, the hydroxide correction was insignificant with regard to the first hydrolysis reaction, but became important during the course of the second reaction, so the uncertainty in the rate constant for the second reaction is largely attributable to the variations in the hydroxide attack, which in turn are attributable to variations in the surface condition of the glass.

The temperature dependence of both rate constants is given in Fig. 7, from which the calculated values for $\Delta H^\ddagger$, $\Delta F^\ddagger$, and $\Delta S^\ddagger$ are 18.0 kcal, 22.9 kcal, and -16 cal/°K respectively for the first base hydrolysis, and 19.1 kcal, 25.3 kcal, and -21 cal/°K respectively for the second base hydrolysis reaction. Because of the uncertainty in the rate constant for the second hydrolysis reaction at 35°C, there is a resultant uncertainty in the thermodynamic quantities for this reaction. In addition, the usual accuracy with which the activation energy can be determined is only on the order of ± 2 kcal, which introduces an additional uncertainty in the entropy of activation.
Figure 5. Logarithmic plot of a portion of the corrected conductivity curve given in Fig. 4, and the resolution of this logarithmic curve into its components. The components represent the reaction periods for the first and second hydrolysis reactions for this particular experiment, and also show that portion of the experimental results which was employed in the determination of the rate constants.
Figure 6. Composite of the correction curves which were employed in the various conductometric experiments of this study. Each curve represents the attack of hydroxide upon the glass of the conductivity cell under the conditions stated. Because these are corrections, they are presented as the correction increment which must be added to the experimental results. The time is the time after the addition of the hydroxide to the solution at which the conductivity was measured.
Figure 7. Temperature dependence of the base hydrolysis rate constant for the first and second base hydrolysis reactions of $t=\text{[Pt(NH$_3$)$_2$Cl$_2$]}$. For the first reaction $\Delta H^\dagger = 18.0 \text{ kcal/mole, } \Delta S^\dagger = -16 \text{ cal/}^\circ\text{K}$. For the second reaction $\Delta H^\dagger = 19.1 \text{ kcal/mole, } \Delta S^\dagger = -21 \text{ cal/}^\circ\text{K}$. 
Fig. 8 shows the changes observed in the reversal of the reaction with time, being a plot of the optical density at three different wavelengths vs the time at which the reaction was reversed.
Figure 8. Plot of the ultraviolet absorption measured at three frequencies for the reversed base hydrolysis reaction. The absorption is that found when an aliquot of the base hydrolysis reaction was acidified with HCl and allowed to approach the starting complex. The time is the time after the inception of the base hydrolysis reaction at which the reaction was reversed by the addition of HCl.
V. DISCUSSION

Examination of the rate constants given in Table 1 above reveals that neither of the reactions is dependent upon the concentration of hydroxide; the reactions are first order in the Pt complex, however. The reasons for undertaking a conductometric study of this reaction were to ascertain whether an initial rapid reaction of the hydroxide with the complex occurs, and whether there is any hydroxide dependence for the reactions, as well as determining the rate constants for the reactions. While the extreme temperature dependence of the conductivity prevented obtaining experimental points during the initial minutes of the reaction, an extrapolation to zero time of the logarithmic plots of the conductivity changes as a function of time so closely duplicated similar extrapolations of the reference cell, which contained no complex, but had similar concentrations of the ionic species found in the experimental solutions, that the possibility of any initial fast reaction can definitely be ruled out. With such a reaction having been excluded, and the rates of reaction for the other reactions having been shown to be independent of hydroxide concentration, the base hydrolysis of the whole system can be stated to be independent of the hydroxide concentration.

The mechanism for the reaction becomes apparent when the rate constant for the first base hydrolysis is compared with the acid hydrolysis rate constant for the same complex as is seen in Table 2. As was stated in Chapter I, one of the paths which occur in the reactions of Pt(II) complexes is the reaction with a solvent molecule to form an intermediate which then undergoes a rapid reaction with the incoming ligand due to the
high lability of the Pt(II) aqua-complexes. In fact, recent studies indicate that all of the first-order reactions of the Pt(II) complexes are attributable solely to the reaction of the complex with solvent followed by a rapid reaction with the incoming ligand (43). In the case of base hydrolysis, the rapid step of the reaction would be a proton transfer from the water molecule coordinated to the Pt, to a hydroxide ion in the solution. This mechanism, which is the mechanism postulated for the reactions under consideration, is illustrated in Fig. 9.

Table 2. Acid hydrolysis rate constants of the chloroamine complexes of platinum(II) at 25°C and 0.318 ionic strength

<table>
<thead>
<tr>
<th>Complex</th>
<th>$k_1$</th>
<th>$k/n$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(x 10^5 sec⁻¹)</td>
<td>(x 10^5 sec⁻¹)</td>
<td></td>
</tr>
<tr>
<td>$[\text{PtCl}_4]^{-}$</td>
<td>3.9</td>
<td>0.98</td>
<td>(1)</td>
</tr>
<tr>
<td>$[\text{Pt(NH}_3\text{Cl}_3]^{-}$</td>
<td>cis- 5.6</td>
<td>2.8</td>
<td>(11)</td>
</tr>
<tr>
<td></td>
<td>trans- 0.62</td>
<td>0.62</td>
<td>(11)</td>
</tr>
<tr>
<td>$\text{cis-}[\text{Pt(NH}_3\text{)}_2\text{Cl}_2]$</td>
<td>2.5</td>
<td>1.3</td>
<td>(6)</td>
</tr>
<tr>
<td>$\text{trans-}[\text{Pt(NH}_3\text{)}_2\text{Cl}_2]$</td>
<td>9.8</td>
<td>4.9</td>
<td>(8)</td>
</tr>
<tr>
<td>$[\text{Pt(NH}_3\text{)}_3\text{Cl}]^+$</td>
<td>2.6</td>
<td>2.6</td>
<td>(9)</td>
</tr>
</tbody>
</table>

$^a$ Acid hydrolysis rate constant divided by the number of equivalent chlorides n for the hydrolysis reaction.

The postulation of this mechanism for the reaction of the second chloride ligand is of a more tenuous nature because the acid hydrolysis rate for neither $\text{cis-}[\text{Pt(NH}_3\text{)}_2(\text{H}_2\text{O})\text{Cl}]^+$ nor $\text{trans-}[\text{Pt(NH}_3\text{)}_2\text{Cl(OH)}]$ has been determined. On the basis of the arguments given in Chapter I for the
Figure 9. Mechanism for the base hydrolysis reaction of \( \text{L-}[\text{Pt}(\text{NH}_3)_2\text{Cl}_2] \), and of \( \text{L-}[\text{Pt}(\text{NH}_3)_2\text{Cl}(\text{OH})] \). \( L = \text{Cl} \) or \( \text{OH} \)
existence of the trigonal bipyramid intermediate, and for the rejection of an SN1 mechanism involving bond breaking as the rate determining step, and the existence of this mechanism in the case of the first hydrolysis reaction, coupled with the findings cited above on the nature of first-order reactions (43), this mechanism is eminently appropriate for this reaction also. Both the first and the second base hydrolysis reactions involve the formation of the aquo intermediate by means of the trigonal bipyramid intermediate, with the aquo complex then reacting with a hydroxide by proton transfer. The trigonal bipyramid is chosen as the intermediate because of its closer approximation to all of the experimental data on the reactions of Pt(II) complexes (43), and because it is energetically more favorable (29, p. 424).

Question arises, of course, as to why the hydrolysis of the second ligand should proceed at a reaction rate which is slower than that for the first hydrolysis reaction. The answer to this question lies with the trans-effect of the chloride as compared to the hydroxide, as well as with the nature of the two complexes. Little work has been done with the hydroxy complexes of Pt(II), so there is little other experimental work to compare the trans labilizing influence of these two ligands. That such a difference should exist can be surmised by other considerations, however. Comparison of the ultraviolet spectrum for t-[Pt(NH3)2Cl2] and t-[Pt(NH3)2Cl(OH)] as given in Fig. 3 above shows that the replacement of a chloride by an hydroxide causes the absorption peaks of the complex to shift to higher frequencies, which means that the crystal field splitting due to the hydroxide ligand is greater than that for the
chloride—a result which is expected from spectrochemical series (7, p. 27). Because the formation of the intermediate involves the formation of an additional bond to the Pt(II), in the case where there is a greater splitting of the energy levels there is a greater energy required for the formation of that bond, all other factors being the same. In addition, the polarizability and capacity to form π-bonds to some degree with the Pt, which are found more pronouncedly in the chloride ligand than in the hydroxide, are germane to explaining why the rate for the one reaction should be faster than the reaction rate for the other. Consideration of the thermodynamic properties of the two reactions leads to a similar conclusion. The lower activation energy for the first hydrolysis reaction would indicate that it should be a more favored reaction in this respect than the second hydrolysis reaction; the entropy of activation being negatively less for the first reaction would indicate a higher probability for the formation of the transition state for this reaction than for the second reaction.

Comparison of the base hydrolysis of $[\text{Pt(NH}_3\text{)}_2\text{Cl}_2]$ with the base hydrolysis of $[\text{PtCl}_4]^-$ is of interest because the ultraviolet spectrum of each reveals that there is a lower ligand field strength for $[\text{PtCl}_4]^-$ . Comparison of the thermodynamic properties of the reactions—18.2 kcal activation enthalpy for the reaction of $[\text{PtCl}_4]^-$ with base, with a rate constant of $3.81 \times 10^{-5}$ sec$^{-1}$ (10)—shows that the first base hydrolysis reaction of the trans-complex has an activation energy approximately the same as that of the base hydrolysis of the tetrachloroplatinate(II), but that the reaction rate for the trans-complex is higher.
That there is a significant difference in the entropies of activation would indicate that there is a higher probability for the formation of the intermediate in the case of trans-complex, but not too much reliance can be put in such a relatively small difference because of the inherent difficulty in obtaining highly accurate thermodynamic data. If the entropies of activation do reflect a difference in the probability of forming the intermediate for each of the complexes, then part of the difference of reaction rate can be attributed to the difference in the solvation of the two intermediates. An additional explanation for the observed difference of reaction rates is the cis-effect of Grinberg (44). While the trans-effect is inadequate to explain the case under consideration because both of the reactions involve a trans chloride, and, although the leaving group can be a determinant in the reaction rate, both of the complexes have the same leaving group, the modification of the trans-effect found in the cis-effect is important here.

As was stated in Chapter I, the trans-effect is regarded as being the product of two different factors, the stabilization of the intermediate because of the biphilic nature of the trans labilizing group, and the weakening of the bond of the leaving group due to the polarization of the trans labilizing group, or possibly a combination of both of these in the case of some ligands. The cis-effect is explained by Grinberg as the enhancement or reduction of the trans-effect, rather than any direct interaction with the leaving group. Possibly a better formulation of this would be to say that the ligands which form the inner coordination sphere of the Pt complex will contribute certain characteristics
to the complex no matter where they are located in the coordination plane, so that any ligand which has the properties associated with trans labilizing influence will exhibit these properties even while located cis to the leaving group, with the net result that a ligand which is trans to the leaving group will have its ability to interact with the central atom appropriately effected by the ligands in the cis position. As a general rule, whenever a good trans labilizing ligand is found cis to the reacting ligand, the reaction rate is less than that found when a poor trans labilizing ligand is located in the cis position. That the cis-effect is operative in the comparison of the reaction rates of the tetra-chloro and the trans-diammine is further evidenced by consideration of the rate of acid hydrolysis of the complexes, listed in Table 2. A consideration of the acid hydrolysis rates is justified by this reaction being the rate determining step in the reaction of all of these complexes with hydroxide. All of these reaction rates have been found to be independent of the ionic strength. In order that the various rate constants can be compared, the value of \( k_1/n \) has been included in Table 2, where \( n \) is the number of equivalent chlorides that can undergo the hydrolysis reaction. The only entry which is not self-explanatory is that for \([\text{Pt(NH}_3\text{)}\text{Cl}_3]^-\), because it contains nonequivalent chlorides; the reaction of the two chlorides which are cis to the ammine are designated \( k_c \), while the reaction of the chloride trans to the ammine is designated by \( k_t \).

Comparison of the reaction rates for the series \([\text{PtCl}_4^-]\), \( k_c \) for \([\text{Pt(NH}_3\text{)}\text{Cl}_3]^-\), and \( k_t \) for \([\text{Pt(NH}_3\text{)}_2\text{Cl}_2]^-\), and for the series \( k_t \) for
[Pt(NH₃)Cl₃]⁻, [Pt(NH₃)₂Cl₂], and [Pt(NH₃)₃Cl]⁺ shows that the substitution of an ammine for a chloride in the cis position yields an approximate doubling of the reaction rate for acid hydrolysis. That this is not the result of the charge on the complex is indicated by the independence of these reactions towards large increases in ionic strength of the solution in which the reaction is occurring (9), and by the comparison of the rates of negatively charged complexes with positively charged—coulombic effects would be of much greater magnitude than any differences noted here. A further comparison of kₜ for [Pt(NH₃)Cl₃]⁻ with [PtCl₄]⁻, kₒ for [Pt(NH₃)Cl₃]⁻ with [Pt(NH₃)₂Cl₂], and of t⁻ [Pt(NH₃)₂Cl₂] with [Pt(NH₃)₃Cl]⁺ shows that substitution of an ammine ligand by a chloride ligand in the trans position to the leaving ligand causes approximately a doubling of the reaction rate (the value of the adjusted reaction rate for the tetrachloro is slightly out of line in these comparisons but not by too great a magnitude). All of this seems to indicate that there is a factor of 2 or 0.5 involved whenever a chloride ligand is substituted by an ammine ligand, depending on whether the substitution is in the trans or the cis position to the reacting ligand. Whether this relationship is just fortuitous or is a pattern followed by all of the groups in their labilizing influence is a matter requiring more consideration, because there is a lack of systematic studies of the various series of Pt(II) complexes.

Some extensions of the present study which would seem to be apparent are the following: the measurement of the acid hydrolysis rates for t⁻ [Pt(NH₃)₂(H₂O)Cl] and t⁻ [Pt(NH₃)₂(OH)Cl] — in this consideration
there is some interest to see whether the rates will be the same, because some unpublished spectra (10) show that the crystal field energy for the aquo complex is less than that for the hydroxide; a study of the effect of substituting various other amines for ammonia in the trans-complex, and among these some ligands which would cause steric hindering of the axial positions of the complex; the determination of the effect of various solvents on the rate of reaction and the mechanism of the base hydrolysis; and a comprehensive treatment of the subsequent reactions which are occurring in the reaction system studied herein.
VI. LITERATURE CITED


