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Kinetics of ligand substitution for platinum(II) complexes

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KINETICS OF LIGAND SUBSTITUTION FOR PLATINUM(II) COMPLEXES

by

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Dean of Graduate College

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Ames, Iowa

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TABLE OF CONTENTS

I. INTRODUCTION

The purpose of this research has been to investigate the kinetics of the reaction of aqueous ammonia with the tetrachloroplatinate(II) ion. This work was a continuation of the studies of the chloro-ammine-platinum(II) series previously begun in this Laboratory (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11).

The chloro-ammine-platinum(II) series has been studied for over a hundred years. In 1840, Reiset (12) first prepared what is now called trans-dichlorodiammineplatinum(II). This compound is also sometimes called "Reiset's salt". Five years later Peyrone (13) prepared a compound with the same composition but with different properties. This compound is now called cis-dichlorodiammineplatinum(II) or sometimes referred to simply as "Peyrone's salt".

Later Jorgenson (14) also prepared both of these compounds. He discovered that different products were formed when substitution reactions of the following type were undertaken.

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

$$[PtX_4^{=}] + 2A \longrightarrow [PtA_2X_2] + 2X^- \qquad (I.2)$$
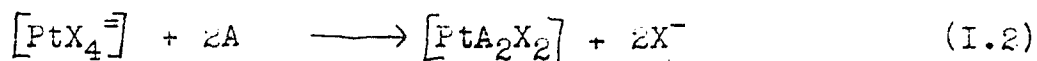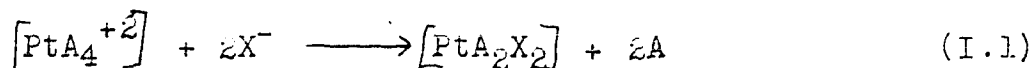
In the above reactions A was ammonia or an organic amine, while X^- was a halide. In 1893, Werner (15) proposed that these compounds were the cis and trans isomers of each other. He postulated that the amine and the halide ligands were in a square planar arrangement about the central platinum atom.

It has since been shown that this is the normal configura-
tion for all platinum(II) complexes, but it was some time be-
fore acceptance of this idea was complete. Werner's theory
was based only on chemical evidence and Reihlen and Nestle
(16) claimed in 1926 that trans-dichlorodiammineplatinum(II)
was only the dimeric form of cis-dichlorodiammineplatinum(II).
Drew et al. (17) claimed in 1932 to have discovered a third
isomer of dichlorodiammineplatinum(II). Since only two iso-
mers are possible under Werner's theory, this third isomer
would have disproved Werner's idea. Later work, however,
failed to confirm the existence of this third isomer and
finally structural studies (18) in 1954 confirmed Werner's
square planar configuration.

The aquation of platinum(II) compounds has been studied
by many people. Werner and Miolati (19) reported the reaction
of cis-dichlorodiammineplatinum(II) with water. They observed
the increased conductivity of the solution upon aging, and mis-
takingly interpreted the results as an ionization process. It
is now known that the following aquation reactions, or more
accurately the acid hydrolyses, were taking place.

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

$$(I.3)$$

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

$$(I.4)$$
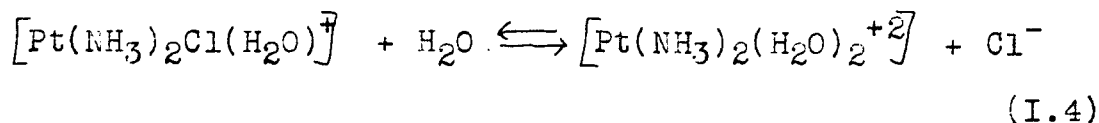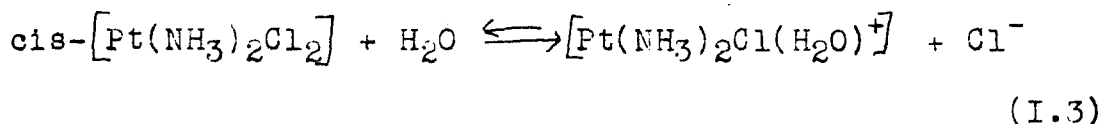
Other authors have also used conductivity measurements

to study the aquation of platinum(II) compounds. Among those to use this method were Drew et al. (17), Jensen (20), and King (21, 22). King worked with many compounds of the type $[Pt(NH_3)_2X_2]$ and $[Pt(NH_3)_3X]X$. He divided these compounds into two classes depending on the extent of hydrolysis which took place within a short time of dissolving the compounds. He found that when X was Cl^-, Br^-, or NO_2^-, the compounds acted as non-electrolytes in the case of the diamines and as salts of univalent cations in the triamines. When X was NO_3^-, $SO_4^=$, or picrate, he found complete or nearly complete hydrolysis in all cases.

Yakshin (23) studied the hydrolysis of cis- and trans-dithiosulfatoplatinate(II). He found that the rate of hydrolysis of the cis isomer was much greater than for the trans isomer.

The aquation of $[PtCl_4]^=$ has been studied by Grantham et al. (1). They used radioactive tracers to follow the exchange of chloride between the complex and the solution. They observed that the exchange could be explained by an acid hydrolysis mechanism with a direct, chloride independent, exchange occurring with $[PtCl_3(H_2O)]^-$.

Sanders and Martin (5) later restudied this reaction and found that it was necessary to include the second aquation product, $[PtCl_2(H_2O)_2]$, in the reaction mechanism. They determined equilibrium constants for both the first and second

aquation reactions which showed that for a 0.001 M solution of K_2PtCl_4, the equilibrium concentrations of the first and second aquation products were of the same order of magnitude with only small amounts of $[PtCl_4]^=$ remaining.

The *cis* and *trans* forms of dichlorodiammineplatinum(II) were studied by Reishus and Martin (6) and by Adams and Martin (8) respectively. For these compounds it was found that the rate of aquation of the *trans* compound was about four times that of the *cis* compound. For each of these compounds the exchange of radioactive chloride between the solution and the complex was followed, and the extent of hydrolysis was determined as a function of time by titration methods. The exchange of chloride in the *cis* compound was found to be first order in the complex and was independent of the chloride ion concentration in the solution. The exchange was attributed to an acid hydrolysis mechanism. The acid hydrolysis was also important for the chloride exchange of the *trans*-compound. In this compound, however, the rate law for the chloride exchange also contained a second term, which was first order in the chloride ion concentration. Thus for the *trans*-compound, both a direct exchange mechanism and an acid hydrolysis mechanism were needed to explain the kinetics for the chloride exchange.

The acid hydrolysis and chloride exchange for $[PtCl_3(NH_3)]^-$ were studied by Elleman et al. (3, 4). They observed that the chloride exchange was more rapid than could

be explained directly by the measured acid hydrolysis. This
was explained by the non-equivalence of the chlorides in
$[PtCl_3(NH_3)]^-$. The aquation rate for all three chlorides was
of the same order of magnitude; however the equilibrium con-
stants for the aquation reactions might differ for the
chloride ligands which are _cis_ or _trans_ to the ammonia group.
Thus the chloride exchange due to the aquation of the ligand
having the lowest equilibrium constant would be more rapid
during the early portion of the reaction. They also found it
necessary to include the second aquation product in order to
explain the observed exchange phenomena.

Aprile and Martin (9) studied the chloride exchange for
$[PtCl(NH_3)_3]^+$. They found that the exchange was dependent on
the chloride concentration in solution. Thus a second order
reaction between the complex and chloride was needed in order
to explain the observed results.

Grinberg and Filinow (24) studied the exchange of bromide
in $[PtBr_4]^=$ using bromine-80 as a tracer. This work was ex-
tended by Grinberg and Nikol'skaya (25). They observed reac-
tions of the type,

$$[PtX_4]^= + X^{*-} \rightleftharpoons [PtX_3X^*]^= + X^- , \qquad (I.5)$$
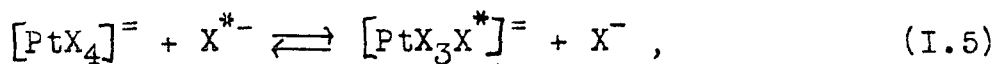
where X was CN^-, I^-, Br^-, or Cl^-. They found that the ex-
change rates were in the order: CN^- I^- Br^- Cl^-. The
stabilities of these complexes toward dissociation were in the
same order, with the cyanide being the most stable. In other
words the ΔF^O's for the reaction

$$4X^-(aq.) + Pt^{+2}(aq.) \longrightarrow [PtX_4]^= (aq.) \qquad (I.6)$$
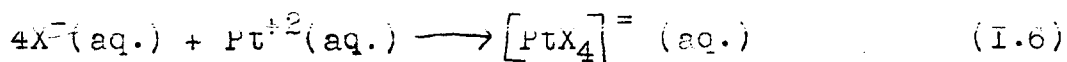
were in the order $Cl^- > Br^- > I^- > CN^-$. Thus they claimed the exchange could not be explained on the basis of a simple dissociation mechanism.

Many things have been found to catalyze the reactions of platinum complexes. Rich and Taube (26) have shown that oxidizing agents like $[Fe(CN)_6]^{-3}$ and $[IrCl_6]^=$ greatly increased the chloride exchange rate of $[PtCl_4]^=$. They concluded from this that the reaction proceeded through Pt(III) as an intermediate with a very high lability.

Ultraviolet light has also been shown in many cases to affect the reaction rate of platinum complexes. Rich and Taube (26) have shown that the chloride exchange in $[PtCl_6]^=$ is greatly accelerated in the presence of light, although the exchange in $[PtCl_4]^=$ does not seem to be so strongly affected. In Pt(II) compounds, Adamson[1] has indicated that the aquation of cis-$[Pt(NH_3)Cl_2]$ and $[PtCl_4]^=$ is accelerated by the use of intense light sources. Grinberg (27) found that the reaction of $K_2 PtBr_4$ with ammonia is strongly accelerated in the presence of light, while the ammoniation of $[PtCl_4]^=$ and $[PtCl_3(NH_3)]^-$ were not similarly affected.

Grinberg, with his coworkers (27, 28, 29, 30), have studied the reactions of $[PtCl_4]^=$, $[PtBr_4]^=$, $[PtCl_3(NH_3)]^-$,

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[1]Arthur Adamson, Los Angeles, California. Photochemistry of platinum complexes. Private communication. 1961.

$[PtCl(NH_3)_3]^+$, $[PtBr_3(NH_3)]^-$, and $[PtCl_3(py)]$, with hydroxide, ammonia, and pyridine. They found the reaction of these compounds with amines to be second order reactions. The reaction of these compounds with hydroxide, which is often referred to as alkaline hydrolysis, were found to be first order, the rate depending only on the concentration of the complex. They found the rate for the alkaline hydrolysis to be very nearly equal to the rate for the acid hydrolysis. They therefore described the reaction with hydroxide as consisting of two steps. A slow aquation reaction was followed by the rapid neutralization of the acidic proton in the aquo species to form the corresponding hydroxo-complex.

Taube (31) has classified the complex ions according to the rate of their substitution reactions. He arbitrarily defines those ions as labile for which the reactions are essentially complete within less than one minute. All other ions he considers as inert. Under this definition most Pt(II) complexes would be inert. Taube correlated the reactivity of various octahedral complexes with their electronic structure which in turn could frequently be inferred from their magnetic characteristics. As a general rule it is found that a central atom with a relatively stable unoccupied low energy orbital will be labile. In some cases an orbital becomes available through the pairing of electrons into a single orbital. Thus the spin free complexes of cobalt(III), such as $[Co(H_2O)_6]^{+3}$,

are labile as would be predicted from the presence of unpaired electrons as shown by magnetic susceptability data. The spin paired complexes of complexes of cobalt(III), however, are inert. In this case the first unoccupied orbital has an energy so high that it is more profitable to crowd the electrons in the lower orbitals. This feature implies that the substitution mechanism involves the formation of an additional bond to give a co-ordination number of seven in the transition state if the energy cost of the necessary additional orbital is not too high.

The *trans* effect has been studied for many years. In 1926 Chernyaev (32) noticed that negative groups in platinum(II) complexes caused the ligands in the position *trans* to this negative group to become more reactive than those in the *cis* position. With this rule it is possible to predict whether the *cis* or *trans* isomer will result from a given reaction. For example, if $\left[Pt(NH_3)Cl_3\right]^-$ is reacted with ammonia, *cis*-$\left[PtCl_2(NH_3)_2\right]$ will result since chloride is a stronger *trans* director than ammonia. The *trans* effect acts through kinetic rates and not through chemical equilibrium since *trans*-$\left[PtCl_2(NH_3)_2\right]$ is formed by the reaction of $\left[Pt(NH_3)_4\right]^{+2}$ with chloride.

Grinberg (33) was one of the earlier workers to propose a structural mechanism for the *trans* effect. He postulated that the bond *trans* to an electronegative group was weakened

due to the induced dipole moment. For better results the permanent dipole moment, the electrical charge, and the size of the ligands should also be considered in order to determine the total electrical potential in the vicinity of the trans group.

Grinberg's theory works reasonably well for ligands having no π bonding character. However the increase in reactivity of a group due to the trans effect is not always due to the weakening of the bond to the ligand trans to that of the trans-directing group. In some instances it has been shown that this bond is actually strengthened. Chatt et al. (34) explain this on the basis of a bimolecular S_N2 mechanism. Since substitution in platinum(II) compounds is nucleophilic in nature, a decrease in the electronic cloud surrounding the leaving group should increase the reaction rate by facilitating the approach of the entering group. Let us consider the ligands of the complex to be in the xy plane, with the x-axis directed toward the π bonded ligand. The π bonding will cause the angular probability density of the electrons in the d_{xz} orbitals of the platinum atom to be shifted toward the bonding ligand, with a resulting decrease in electronic density in the lobes directed toward the trans position. Thus ligands capable of π bonding should have a high trans effect. Orgel (35) independently proposed the same mechanism to account for the trans effect of π bonding groups. He used

a trigonal bipyramid for the transition state.

Chatt et al. (34) have given the following series as being the approximate order of the trans directing power of various ligands. $H_2O < OH^- < NH_3 \approx R < $ pyridine $ < Cl^- < Br^- < NCS \approx I^- \approx NO_2^- \approx SO_3H^- \approx PR_3 \approx R_2S \approx SC(NH_2)_2 < NO \approx CO \approx C_2H_4 \approx CN^-$

Bannerjea et al. (36) investigated the effect of the reactant on the rate of reaction of various platinum(II) complexes. They found that the reactions with a given complex could be divided into two classes. The first was a slow first order reaction, the rate depending only on the concentration of the complex. All reactions of this type had approximately the same rate constant for a given complex. The second class of reactions were of second order, the rate being proportional to both the complex and the reactant. The rates for these reactions were much greater than for those of the first class. In general they found the reactants for the second order reactions to have high trans directing properties, while the reactants for the first order reactions had low trans effects. They assumed that π bonding in the transition state for the second order reactions would help to stabilize the intermediate complex and thus partially counteract the change in crystal field stabilization energy in going from the square planar configuration to a trigonal bipyramid.

Grinberg (29, 30) cites evidence for a "cis" effect. He shows that the reaction of a leaving group is influenced by

the group _cis_ to it as well as the _trans_ group. As an example
he points out that the reaction of ammonia with $[PtCl_3(NH_3)]^-$
is much faster than the reaction of ammonia with $[PtCl_4]^=$.
The _cis_ effect seems to have its largest influence on systems
which also have a large _trans_ effect. Grinberg explains the
cis effect as a modification of the _trans_ effect. The _cis_
groups alter the influence of the _trans_ group on the reaction
rate. For instance, a π -bonding group in the _cis_ position
will compete with a π -bonding group in the _trans_ position for
the π -bonding ability of the platinum atom, and thus decrease
the _trans_ directing strength of the _trans_ group.

Basolo and Pearson (37), in their book, have proposed a
mechanism for substitution in square planar compounds. The
mechanism is a slight modification of the theories of Chatt
(34) and of Orgel (35). If either the reactant or the orig-
inal complex contains a π bond, a reaction intermediate with
a trigonal bipyramid structure will be stabilized. The trans-
ition state will then be as follows, with X and Y being the
leaving and entering groups respectively. The L, X, and Y
groups form a plane which includes the platinum atom, with the
A groups being above and below this plane.
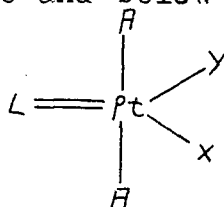
The transition state is stabilized by the π bonding in

a similar manner to that described earlier in Chatt's (34)

explanation of the _trans_ effect.

Basolo (37) suggested the following mechanism for the

substitution in the square planar compounds of platinum(II).

S solvent

- - - - weak bond
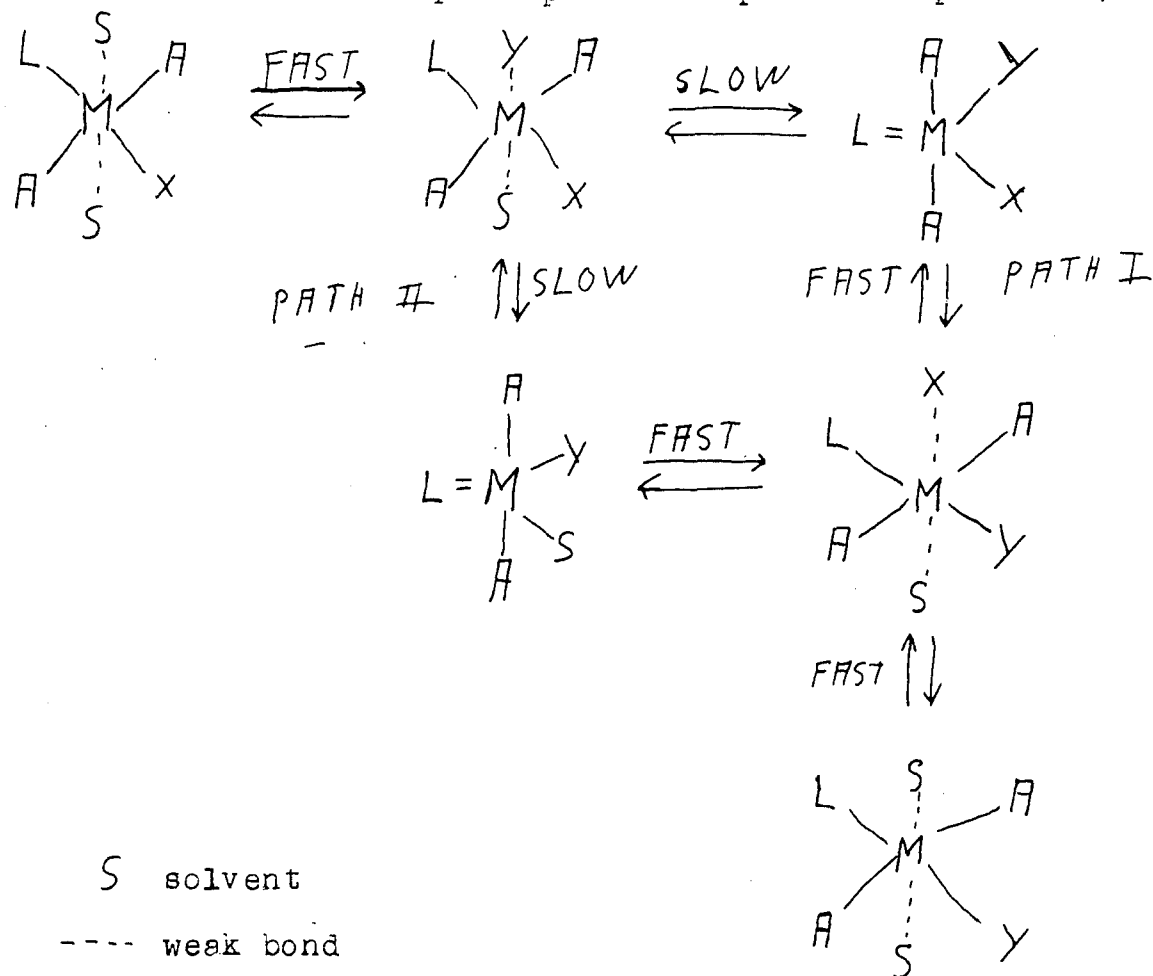
According to this mechanism the reaction should be bi-

molecular with a first order dependence on the entering group.

However in some cases water may act initially as the reactant

with a further immediate reaction with another reagent, so

that the overall reaction is not dependent on the concentration

of the eventual reagent. This latter possibility is necessary in order to account for the fact that the reactions of platinum(II) complexes may be either first or second order, or even a mixture of the two.

14

II. EXPERIMENTAL

A. Materials

1. Pt

The platinum used in this work was obtained either in the
form K_2PtCl_6 or as $H_2PtCl_6 \cdot 6H_2O$. Platinum was also obtained
from the recovered wastes of previous experiments. To purify
these products from iridium, which might have a catalytic
effect on the reactions to be studied, the following procedure
was used. The platinum compounds were dissolved in water, the
solution was made basic (pH 10) with sodium hydroxide, and the
platinum was then reduced to metallic platinum with hydrazine.
After coagulation, the platinum was dissolved in aqua regia
and evaporated to dryness three times with hydrobromic acid.
The H_2PtBr_6 was taken up in a minimum amount of hot water
from which K_2PtBr_6 was precipitated by the use of an excess
of KBr. The K_2PtBr_6 was then recrystallized three times with
hot water.

2. K_2PtCl_4

The K_2PtBr_6, previously purified from iridium by the
above procedure, was dissolved in water. The solution was
then made basic with sodium hydroxide and Pt^o precipitated
with hydrazine. The Pt^o was washed with water, hydrochloric
acid, and nitric acid, and then dissolved in aqua regia.

After evaporating to dryness three times with HCl, K_2PtCl_6 was precipitated by adding excess KCl. The K_2PtCl_6 was reduced to K_2PtCl_4 by refluxing it with a stoichiometric amount of $K_2C_2O_4$. The K_2PtCl_4 was recovered by cooling the solution in an ice bath before filtering. It was usually necessary to recrystallize the impure K_2PtCl_4 from water at least ten times before the desired purity was obtained. The ultraviolet absorption spectrum of a preparation in solution served as a criterion for its purity. Special attention was paid to the depth of the valley at 293 mμ, since impurities had a strong tendency to increase the optical density at this wave length. The highest value obtained for the ratio of the O.D. at the peak at 331 mμ to the above valley was 4.0.

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

Cis-$[Pt(NH_3)_2Cl_2]$ was prepared by a method similar to that devised by Lebedinskii and Golovaya (38). Six grams of K_2PtCl_4 and six grams of KCl were dissolved in a 5% solution of $(NH_4)(C_2H_3O_2)$ and refluxed for half an hour. The impure cis-$[Pt(NH_3)_2Cl_2]$ was recovered by filtering the cold solution, after which it was recrystallized several times from water.

4. Water

The water used in these experiments was redistilled from alkaline permanganate solutions.

3. Other reagents

The sulfamic acid, which was used to standardize the ammonia solutions, was purchased from the Matheson Company. All other chemicals were reagent grade chemicals obtained from either the Baker Chemical Company or the Fisher Scientific Company.

B. Equipment

1. Constant temperature baths

The constant temperature baths used in this work were manufactured by the Sargent Company. Intermittent heaters balanced refrigerated cooling coils to keep the temperature within $\pm$ 0.1° C.

2. Spectrophotometers

Most of the spectra for this work were obtained with the Cary Recording Spectrophotometer, Model 12, manufactured by the Applied Physics Corporation. A few spectra were taken with the Beckman ratio Recording Spectrophotometer, Model DK-2. With both of these machines it was impossible to control the temperature of the cell compartment while spectra were recorded. Silica cells were used with path lengths of 20, 50, or 100 mm.

5. Computer

An IBM 704 computer, operated by the University of Wisconsin, was used in the calculation of the rate constants. An IBM 66 printing data transceiver between Madison, Wisconsin, and Ames, Iowa, made possible the rapid transferance of information on IBM cards. This permitted the efficient use of the computer while remaining in Ames.

C. Procedures

1. Spectra determinations

In order to determine the spectra of $[PtCl_3(H_2O)]^-$, $[PtCl_2(H_2O)_2]$, $[PtCl_3(OH)]^=$, and $[PtCl_2(OH)_2]^=$, solutions of K_2PtCl_4 at different concentrations were allowed to age at 25° C. for about one day to insure equilibrium. Ultraviolet spectra for these solutions were then recorded. The solutions were made basic with NaOH and the spectra were redetermined immediately. With the use of the known equilibrium constants and with the assumption of only a slow aquation of $[PtCl_3(OH)]^=$ and $[PtCl_2(OH)_2]^=$, the spectra of $[PtCl_3(H_2O)]^-$, $[PtCl_2(H_2O)_2]$, $[PtCl_3(OH)]^=$ and $[PtCl_2(OH)_2]^=$ were calculated as shown in the following section.

2. <u>Kinetic runs</u>

The reaction of ammonia with $[PtCl_4]^=$ was studied by adding aqueous NH_3, previously standardized against sulfamic acid, to a freshly prepared solution of K_2PtCl_4. The ammonia and the water used to dissolve the K_2PtCl_4 had previously been allowed to come to equilibrium in a constant temperature bath of the desired temperature. Following the addition of the ammonia, which was taken as zero time, the solution was put back into the constant temperature bath. At intervals samples were withdrawn and their ultra-violet spectra were recorded immediately. Since the temperature of the samples were not controlled during the periods that they were introduced into the spectrophotometer, errors due to this cause were inevitable. These errors were probably least for the experiments at 25° C. and did not appear to lead to inconsistencies at this temperature. They did appear to be the source of some difficulty at other temperatures.

III. TREATMENT OF DATA

A. Spectra

In order to follow the kinetics of the reaction of $[PtCl_4]^=$ with aqueous ammonia, it was first necessary to obtain the ultraviolet spectrum for each of the species involved in the reaction. The spectra of $[PtCl_4]^=$, cis-$[Pt(NH_3)_2Cl_2]$, and $[Pt(NH_4)_4]^{++}$ were obtained directly from freshly prepared solutions of pure compounds. The spectra used for $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(OH)]^-$ were from the work of Elleman et al. (3, 4). The spectrum of $[Pt(NH_3)_3Cl]^+$ was obtained from Aprile and Martin (9).

Since it was impossible to isolate pure $PtCl_3(H_2O)^-$, $[PtCl_2(H_2O)_2]$, $[PtCl_3(OH)]^=$, or $[PtCl_2(OH)_2]^=$, the spectra for these species had to be obtained from solutions of mixtures. Solutions of K_2PtCl_4 at various concentrations were allowed to age at 25° C. for about one day. Equilibrium constants were given by Sanders and Martin (5) as follows,

$$[PtCl_4]^= + H_2O \rightleftharpoons [PtCl_3(H_2O)]^- + Cl^- \qquad K_1 \quad \text{(III.1)}$$

$$[PtCl_3(H_2O)]^- + H_2O \rightleftharpoons [PtCl_2(H_2O)_2] + Cl^- \quad K_2 \quad \text{(III.2)}$$
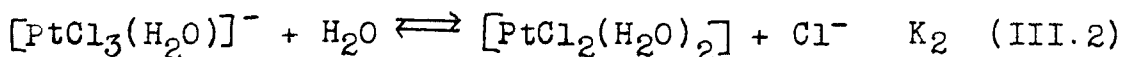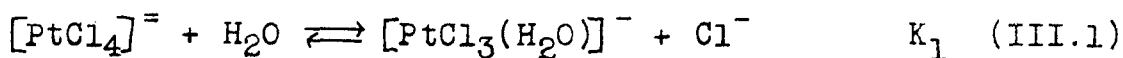
where

$$K_1 = 3.0 \times 10^{-2}$$
$$K_2 = 1.0 \times 10^{-3}.$$

The equilibrium constants cited were for zero ionic strength and had to be corrected for the activity coefficients

as the ionic strength changed. The ionic strength is defined
by

$$s = 1/2 \sum_i m_i z_i ,$$

where "m_i" is the molarity and "z_i" is the charge of the ith
ion.

Under the conditions of the experiments only ionic
strengths of about .04 or less were used. In reaction III.2
both reactants and products have one neutral molecule and one
ion with a single negative charge. Thus to a first approxima-
tion the ratio of the activity coefficients, and thus the
equilibrium constant, should be approximately independent of
ionic strength for this reaction. For reaction III.1, how-
ever, the products have different charges from the reactants.
Thus the ratio of the activity coefficients are expected to
vary with the ionic strength even at these low ionic strengths.
Γ_1 is defined

$$\Gamma_1 = \frac{\gamma_{[PtCl_4^=]}}{\gamma_{[PtCl_3(H_2O)]} \, \gamma_{Cl^-}} ,$$

where the γ's are the activity coefficients for the indicated
ions.

To determine Γ_1 as a function of ionic strength, the
results of Pinching and Bates (39) were used. They determined
a value for the second dissociation constant of oxalic acid
in solutions containing chloride ions by measuring the electro-
motive force of a cell without a liquid junction. The system

studied was

$$Pt; \; H_2(g), \; KHC_2O_4(m_1), \; Na_2C_2O_4(m_2), \; NaCl(m_3), \; AgCl(s); \; Ag.$$

The relation between the second dissociation constant and the electromotive force of the cell was taken as

$$pK_2 = -\log K_2 = (E-E^O)F/2.3026RT + \log(m_1m_3/m_2) + \log(f_1f_3/f_2)$$

$$(III.4)$$

where

E^O = standard electromotive force,

E = measured electromotive force,

R = gas constant,

T = temperature of cell,

m_1 = molality of $[HC_2O_4]^-$,

m_2 = molality of $[C_2O_4]^=$,

m_3 = molality of Cl^-,

f_1 = activity coefficient of $[HC_2O_4]^-$,

f_2 = activity coefficient of $[C_2O_4]^=$,

f_3 = activity coefficient of Cl^-.

K_2 was defined by the equation

$$K_2 = (a_{H^+})(a_{[C_2O_4]^=})/(a_{[HC_2O_4]^-}) \; ,$$

where

a_{H^+} = activity of H^+,

$a_{[C_2O_4^=]}$ = activity of $[C_2O_4]^=$,

$a_{[HC_2O_4]}$ = activity of $[HC_2O_4]^-$.

Pinching and Bates (39) gives tables of $\log(f_1f_3/f_2)$ as

a function of molality. From the calculated ionic strengths

obtained from the listed molalities from this table, a graph,

Figure 1, was drawn of the value of (f_1f_3/f_2) vs. the square

root of the ionic strength. The reciprocal of this value was

used as an approximation for the ratio of activity coeffi-

cients, Γ_1, since the ionic charges in both reactions were

the same.

The concentrations of the species in equilibrium with

$[PtCl_4]^=$ were calculated in the following manner.

Let

a = total concentration of platinum species in solution,

$x = [PtCl_3(H_2O)]^-$,

$y = [PtCl_2(H_2O)_2]$.

Since one chloride is replaced to form $[PtCl_3(H_2O)]^-$ and

two chlorides are replaced to form $[PtCl_2(H_2O)_2]$, the concen-

tration of chloride is given by

$$[Cl^-] = x + 2y . \qquad (III.5)$$

Substituting in the equations for the equilibrium constants

for reactions III.1 and III.2 we have

$$\Gamma_1 k_1 = x[Cl^-] / [PtCl_4^=] = x[Cl^-]/(a-x-y) , \qquad (III.6)$$
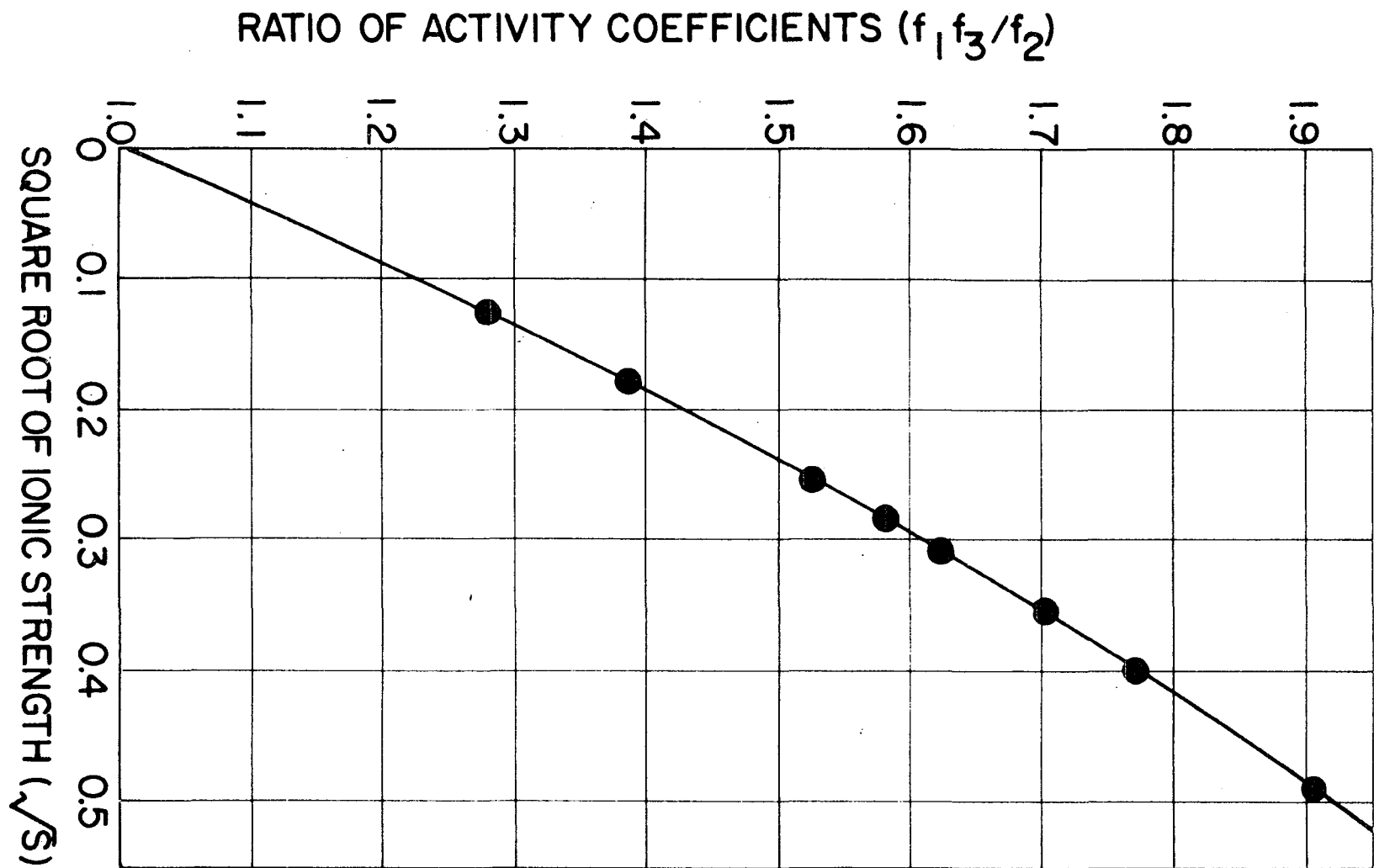
$$K_2 = y[Cl^-] /x . \qquad (III.7)$$

The elimination of x between equations III.5 and III.7 yields

$$K_2 = y[Cl^-] /([Cl^-] -2y) .$$

From this equation an explicit function for y may be obtained

as follows,

Figure 1. Ratio of activity coefficient function versus
square root of ionic strength

RATIO OF ACTIVITY COEFFICIENTS ($f_1 f_3/f_2$)

SQUARE ROOT OF IONIC STRENGTH ($\sqrt{S}$)

$$y = K_2 [Cl^-] / ([Cl^-] + 2K_2) \ . \qquad\qquad (III.8)$$

The quantity y may also be eliminated between equations III.5 and III.7. Solving the resulting equation yields

$$x = [Cl^-]^2 / ([Cl^-] + 2K_2) \ . \qquad\qquad (III.9)$$

Finally the expressions for x and y from equations III.8 and III.9 may be substituted into equation III.6 which upon rearrangement gives,

$$\Gamma_1 K_1 \ Cl^- \ (a-[Cl^-]) + \Gamma_1 K_1 K_2 (2a-[Cl^-]) = [Cl^-]^3 \ . $$

$$\qquad\qquad\qquad\qquad\qquad\qquad (III.10)$$

In order to determine the equilibrium concentrations of these species in an aged solution of K_2PtCl_4, an approximate value for the ionic strength was estimated. The value of Γ_1 was then obtained from Figure 1 and equation III.10 solved for $[Cl^-]$ by approximation methods. The concentrations of $[PtCl_3(H_2O)]^-$ and $[PtCl_2(H_2O)_2]$ were then obtained from equations III.9 and III.8. $[PtCl_4]^=$ was obtained by difference. A better value for the ionic strength was then calculated from this first approximation to the equilibrium concentrations. This new value for the ionic strength was used to give a better value for Γ_1 and the concentrations of the various platinum species were recalculated. This reiterative procedure was continued until agreement was reached between two successive calculations.

To obtain the ultraviolet spectra of $[PtCl_3(H_2O)]^-$ and $[PtCl_2(H_2O)_2]$, the spectra of several equilibrium solutions

of K_2PtCl_4 were recorded. The concentrations of $[PtCl_4]^=$, $[PtCl_3(H_2O)]^-$, and $[PtCl_2(H_2O)_2]$ were calculated by the above procedure. The optical density of the solution at any given wave length is given by

$$O.D./l = [PtCl_4^=] \; \epsilon_{[PtCl_4^=]} + [PtCl_3(H_2O)^-] \; \epsilon_{[PtCl_3(H_2O)^-]}$$

$$+ [PtCl_2(H_2O)_2] \; \epsilon_{[PtCl_2(H_2O)_2]} , \qquad (III.11)$$

where

l = path length,

ϵ_i = extinction coefficient for the species "i".

Using the known concentrations of $[PtCl_4]^=$ and the known spectrum for $[PtCl_4]^=$, the contribution due to $[PtCl_4]^=$ was subtracted from the total spectrum. Thus at any given wave length a linear equation containing the two unknowns,

$\epsilon_{[PtCl_3(H_2O)^-]}$ and $\epsilon_{[PtCl_2(H_2O)_2]}$, may be obtained from each of the spectra taken at different concentrations of K_2PtCl_4. The spectra obtained at the highest and the lowest concentration of K_2PtCl_4 were used in the calculation. The spectra of $[PtCl_3(H_2O)]^-$ and $[PtCl_2(H_2O)_2]$ were calculated at 2 $1/2$ $m\mu$ intervals using the set of equations and two unknowns that were obtained at each wave length.
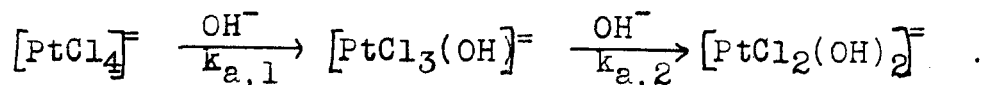
The spectra of $[PtCl_3(OH)]^=$ and $[PtCl_2(OH)_2]^=$ were evaluated in a similar manner. Equilibrium solutions of K_2PtCl_4 in distilled water were made basic with NaOH and the spectra recorded immediately. In the basic solution, the

$[PtCl_3(H_2O)]^-$ and $[PtCl_2(H_2O)_2]$ are converted immediately to $[PtCl_3(OH)]^=$ and $[PtCl_2(OH)_2]^=$ respectively. With the assumption that the reaction of these compounds with water or with hydroxide is negligible in the time required to record a spectrum, the concentrations of the hydroxo-complexes can thus be taken equal to the concentrations of the corresponding aquo-complexes. The spectra of $[PtCl_3(OH)]^=$ and $[PtCl_2(OH)_2]^=$ were then calculated in a manner similar to the calculation of the spectra of the aquo-complexes.

B. Treatment of Kinetic Data

The reaction scheme given in Figure 2 was considered for the reaction of K_2PtCl_4 with aqueous ammonia.

With all of these reactions occurring simultaneously, determination of all the individual rate constants from the observed spectra becomes difficult. Let us first consider only the basic aquation of $[PtCl_4]^=$. The rate constants for these reactions were studied by following the ultraviolet spectra of solutions of K_2PtCl_4 in 0.1 M NaOH. In the basic solution all the aquation products are converted immediately to the corresponding hydroxo-species. Thus in this system only the following net reactions take place;

$$[PtCl_4]^= \xrightarrow[k_{a,1}]{OH^-} [PtCl_3(OH)]^= \xrightarrow[k_{a,2}]{OH^-} [PtCl_2(OH)_2]^=$$

(III.12)

$$[PtCl_4]^= \xrightarrow[k_{1,a}]{NH_3} [PtCl_3(NH_3)]^- \xrightarrow[k_{2,a}]{NH_3} [PtCl_2(NH_3)_2] \xrightarrow[k_{3,a}]{NH_3} [PtCl(NH_3)_3]^+ \xrightarrow[k_{4,a}]{NH_3} [Pt(NH_3)_4]^{+2}$$

$OH^- \downarrow k_{a,1}$ $OH^- \downarrow k_{b,1}$ $OH^- \downarrow k_{c,1}$ $OH^- \downarrow k_{d,1}$

$$[PtCl_3(OH)]^= \xrightarrow[k_{1,b}]{NH_3} [PtCl_2(NH_3)(OH)]^- \xrightarrow[k_{2,b}]{NH_3} [PtCl(NH_3)_2(OH)] \xrightarrow[k_{3,b}]{NH_3} [Pt(NH_3)_3(OH)]^+$$

$OH^- \downarrow k_{a,2}$ $OH^- \downarrow k_{b,2}$ $OH^- \downarrow k_{c,2}$

$$[PtCl_2(OH)_2]^= \xrightarrow[k_{1,c}]{NH_3} [PtCl(NH_3)(OH)_2]^- \xrightarrow[k_{2,c}]{NH_3} [Pt(NH_3)(OH)_2]$$
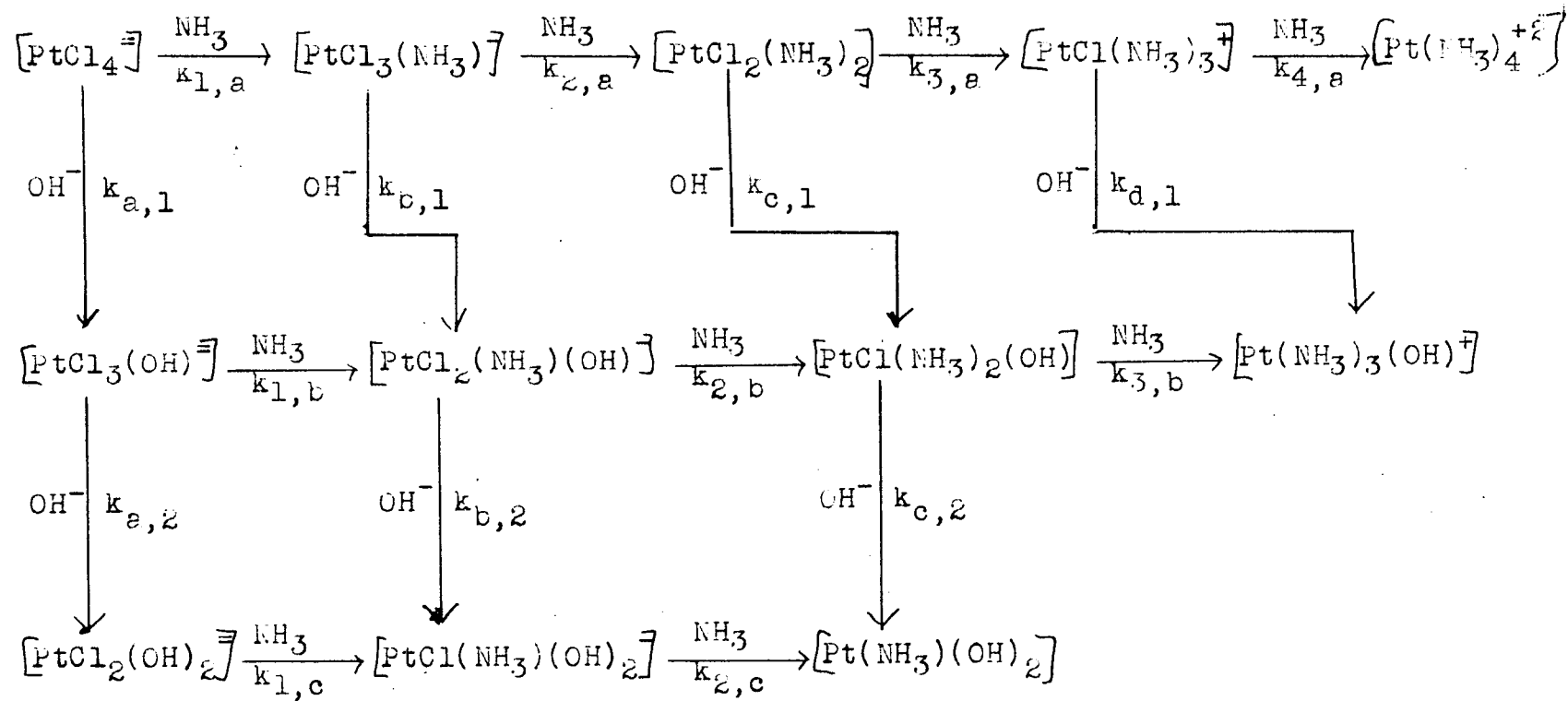
Figure 2. Reaction scheme for reaction of $PtCl_4^=$ with aqueous ammonia

As can be seen in Figure 7, the ultraviolet spectrum of $[PtCl_4]^=$ has a peak at 390 mμ while the extinction coefficients of the reaction products is nearly linear in wave length in the region between 375 and 405 mμ. Thus the height of the peak above the optical density at neighboring wave lengths can be taken as a measure of the $[PtCl_4]^=$ concentration in the solution. A line was drawn between the optical density at 405 mμ and the optical density at 375 mμ. The difference between this line and the optical density of the solution at 390 mμ was then assumed to be proportional to the concentration of $[PtCl_4]^=$. If in the reaction of $[PtCl_4]^=$, hydroxide is present in large excess so that a pseudo first order reaction may be assumed, the pseudo rate constant may be determined by plotting $\log[PtCl_4^=]$ against time. The pseudo rate constant is obtained from the initial slope of the straight line on the graph. As will be shown in the next section, this reaction rate is independent of the hydroxide concentration and is first order in $[PtCl_4]^=$ concentration.

Although the above method gives a very rough value for the rate constant $k_{a,1}$, errors were introduced due to the non-linearity of the reaction products in the region 375-405 mμ. Also it was impossible by this method to obtain a value for the rate of the second basic hydrolysis reaction $k_{a,2}$. To avoid these difficulties more elaborate methods of calculations

were used.

Let us again consider only the reactions as given in equation III.12. If at t=0 only $[PtCl_4]^=$ is present, and if we let a_0 equal the initial concentration of $[PtCl_4]^=$, solutions for the concentrations of the various species as a function of time are as follows:

$$[PtCl_4^=] = a_0 e^{-(k_{a,1})t} , \qquad (III.13)$$

$$[PtCl_3(OH)^=] = \frac{a_0(k_{a,1})(e^{-k_{a,1}t} - e^{-k_{a,2}t})}{(k_{a,2} - k_{a,1})} , \qquad (III.14)$$

$$[PtCl_2(OH)_2^=] = a_0 - [PtCl_4^=] - [PtCl_3(OH)^=] . \qquad (III.15)$$

If the concentrations of all the species involved were known, the optical density of the resulting solution could be calculated by summing the product of these concentrations with the corresponding extinction coefficients and multiplying the result by the path length of the cell. Estimates of the rate constants were made and the concentrations of the products calculated from these for the periods that the ultraviolet spectra were obtained. Using these values, the optical densities were calculated and compared to the results obtained experimentally. If the two did not agree, new estimates of the rate constants were made and the process repeated. Using trial and error methods, the rate constants were varied until the best fit to the experimental data was obtained.

Due to the uncertainties in the spectra of $[PtCl_3(OH)]^=$

and $\left[PtCl_2(OH)_2\right]^=$ it was difficult to obtain a good fit to the experimental data throughout the entire ultraviolet region using the above method. The peak in the spectrum of $\left[PtCl_3(OH)\right]^=$ at 365 mμ was considered to be the most reliable point in its spectrum. By neglecting the concentration of $\left[PtCl_2(OH)_2\right]^=$ formed during the early portion of the experiments, an infinite O.D. at this wave length was calculated on the basis of no further reaction following the formation of $\left[PtCl_3(OH)\right]^=$. The log of the difference between this O.D. and the experimental O.D. was plotted versus time. The rate constant for base hydrolysis of $\left[PtCl_4\right]^=$, $k_{a,1}$, was calculated from the initial slope of the above curve.

The rate constant for ammoniation of cis-$\left[PtCl_2(NH_3)_2\right]$ was studied by reacting pure cis-$\left[PtCl_2(NH_3)_2\right]$ with aqueous ammonia and following the ultraviolet spectrum of the solution. During the initial portion of the reaction, the following simplification of the reaction scheme may be used:

$$\text{cis-}\left[PtCl_2(NH_3)_2\right] \xrightarrow[k_{3,a}]{NH_3} \left[PtCl(NH_3)_3\right]^+$$

$$OH^-\Big\downarrow k_{c,1} \qquad\qquad\qquad\qquad (III.16)$$
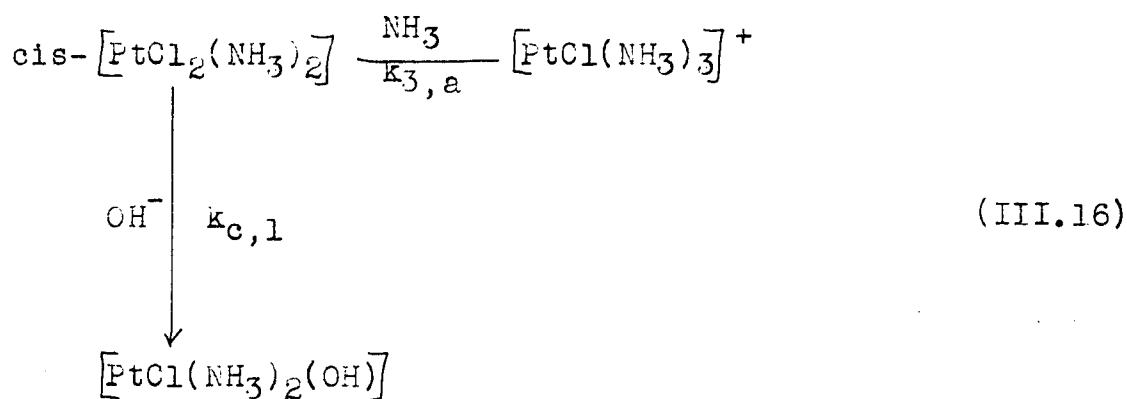
$$\left[PtCl(NH_3)_2(OH)\right]$$

Looking at the ultraviolet spectra for cis-$\left[PtCl_2(NH_3)_2\right]$ and $\left[PtCl(NH_3)_3\right]^+$, Figure 9, we see that the extinction

coefficients have widely separated values at 500 mμ. The optical density of the solution at this wave length was thus followed as a function of time. This data was used to calculate the rate constants as follows:

$$O.D./l = [PtCl_2(NH_3)_2] \, \epsilon_{[PtCl_2(NH_3)_2]}$$

$$+ [PtCl(NH_3)_3^+] \, \epsilon_{[PtCl(NH_3)_3^+]}$$

$$+ [PtCl(NH_3)_2(OH)] \, \epsilon_{[PtCl(NH_3)_2(OH)]} \qquad (III.17)$$

$$\frac{d[PtCl(NH_3)_3^+]}{dt} = [PtCl_2(NH_3)_2] \, k_{3,a} \, , \qquad (III.18)$$

$$\frac{d[PtCl(NH_3)_2(OH)]}{dt} = [PtCl_2(NH_3)_2] \, k_{c,1} \, , \qquad (III.19)$$

$$\frac{d[PtCl_2(NH_3)_2]}{dt} = - [PtCl_2(NH_3)_2] \, (k_{3,a} + k_{c,1}) \qquad (III.20)$$

At $t=0$,

$$c - [PtCl_2(NH_3)_2] = A_0 \, ,$$

and

$$[PtCl(NH_3)_3^+] = [PtCl(NH_3)_2(OH)] = 0 \, ,$$

$$\frac{[PtCl(NH_3)_3^+]}{[PtCl(NH_3)_2(OH)]} = \frac{k_{3,a}}{k_{c,1}} \qquad (III.21)$$

$$\frac{[PtCl(NH_3)_3^+]}{[PtCl(NH_3)_3^+] + [PtCl(NH_3)_2(OH)]} = \frac{k_{3,a}}{k_{3,a} + k_{c,1}} \qquad (III.22)$$

$$\frac{\left[PtCl(NH_3)_2(OH)\right]}{\left[PtCl(NH_3)_3^+\right] + \left[PtCl(NH_3)_2(OH)\right]} = \frac{k_{c,1}}{k_{3,a} + k_{c,1}} \qquad (III.23)$$

But,

$$A_0 = \left[PtCl_2(NH_3)_2\right] + \left[PtCl(NH_3)_3^+\right] + \left[PtCl(NH_3)_2(OH)\right] , \qquad (III.24)$$

or the equivalent expression,

$$\left[PtCl(NH_3)_3^+\right] + \left[PtCl(NH_3)_2(OH)\right] = A_0 - \left[PtCl_2(NH_3)_2\right] . \qquad (III.25)$$

Substituting this expression for $\left[PtCl(NH_3)_3^+\right] + \left[PtCl(NH_3)_2(OH)\right]$ into equations III.22 and III.23, we have,

$$\left[PtCl(NH_3)_3^+\right] = \frac{k_{3,a}(A_0 - \left[PtCl_2(NH_3)_2\right])}{k_{3,a} + k_{c,1}} , \qquad (III.26)$$

$$\left[PtCl(NH_3)_2(OH)\right] = \frac{k_{c,1}(A_0 - \left[PtCl_2(NH_3)_2\right])}{k_{3,a} + k_{c,1}} . \qquad (III.27)$$

Substitution of these quantities into III.17 yields,

$$\frac{O.D.}{l} = \left[PtCl_2(NH_3)_2\right] \epsilon_{PtCl_2(NH_3)_2}$$

$$+ \frac{k_{3,a}(A_0 - \left[PtCl_2(NH_3)_2\right]) \epsilon_{\left[PtCl(NH_3)_3^+\right]}}{k_{3,a} + k_{c,1}}$$

$$+ \frac{k_{c,1}(A_0 - \left[PtCl_2(NH_3)_2\right]) \epsilon_{\left[PtCl(NH_3)_2(OH)\right]}}{k_{3,a} + k_{c,1}} . \qquad (III.28)$$

Rearranging the right side of the above equation yields,

$$\frac{O.D.}{l} = \left[PtCl_2(NH_3)_2\right] \left\{ \epsilon_{[PtCl_2(NH_3)_2]} \right.$$

$$- \frac{k_{3,a}\ \epsilon_{[PtCl(NH_3)_3^+]} + k_{c,1}\ \epsilon_{[PtCl(NH_3)_2(OH)]}}{k_{3,a} + k_{c,1}} \Bigg)$$

$$+ \frac{A_o k_{3,a}\ \epsilon_{[PtCl(NH_3)_3^+]} + A_o k_{c,1}\ \epsilon_{[PtCl(NH_3)_2(OH)]}}{k_{3,a} + k_{c,1}} .$$

$$(III.29)$$

Further rearrangement of this equation yields,

$$\frac{O.D.}{l} - \frac{A_o k_{3,a}\ \epsilon_{[PtCl(NH_3)_3^+]} + A_o k_{c,1}\ \epsilon_{[PtCl(NH_3)_2(OH)]}}{k_{3,a} + k_{c,1}}$$

$$= \left[PtCl_2(NH_3)_2\right] \left\{ \epsilon_{[PtCl_2(NH_3)_2]} \right.$$

$$- \frac{k_{3,a}\ \epsilon_{[PtCl(NH_3)_3^+]} + k_{c,1}\ \epsilon_{[PtCl(NH_3)_2(OH)]}}{k_{3,a} + k_{c,1}} \Bigg) .$$

$$(III.30)$$

Let

$$\frac{(O.D.)'}{l} = \frac{A_o k_{3,a}\ \epsilon_{[PtCl(NH_3)_3^+]} + A_o k_{c,1}\ \epsilon_{[PtCl(NH_3)_2(OH)]}}{k_{3,a} + k_{c,1}} .$$

$$(III.31)$$

Equation III.30 then reduces to

$$\frac{(O.D.)}{l} - \frac{(O.D.)'}{l} = \left[PtCl_2(NH_3)_2\right] \left\{ \epsilon_{[PtCl_2(NH_3)_2]} \right.$$

$$- \frac{k_{3,a}\ \epsilon_{[PtCl(NH_3)_3^+]} + k_{c,1}\ \epsilon_{[PtCl(NH_3)_2(OH)]}}{k_{3,a} + k_{c,1}} \Bigg) . \quad (III.32)$$

The expression on the left hand side of equation III.32 is thus proportional to the concentration of cis-$[PtCl_2(NH_3)_2]$. If the log of this expression could be plotted against time, the initial slope of the line would be proportional to the total pseudo first order rate constant for the reaction of cis-$[PtCl_2(NH_3)_2]$, if the reaction followed a pseudo first order reaction kinetics under the conditions of the experiment. Since this rate is the sum of two reactions, the pseudo first order rate constant for the ammoniation of cis-$[PtCl_2(NH_3)_2]$ may be calculated by subtracting from this total rate the known rate for the aquation of cis-$[PtCl_2(NH_3)_2]$ as given by Reishus and Martin (6).

(O.D.)$'$ is the value for the O.D. that would result at infinite time if the first reaction products, $[PtCl(NH_3)_2(OH)]$ and $[PtCl(NH_3)_3^+]$, did not undergo further reactions. Since this is not the case, it is not possible to obtain this quantity directly from experiment, and reiteration methods were employed. Since the solutions contained high concentrations of aqueous ammonia, the ammoniation rate was about ten times the rate of aquation. Therefore, to a first approximation, the aquation may be neglected. Equation III.30 then reduces to

$$\frac{O.D.}{1} - A_0 \quad \epsilon_{[PtCl(NH_3)_3^+]}$$

$$= [PtCl_2(NH_3)_2] \left\{ \epsilon_{[PtCl_2(NH_3)_2]} - \epsilon_{[PtCl(NH_3)_3^+]} \right\} .$$

$$(III.33)$$

The log of the left hand side of this equation was then plotted against time and the first approximation to the rate constant obtained from the slope. This value was then used to calculate a value of $(O.D.)'$ from equation III.31. Using equation III.3z, the log of $(O.D.)/1 - (O.D.)'/1$ was plotted against time and a better value for the rate constant obtained from the slope. A new value for $(O.D.)'$ was then calculated and the rate constant recalculated in a similar fashion. The process was repeated until agreement was reached between two successive calculations. Two or three reiterations were usually sufficient to obtain an accurate value.

The ammoniation of $[PtCl_4]^=$ was studied by following the ultraviolet spectrum of 0.01 M solutions of K_2PtCl_4 in various concentrations of ammonia. During the initial portion of the reaction, the principle reactions taking place are

$$[PtCl_4^=] \xrightarrow[k_{1,a}]{NH_3} [PtCl_3(NH_3)^-]$$

$$OH^- \downarrow k_{a,1}$$

$$[PtCl_3(OH)^=] .$$

$$(III.34)$$
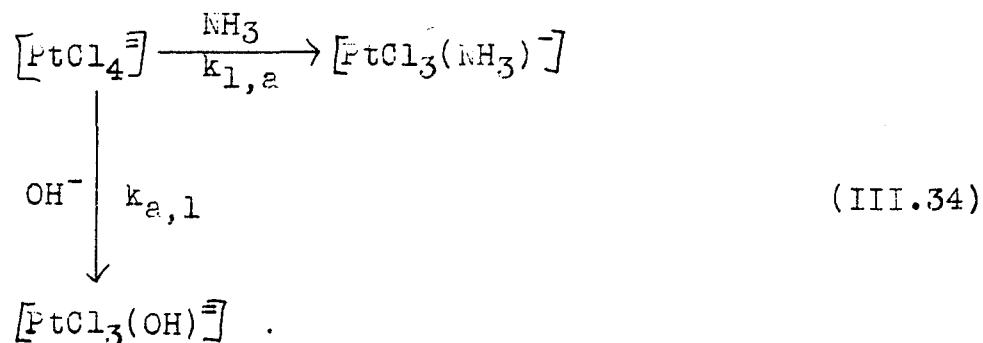
A reasonably good value for the rate constant, $k_{1,a}$, may be obtained in a manner similar to the determination of the basic aquation rate, $k_{a,1}$. Again the assumption was made that the spectra of the principal reaction products was linear in the region 375-405 mμ. The log of the difference between the optical density of the solution at 390 mμ and the average of the optical densities at 375 mμ and 405 mμ was plotted versus time. The slope of the straight line on this plot then gave the pseudo first order rate constant for the decrease in $[PtCl_4]^=$ concentration. These pseudo first order rate constants were plotted versus the concentration of NH_3. The slope of this curve gives the second order rate constant for the reaction of $[PtCl_4]^=$ with aqueous NH_3, while the intercept at $NH_3 = 0$ should again give the basic hydrolysis rate constant $k_{a,1}$.

The above treatment gives fairly good values for the rate constant, however errors were again introduced due to the slight nonlinearity of the reaction products in the region 375-405 mμ. In order to avoid this difficulty and also to obtain a value for the ammoniation of $[PtCl_3(NH_3)]^-$, more elaborate methods of calculation were used. The solutions for the concentrations of reaction products in a chain of first order reactions are as follows.

If

$$N_1 \xrightarrow{k_1} N_2 \xrightarrow{k_2} N_3 \xrightarrow{k_3} \cdots N_n , \qquad \text{(III.35)}$$
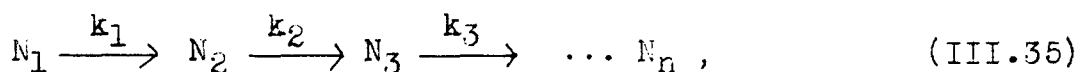
then

$$N_n = C_1 e^{-(k_1 t)} + C_2 e^{-(k_2 t)} + C_3 e^{-(k_3 t)} + \dots C_n e^{-(k_n t)}$$

$$(III.36)$$

where

$$C_1 = \frac{k_1 k_2 \dots k_{n-1} N_1^0}{(k_2 - k_1)(k_3 - k_1)(k_4 - k_1) \dots (k_n - k_1)}$$

$$C_2 = \frac{k_1 k_2 \dots k_{n-1} N_1^0}{(k_1 - k_2)(k_3 - k_2)(k_4 - k_2) \dots (k_n - k_2)}$$

etc.

The general reaction scheme for the reaction of $[PtCl_4^=]$ with ammonia, as given in Figure 2, was slightly simplified to that given in Figure 3.

The reaction products omitted do not make any measurable contribution to the ultraviolet spectrum during the period that the reaction was followed. The first order or pseudo first order rate constants are labeled as defined on the reaction scheme.

If a large excess of aqueous ammonia is used so that the ammonia concentration may be assumed to be constant, if at $t=0$ only $[PtCl_4]^=$ and aqueous ammonia are present and if the initial concentration of $[PtCl_4]^=$ is equal to a_0, equation III.36 gives the solutions for the concentrations of the reaction products as a function of time, as given in equations III.37-III.44.

$$[PtCl_4]^= \xrightarrow[k_{1,a}]{NH_3} [PtCl_3(NH_3)]^- \xrightarrow[k_{2,a}]{NH_3} [PtCl_2(NH_3)_2] \xrightarrow[k_{3,a}]{NH_3} [PtCl(NH_3)_3]^+ \xrightarrow[k_{4,a}]{NH_3} [Pt(NH_3)_4]^{+2}$$

$$OH^- \downarrow k_{a,1} \qquad OH^- \downarrow k_{b,1}$$

$$[PtCl_3(OH)]^= \xrightarrow[k_{1,b}]{NH_3} [PtCl_2(NH_3)(OH)]^-$$
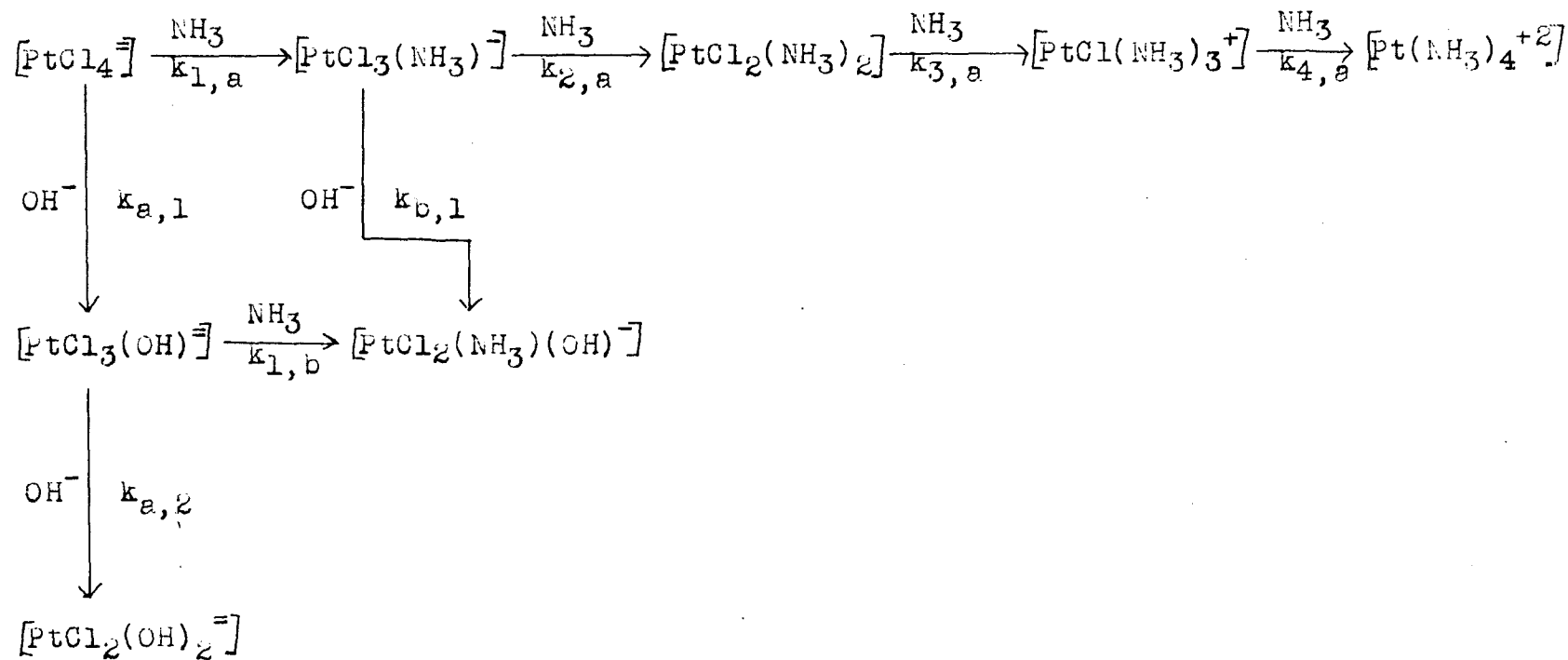
$$OH^- \downarrow k_{a,2}$$

$$[PtCl_2(OH)_2]^=$$

Figure 3. Simplified reaction scheme for reaction of $[PtCl_4]^=$ with aqueous ammonia

$$[PtCl_4^=] = a_0 e^{-(k_{1,a} + k_{a,1})t} \tag{III.37}$$

$$[PtCl_3(OH)^=] = \frac{a_0(k_{a,1})(e^{-(k_{1,a} + k_{a,1})t} - e^{-(k_{1,b} + k_{a,2})t})}{(k_{a,2} + k_{1,b} - k_{a,1} - k_{1,a})} \tag{III.38}$$

$$[PtCl_2(OH)_2^=] = \frac{a_0(k_{a,1})(k_{a,2})e^{-(k_{1,a} + k_{a,1})t}}{(k_{a,2} + k_{1,b} - k_{1,a} - k_{a,1})(-k_{1,a} - k_{a,1})}$$

$$+ \frac{a_0(k_{a,1})(k_{a,2})e^{-(k_{1,b} + k_{a,2})t}}{(k_{1,a} + k_{a,1} - k_{1,b} - k_{a,2})(-k_{1,b} - k_{a,2})}$$

$$+ \frac{a_0(k_{a,1})(k_{a,2})}{(k_{1,a} + k_{a,1})(k_{1,b} + k_{a,2})} \tag{III.39}$$

$$[PtCl_3(NH_3)^-] = \frac{a_0(k_{1,a})e^{-(k_{1,a} + k_{a,1})t}}{(k_{2,a} + k_{b,1} - k_{1,a} - k_{a,1})}$$

$$+ \frac{a_0(k_{1,a})e^{-(k_{2,a} + k_{b,1})t}}{(k_{1,a} + k_{a,1} - k_{2,a} - k_{b,1})} \tag{III.40}$$

$$c-[PtCl_2(NH_3)_2] = \frac{a_0(k_{1,a})(k_{2,a})e^{-(k_{1,a} + k_{a,1})t}}{(k_{2,a} + k_{b,1} - k_{1,a} - k_{a,1})(k_{3,a} - k_{1,a} - k_{a,1})}$$

$$+ \frac{a_0(k_{1,a})(k_{2,a})e^{-(k_{2,a} + k_{b,1})t}}{(k_{a,1} + k_{1,a} - k_{2,a} - k_{b,1})(k_{3,a} - k_{2,a} - k_{b,1})}$$

$$+ \frac{a_0(k_{1,a})(k_{2,a})e^{-(k_{3,a})t}}{(k_{1,a} + k_{a,1} - k_{3,a})(k_{2,a} + k_{b,1} - k_{3,a})} \tag{III.41}$$

$$[PtCl_2(NH_3)(OH)^-] = \frac{a_0(k_{1,a})(k_{b,1})e^{-(k_{1,a} + k_{a,1})t}}{(k_{2,a} + k_{b,1} - k_{1,a} - k_{a,1})(-k_{1,a} - k_{a,1})}$$

$$+ \frac{a_0(k_{1,a})(k_{b,1})e^{-(k_{2,a} + k_{b,1})t}}{(k_{1,a} + k_{a,1} - k_{2,a} - k_{b,1})(-k_{2,a} - k_{b,1})}$$

$$+ \frac{a_0(k_{1,a})(k_{b,1})}{(k_{1,a} + k_{a,1})(k_{2,a} + k_{b,1})}$$

$$+ \frac{a_0(k_{a,1})(k_{1,b})e^{-(k_{1,a} + k_{a,1})t}}{(k_{1,b} + k_{a,2} - k_{1,a} - k_{a,1})(-k_{1,a} - k_{a,1})}$$

$$+ \frac{a_0(k_{a,1})(k_{1,b})e^{-(k_{a,2} + k_{1,b})t}}{(k_{1,a} + k_{a,1} - k_{a,2} - k_{1,b})(-k_{a,2} - k_{1,b})}$$

$$+ \frac{a_0(k_{a,1})(k_{1,b})}{(k_{1,a} + k_{a,1})(k_{a,2} + k_{1,b})} \tag{III.42}$$

Due to the difficulty in solving explicitly for the rate constants, a type of trial and error solution was tried. Estimates of the rate constants were made and the concentrations of the reaction products were calculated from these for the times the ultraviolet spectra were taken. Using the ultraviolet spectra previously determined for these species, the composite spectra were calculated on the basis of the concentrations calculated from the trial rate constants. These spectra were compared to the experimentally determined spectra, and if necessary new rate constants were then tried.

$$[\text{PtCl}(\text{NH}_3)_3{}^+] = \frac{a_0(k_{1,a})(k_{2,a})(k_{3,a})e^{-(k_{1,a} + k_{a,1})t}}{(k_{2,a} + k_{b,1} - k_{1,a} - k_{a,1})(k_{3,a} - k_{1,a} - k_{a,1})(k_{4,a} - k_{1,a} - k_{a,1})}$$

$$+ \frac{a_0(k_{1,a})(k_{2,a})(k_{3,a})e^{-(k_{2,a} + k_{b,1})t}}{(k_{1,a} + k_{a,1} - k_{2,a} - k_{b,1})(k_{3,a} - k_{2,a} - k_{b,1})(k_{4,a} - k_{2,a} - k_{b,1})}$$

$$+ \frac{a_0(k_{1,a})(k_{2,a})(k_{3,a})e^{-(k_{3,a})t}}{(k_{1,a} + k_{a,1} - k_{3,a})(k_{2,a} + k_{b,1} - k_{3,a})(k_{4,a} - k_{3,a})}$$

$$+ \frac{a_0(k_{1,a})(k_{2,a})(k_{3,a})e^{-(k_{4,a})t}}{(k_{1,a} + k_{a,1} - k_{4,a})(k_{2,a} + k_{b,1} - k_{4,a})(k_{3,a} - k_{4,a})}$$

Figure 4. Equation III.43, concentration of $[\text{PtCl}(\text{NH}_3)_3]^+$ as a function of time

$$[Pt(NH_3)_4^{+2}] = \frac{a_0(k_{1,a})(k_{2,a})(k_{3,a})(k_{4,a})e^{-(k_{1,a}+k_{a,1})t}}{(k_{2,a}+k_{b,1}-k_{1,a}-k_{a,1})(k_{3,a}-k_{1,a}-k_{a,1})(k_{4,a}-k_{1,a}-k_{a,1})(-k_{1,a}-k_{a,1})}$$

$$+ \frac{a_0(k_{1,a})(k_{2,a})(k_{3,a})(k_{4,a})e^{-(k_{2,a}+k_{b,1})t}}{(k_{1,a}+k_{a,1}-k_{2,a}-k_{b,1})(k_{3,a}-k_{2,a}-k_{b,1})(k_{4,a}-k_{2,a}-k_{b,1})(-k_{2,a}-k_{b,1})}$$

$$- \frac{a_0(k_{1,a})(k_{2,a})(k_{4,a})e^{-(k_{3,a})t}}{(k_{1,a}+k_{a,1}-k_{3,a})(k_{2,a}+k_{b,1}-k_{3,a})(k_{4,a}-k_{3,a})}$$

$$- \frac{a_0(k_{1,a})(k_{2,a})(k_{3,a})e^{-(k_{4,a})t}}{(k_{1,a}+k_{a,1}-k_{4,a})(k_{2,a}+k_{b,1}-k_{4,a})(k_{3,a}-k_{4,a})}$$

$$+ \frac{a_0(k_{1,a})(k_{2,a})}{(k_{1,a}+k_{a,1})(k_{2,a}+k_{b,1})}$$

Figure 5. Equation III.44, concentration of $[Pt(NH_3)_4]^{+2}$ as a function of time

In practice the only rate constants which could be determined with any accuracy by this method were $(k_{1,a})$ and $(k_{2,a})$. The values previously determined were used for the rate constants $(k_{a,1})$, $(k_{a,2})$, and $(k_{3,a})$. The basic equation rate for $[PtCl_3(NH_3)_3]^-$ was from the work of Elleman et al. (4). Variations in the spectra due to changing most of the other rate constants were too small to make the calculation reliable. However even if the estimates of these rate constants were in error the effect on the calculation of the rate constants of interest would not be affected.

A computer was used in order to reduce the labor in calculating the concentrations and converting these to predicted spectra. A program was written for the IBM 704 and run on the University of Wisconsin computer (see Appendix). Efficient use of the computer was possible due to an electronic data link between Ames, Iowa, and Madison, Wisconsin.

IV.   RESULTS AND DISCUSSION

A. Spectra

The ultraviolet absorption spectrum of $[PtCl_4]^=$ is given in Figure 6 and in Table 1. The spectrum was obtained from a freshly prepared solution of K_2PtCl_4 in a 0.1 N solution of HCl to repress the aquation.

To obtain the spectra of $[PtCl_3(H_2O)]^-$ and $[PtCl_2(H_2O)_2]$, solutions of K_2PtCl_4 were aged 2-3 days to insure chemical equilibrium between $[PtCl_4]^=$, $[PtCl_3(H_2O)]^-$, and $[PtCl_2(H_2O)_2]$. The original concentrations of K_2PtCl_4 used in this work were 0.00193 M and 0.01077 M. The ultraviolet spectra of these solutions were then recorded, 2 cm. and 10 cm. cells being used for the more concentrated and the more dilute solutions respectively. The concentrations of the various equilibrium species for these solutions were calculated from equations III.8, III.9, and III.10 using the reiteration method until agreement was reached between two successive calculations. The equilibrium concentrations of the various species are given in Table 3. These values and the previously determined spectrum for $[PtCl_4]^=$ were substituted into equation III.11. Since two different equilibrium solutions were used, it was possible to obtain two equations containing the two unknown extinction coefficients at any given wave length. These equations were solved at 2 1/2 mμ

Table 1. Molar extinction coefficients for various platinum species in the ultraviolet region

Wave length mμ	$[PtCl_4]^=$ $M^{-1}cm^{-1}$	$[PtCl_3(H_2O)]^-$ $M^{-1}cm^{-1}$	$[PtCl_2(H_2O)_2]$ $M^{-1}cm^{-1}$	$[PtCl_3(OH)]^=$ $M^{-1}cm^{-1}$	$[PtCl_2(OH)_2]^=$ $M^{-1}cm^{-1}$
280	60.3	23.0	84.1	34.7	74.2
285	28.45	27.9	79.6	30.0	70.5
290	16.94	35.0	87.8	35.5	72.6
295	15.81	51.0	96.0	44.1	76.8
300	19.89	70.0	102.8	52.6	78.8
305	27.21	88.2	107.2	60.2	78.0
310	36.19	104.4	108.3	66.6	76.2
315	45.65	114.8	100.6	69.1	74.2
320	53.8	118.0	85.2	67.9	73.1
325	59.6	110.0	72.0	63.3	74.2
330	62.15	96.0	60.1	57.5	77.8
335	60.6	80.0	49.4	51.6	82.5
340	55.4	62.8	42.1	49.4	86.7
345	48.05	49.1	39.0	51.6	88.0
350	39.8	40.3	37.9	57.9	86.0
355	33.0	38.0	39.7	66.5	79.8
360	29.75	39.2	40.1	74.0	71.0
365	30.81	43.7	38.0	78.5	61.8
370	35.85	49.8	35.0	78.5	52.6
375	43.6	52.2	32.8	75.0	44.4
380	51.1	52.5	31.0	68.0	37.5
385	54.3	51.5	29.0	59.0	32.3
390	58.5	47.9	27.9	48.5	28.1
395	55.9	42.0	26.8	41.2	25.0
400	50.55	35.2	25.8	34.8	22.6
405	43.6	30.8	25.0	30.0	20.9

Table 2. Molar extinction coefficients for various platinum species in the ultraviolet region

Wave length mμ	$[PtCl_4]^=$ $M^{-1}cm^{-1}$	$[PtCl_3(NH_3)]^-$ $M^{-1}cm^{-1}$	$[PtCl_2(NH_3)(OH)]^-$ $M^{-1}cm^{-1}$	c-$[PtCl_2(NH_3)_2]$ $M^{-1}cm^{-1}$	$[PtCl(NH_3)_3]^+$ $M^{-1}cm^{-1}$	$[Pt(NH_3)_4]^{+2}$ $M^{-1}cm^{-1}$
280	60.3	40.2	86.5	105.0	73.0	34.3
285	28.45	50.5	89.2	110.2	59.0	35.3
290	16.94	60.0	88.4	117.1	45.8	34.8
295	15.81	69.5	85.3	124.7	36.1	32.6
300	18.89	71.0	80.5	131.4	30.1	29.1
305	27.21	69.5	78.1	130.0	27.3	25.3
310	36.19	64.0	77.0	119.2	27.2	20.3
315	45.65	60.1	78.5	103.5	27.5	16.3
320	53.8	62.0	81.8	77.5	28.4	12.9
325	59.6	70.5	84.7	53.8	28.8	9.8
330	62.15	82.3	84.0	41.0	27.8	6.5
335	60.6	95.3	78.8	31.5	26.4	5.1
340	55.4	109.3	69.8	26.6	24.0	4.0
345	46.05	114.0	57.5	24.5	21.0	3.3
350	30.8	108.0	47.6	24.6	17.8	2.8
355	33.0	95.5	39.8	25.5	14.5	2.5
360	29.75	78.0	32.9	26.0	11.7	2.2
365	30.81	62.0	28.0	26.0	9.1	2.0
370	35.85	47.2	24.9	25.5	7.2	1.8
375	43.6	39.2	23.0	24.5	5.6	1.5
380	51.1	34.3	22.0	23.0	4.2	1.3
385	54.3	32.0	21.2	21.3	3.2	1.2
390	58.5	30.5	20.7	19.4	2.4	1.1
395	55.9	30.1	20.4	17.3	2.0	1.0
400	50.55	30.2	20.0	15.2	1.6	.9
405	43.6	30.4	19.6	13.2		

Figure 6. Ultraviolet spectra of $[PtCl_4]^=$, $[PtCl_3(H_2O)]^-$, and $[PtCl_2(H_2O)_2]$
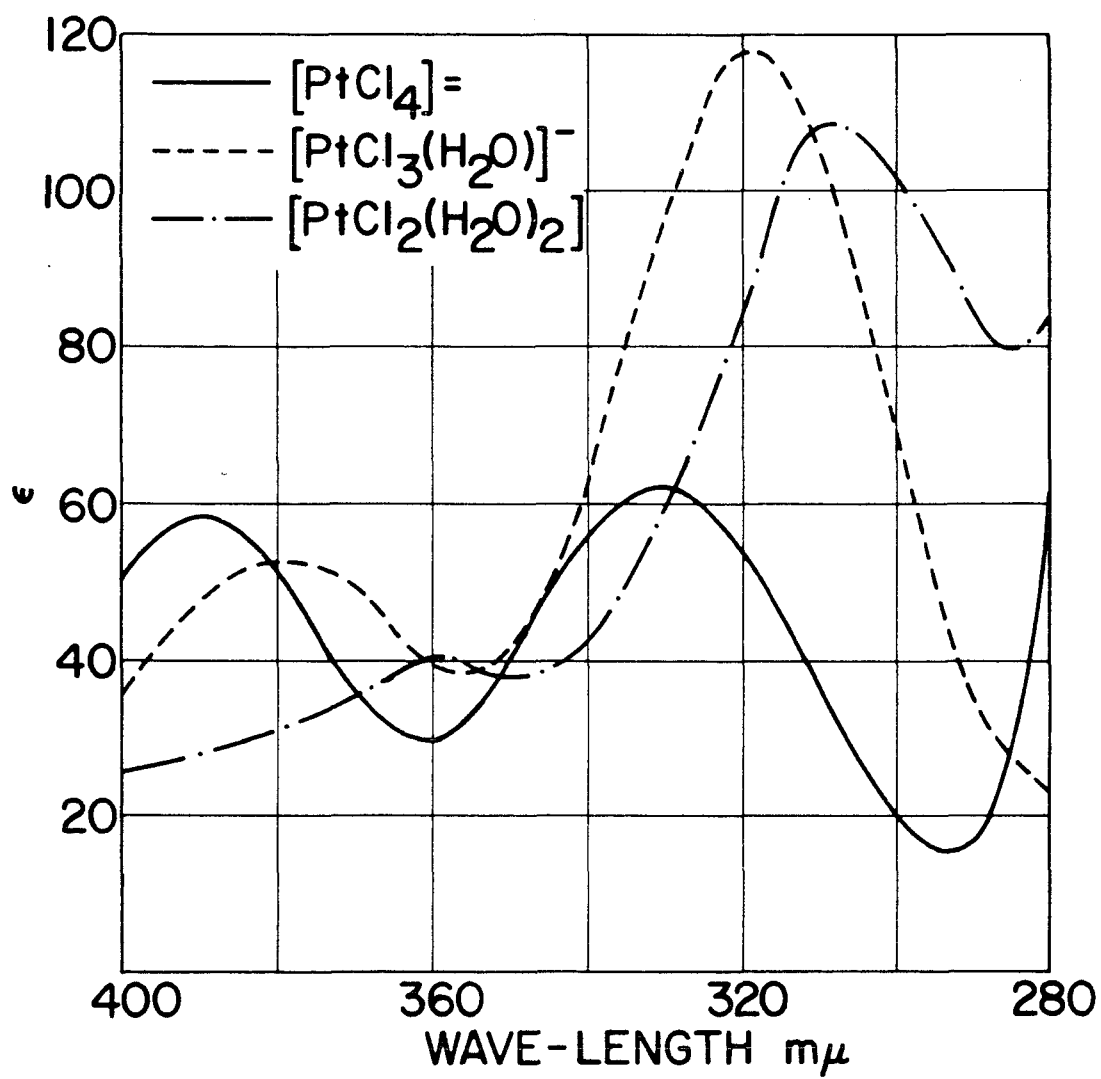
Figure 7. Ultraviolet spectra of $[PtCl_4]^=$, $[PtCl_3(OH)]^-$, and $[PtCl_2(OH)_2]^=$
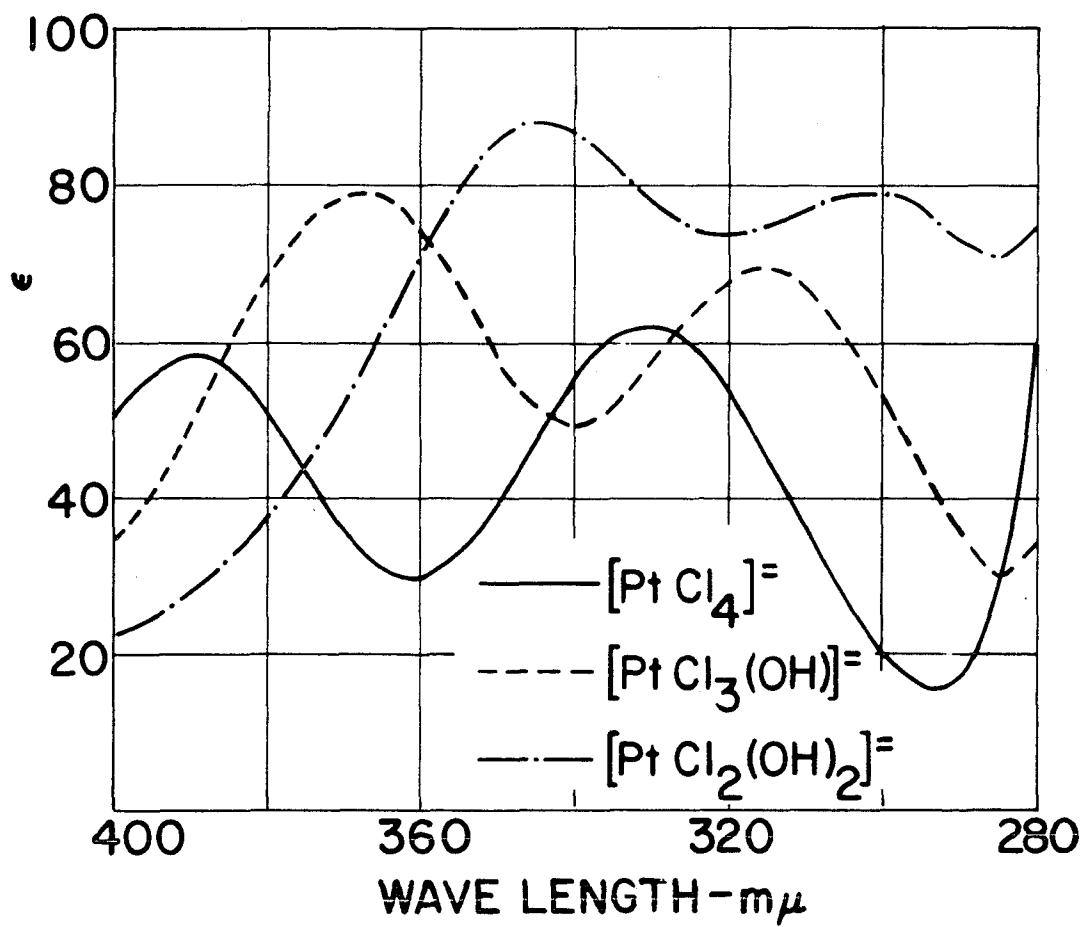
Figure 8.   Ultraviolet spectra of $[\mathrm{PtCl_4}]^=$, $[\mathrm{PtCl_3(NH_3)}]^-$, and $[\mathrm{PtCl_2(NH_3)(OH)}]^-$
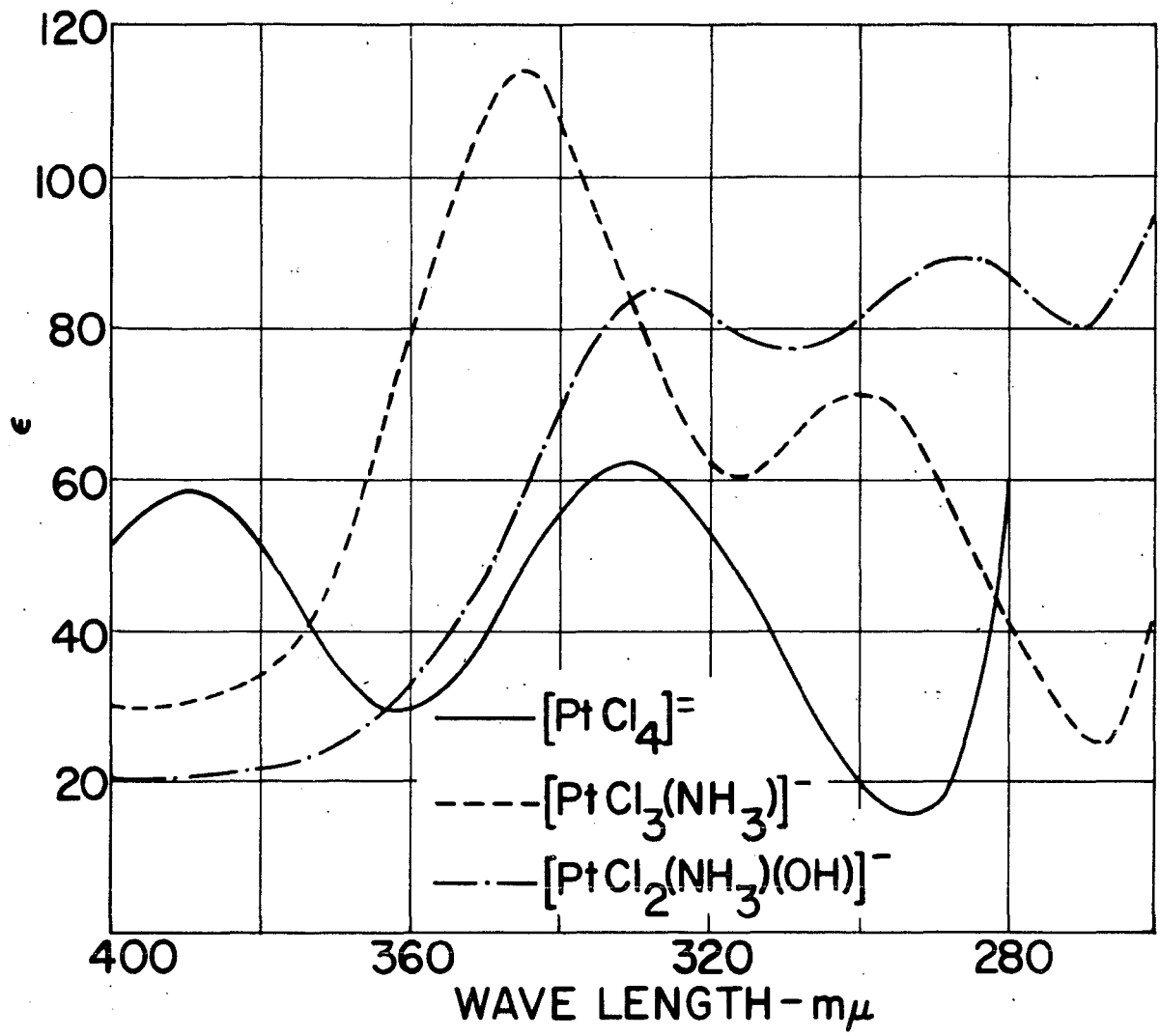
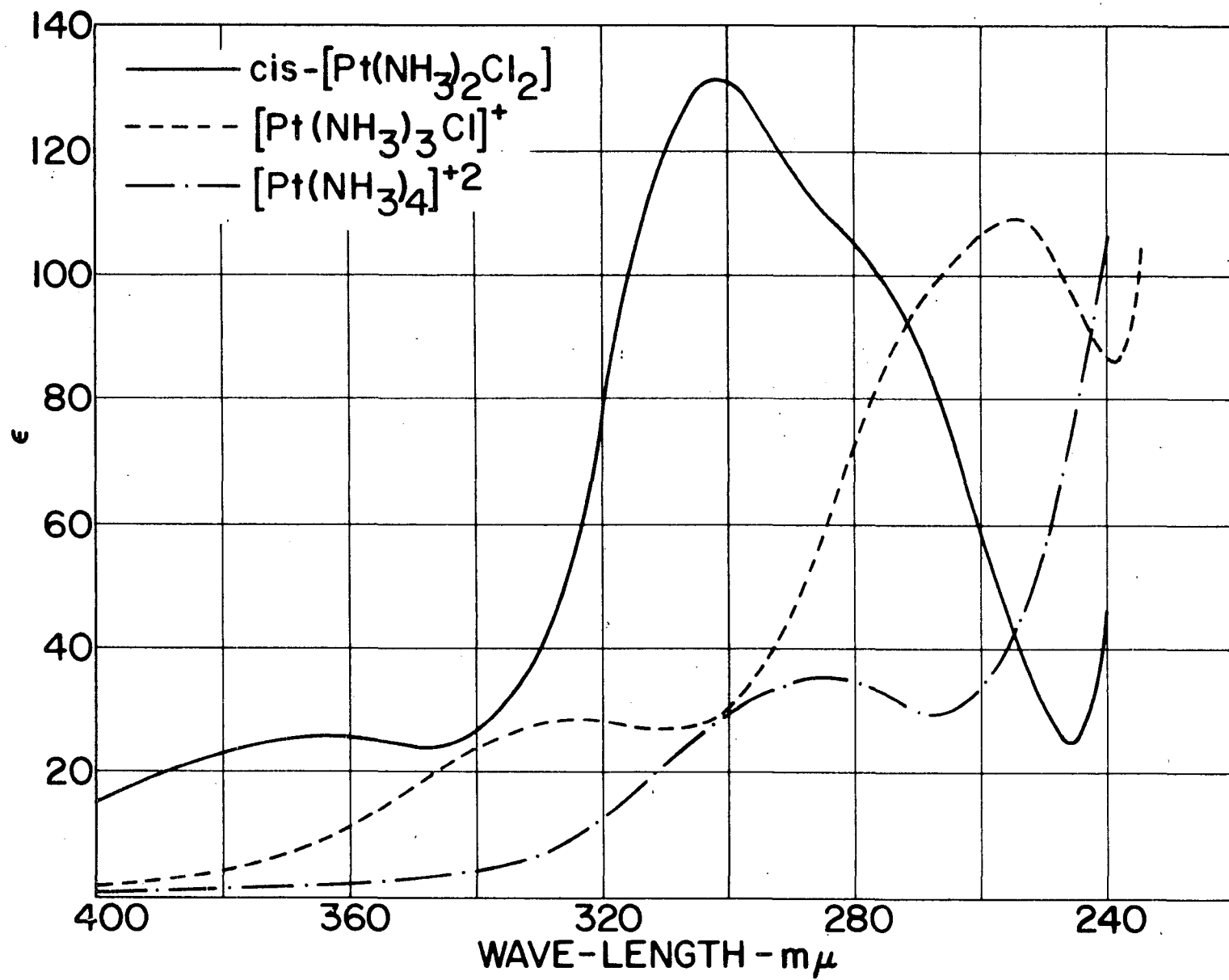Figure 9.   Ultraviolet spectra of cis-$[PtCl_2(NH_3)_2]$, $[PtCl(NH_3)_3]^+$, and $[Pt(NH_3)_4]^{+2}$

Table 3. Concentrations of platinum species in equilibrium
          with $[PtCl_4]^=$ at 25° C.

Total Pt in solution (M.)	$[PtCl_4]^=$ (M.)	$[PtCl_3(H_2O)]^-$ (M.)	$[PtCl_2(H_2O)_2]$ (M.)
.00193	.00009	.00128	.00056
.01077	.00195	.00796	.00086

intervals to give the ultraviolet spectra for $[PtCl_3(H_2O)]^-$
and $[PtCl_2(H_2O)_2]$ as given in Table 1 and Figure 6. The re-
sults are tabulated at 5 mμ intervals.

Uncertainties in the extinction coefficients of
$[PtCl_3(H_2O)]^-$ and $[PtCl_2(H_2O)_2]$ arise because of the uncer-
tainties in the equilibrium constants and in the spectral
data, which are magnified somewhat in the calculations, which
involve small differences between large numbers. However the
positions and the extinction coefficients of the peaks should
be given reasonably well since these would not be affected as
greatly by experimental error as other portions of the spec-
trum. Extinction coefficients for some portions of the
spectra may be uncertain by as much as 20%.

The spectra of $[PtCl_3(OH)]^=$ and $[PtCl_2(OH)_2]^=$ were
obtained in a similar manner. The aged solutions used in the
determination of the aquo-complexes were made basic with NaOH,
and the spectra of the solutions immediately redetermined.

Assuming no other reactions took place during this time except for the rapid conversion of the aquo ligand to the hydroxide group, the concentrations of the hydroxo-complexes were taken equal to the concentrations of the corresponding aquo complex. The spectra of the hydroxo-complexes were then calculated at $1/2$ mμ intervals in a manner similar to that above.

The uncertainties involved in the determination of these spectra should be most apparent in the case of $[PtCl_2(H_2O)_2]$ and $[PtCl_2(OH)_2]^=$ since the equilibrium constant involving the second aquation of $[PtCl_4]^=$ is considered to have a larger uncertainty than the equilibrium constant for the first aquation. Also since the equilibrium concentration of $[PtCl_2(H_2O)_2]$ is less than the concentration of $[PtCl_3(H_2O)]^-$ at even the lowest concentrations of K_2PtCl_4 studied, any error in the determination of the spectra of the equilibrium solutions will have a larger effect on the spectra of $[PtCl_2(H_2O)_2]$ and $[PtCl_2(OH)_2]^=$ than on the spectra of $[PtCl_3(H_2O)]^-$ and $[PtCl_3(OH)]^=$. If it is assumed that the reaction of $[PtCl_2(OH)_2]^=$ with hydroxide, if it exists, is much slower than the reaction of hydroxide with $[PtCl_4]^=$ and $[PtCl_3(OH)]^=$, a reasonably pure solution of $[PtCl_2(OH)_2]^=$ will result from an aged solution of $[PtCl_4]^=$ containing an excess of NaOH, if the aging process is not too prolonged. It was noticed that such a solution yielded a spectrum very similar to that previously calculated for $[PtCl_2(OH)_2]^=$. The valleys

or this experimental spectrum, were even deeper than that obtained from the calculations. Since a deeper valley is usually associated with higher purity, and due to the uncertainties in the calculated values, it was decided to use this later experimental spectrum for the spectrum of $[PtCl_2(OH)_2]^=$. The spectrum for $[PtCl_3(OH)]^=$ was then recalculated from the previous data using this new spectrum for $[PtCl_2(OH)_2]^=$, and the equilibrium concentrations as previously calculated. The resulting spectrum was again slightly modified, as will be shown later, to obtain a slightly better fit with the spectra obtained during the basic aquation of $[PtCl_4]^=$. These later refinements were considered to be within the estimated accuracy of the calculation of these spectra. These final values for the spectra of $[PtCl_3(OH)]^=$ and $[PtCl_2(OH)_2]^=$ are given in Table 1 and Figure 7. Again the spectra are given at 5 mμ intervals.

The values for the positions of the peaks give good agreement to theoretical calculations based on crystal field considerations presented by R. F. Fenske (7).

B. Base Hydrolysis Rate Constants for $[PtCl_4]^=$

The rate constants for the base hydrolysis of $[PtCl_4]^=$ were determined by following the ultraviolet spectrum of .01 M solutions of $[PtCl_4]^=$ in 0.1 M NaOH. Difficulties, however, were found in the methods of calculation as indicated in sec-

tion III. Due to the non-linearity of the spectra of the re-
action products in the region 375-405 mμ, the plot of

$$\log \left[O.D._{390 \text{ m}\mu} - \frac{1}{2}(O.D._{375 \text{ m}\mu} + O.D._{405 \text{ m}\mu}) \right]$$

versus time yields a rate constant much higher than that ex-
pected for the base hydrolysis. Difficulties were also expe-
rienced in the attempts to obtain a good fit to the experi-
mental data using equations III.13-III.15 to calculate the
concentrations of $[PtCl_4]^=$, $[PtCl_3(OH)]^=$, and $[PtCl_2(OH)_2]^=$
from trial rate constants. Any inaccuracies in the spectra
for these species would make it impossible to obtain a good
fit by these methods. The worst fit, as could be expected,
was found in the region 380-405 mμ. In this region the
$[PtCl_4]^=$ peak at 390 mμ made the determination of the spectra
of $[PtCl_3(OH)]^=$ and $[PtCl_2(OH)_2]^=$ difficult since the calcu-
lation involved the small differences of large numbers. The
most reliable values for the spectrum of $[PtCl_3(OH)]^=$ should
be in the region of its peak at 368 mμ, since the spectrum
of $[PtCl_4]^=$ is also in a minimum in this region. At about
365 mμ the extinction coefficients for these two species have
widely separated values. This wave length was thus taken as
the most reliable for the determination of the base hydrolysis
rates. Following the calculations of the theoretical O.D.$_\infty$
at this wave length, as indicated in section III, the log of
the difference between the theoretical O.D.$_\infty$ and the experi-
mental O.D. was plotted against time. The rate constant,

$k_{a,1}$, for base hydrolysis was obtained from the slope of the initial straight portion of the plot. The data from these experiments is given in Table 4, while the results of this calculation are given in Table 5. A typical plot of $\log(O.D._{\infty} - O.D.)$ versus time is given in Figure 10.

Table 4. Optical density measurements for the basic
hydrolysis of $[PtCl_4]^=$

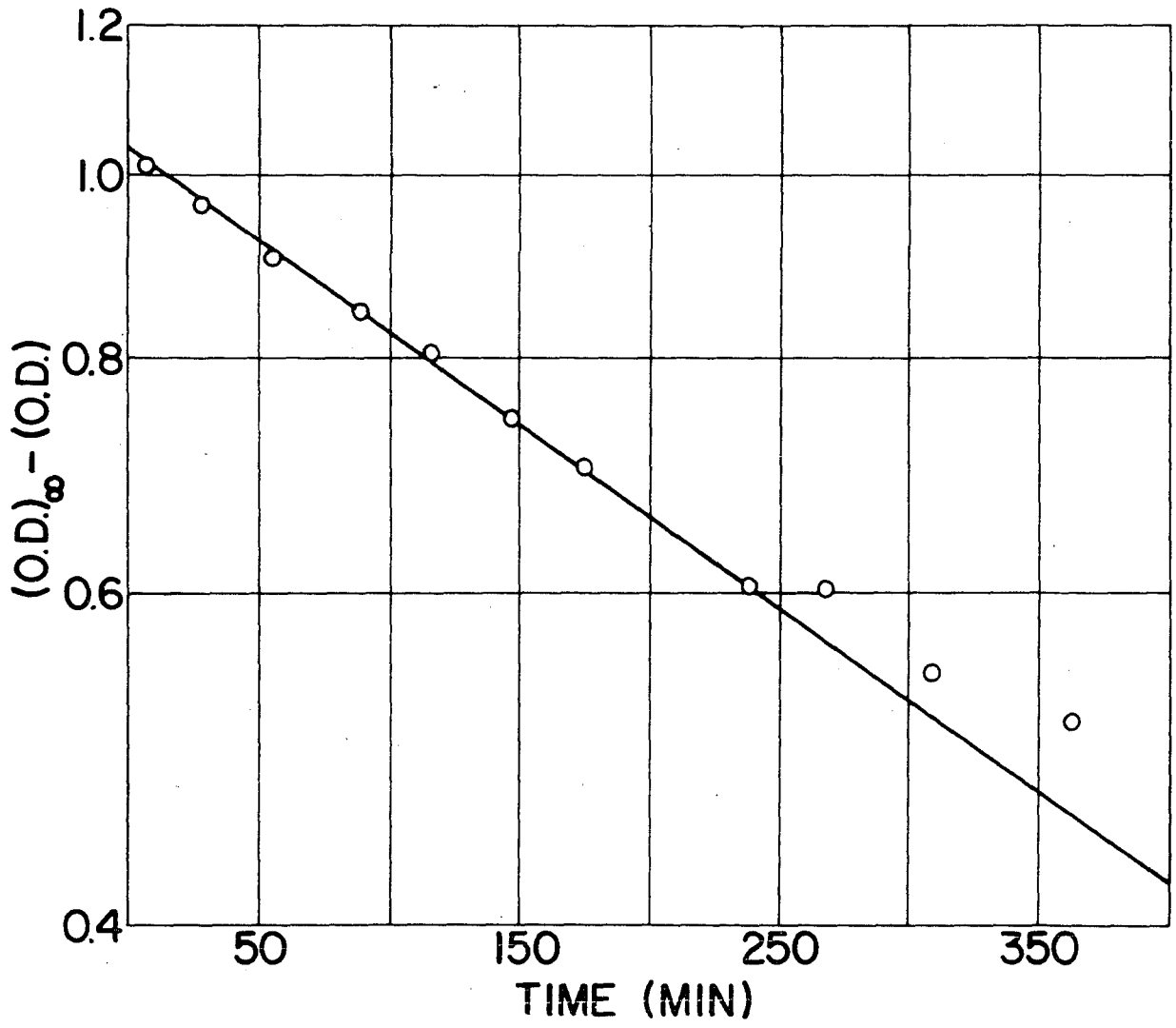| Experiment 1		Experiment 2		Experiment 3	
Time (min.)	$O.D._{365m\mu}$	Time (min.)	$O.D._{365m\mu}$	Time (min.)	$O.D._{365m\mu}$
6 1/2	0.562	7	0.669	7	0.646
33	0.578	28	0.715	22 1/2	0.743
92	0.600	56	0.774	45 1/2	0.845
146	0.632	89 1/2	0.832	63	0.918
192 1/2	0.652	115 1/2	0.878	84 1/2	0.995
277	0.688	148	0.938	101	1.065
356 1/2	0.709	175	0.980	130	1.125
419	0.768	238 1/2	1.072	186 1/2	1.200
523	0.814	266	1.075	210	1.230
653 1/2	0.861	307 1/2	1.135		
720 1/2	0.901	363	1.168		
781	0.939				
855	0.946				
947	0.980				
1001	1.010				

By the use of trial rate constants, the known spectra, and equations III.13-III.15, an attempt was made to determine $k_{2,a}$ by varying this rate constant until the best fit to the experimental data was obtained. Due to the poor fit, it was necessary to make slight refinements in the spectrum of $[PtCl_3(OH)]^=$. Using the previously determined values for

Table 5. Rate constants for the basic hydrolysis of $[PtCl_4]^=$

Expt. no.	Temp. (°C.)	NaOH conc. (M.)	$[PtCl_4]^=$ conc. (M.)	Calculated O.D.$_\infty$ (2 cm. cells)	$k_{a,1}$ (sec^{-1} x 10^4)	$k_{a,2}$ (sec^{-1} x 10^4)
1	15	.1051	.00872	1.367	.125	.10
2	25	.1010	.01052	1.680	.381	.35
3	35	.1013	.00985	1.546	1.046	.81

Figure 10. Typical plot of $\log(O.D._{\infty} - O.D.)$ versus time for the determination of $k_{a,1}$: initial $[PtCl_4]^=$ = 0.01052 M., $[OH]^-$ = 0.1010 M., 2 cm. cells, 25° C.

$k_{a,1}$, and a rough value for $k_{a,2}$, the concentrations of $[PtCl_4]^=$, $[PtCl_3(OH)]^=$, and $[PtCl_2(OH)_2]^=$ were calculated for the solutions from which the ultraviolet spectra were taken during the initial portion of the base hydrolysis experiments. During this period, the concentration of $[PtCl_2(OH)_2]^=$ is relatively low, and errors in the value of $k_{a,2}$ or the spectrum for $[PtCl_2(OH)_2]^=$ will not have a large effect. From this data the spectrum of $[PtCl_3(OH)]^=$ was recalculated using the previously determined values for the spectra of $[PtCl_4]^=$ and $[PtCl_2(OH)_2]^=$. It was found that a much better fit to the experimental data could be obtained if the extinction coefficients for $[PtCl_3(OH)]^=$ were slightly increased in the region 380-405 mμ . Since these values were within the estimated accuracy of the previous calculations, this new spectrum was assumed to be the more accurate and is the one tabulated in Table 1.

Following this refinement of the spectrum for $[PtCl_3(OH)]^=$, another attempt was made to obtain the rate constant for the second base hydrolysis reaction for $[PtCl_4]^=$, $k_{a,2}$. This rate constant was varied until the best fit to the experimental data was obtained. The best values for these rate constants are given in Table 5. However due to the uncertainty in the spectra, these values have the largest uncertainty of any rate constants determined in this work.

As in the case of most other platinum complexes, the

rates for the base hydrolysis of $[PtCl_4]^=$ agree closely with the corresponding rates for the acid hydrolysis. It thus appears that the base hydrolysis proceeds mainly, if not exclusively through an aquation mechanism, with an immediate fast neutralization of the acidic hydrogen of the aquo-complex.

C. Rate Constants for the Ammoniation of cis-$[PtCl_2(NH_3)_2]$

The rate constants for the ammoniation of cis-$[PtCl_2(NH_3)_2]$ were determined by following the ultraviolet spectrum of solutions of cis-$[PtCl_2(NH_3)_2]$ in aqueous ammonia. The data were treated by the use of equations III.31 through III.33, with the reiterative procedure from section III. The rate constants for the aquation of cis-$[PtCl_2(NH_3)_2]$ at 15°, 25°, and 35^oC. are taken from Reishus and Martin (6) as 0.08×10^{-4}, 0.25×10^{-4}, and 0.72×10^{-4} sec^{-1} respectively. The assumption was made that these values for the rates for the acid hydrolysis are equal to the rates for aquation in basic solution, $k_{c,1}$. The spectrum for cis-$[PtCl_2(NH_3)_2]$ was obtained from Reishus and Martin (6) and is given in Figure 9 and Table 2. The spectrum for $[PtCl_3(NH_3)]^+$ was obtained from Aprile and Martin (9) and is also given in Figure 9 and in Table 2. A rough value for the extinction coefficient for $[PtCl(NH_3)_2(OH)]$ at 300 $m\mu$ was obtained from the data of

Reishus and Martin.[1] An uncertainty of 15-20% in the value
used, 60 moles^{-1}cm^{-1}, would not make an appreciable error in
the calculated values for the rate constants. Data from these
experiments are given in Table 6. Equation III.33 was used
to obtain a first approximation to the rate constant $k_{3,a}$.
The quantity (O.D.)′ was then calculated from equation III.31
and log (O.D.) - (O.D.)′ was plotted against time. The total
pseudo first order rate constant and the net pseudo first
order rate constant were then calculated from the initial
slope of this curve with the use of equation III.3x. If
necessary the process was repeated until agreement was
reached between two consecutive calculations. The second
order rate constants for the reactions were then obtained by
dividing by the concentration of the ammonia in the solutions.
The results of these experiments are given in Table 7. A
typical plot of log (O.D.) - (O.D.)′ versus time is given
in Figure 11.

D. Rate Constants for the Ammoniation
of $[PtCl_4]^=$ and $[PtCl_3(NH_3)]^-$

The rate constants for the reaction of ammonia with
$[PtCl_4]^=$ and $[PtCl_3(NH_3)]^-$ were determined by following the

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[1]J. W. Reishus and D. S. Martin, Jr., Ames, Iowa.
Ultraviolet spectra of $[PtCl(NH_3)_2(OH)]$. Private communi-
cation. 1960.

Table 6. Optical density measurements at 300 mμ for the ammoniation of cis-[PtCl$_2$(NH$_3$)$_2$]

Experiment 4		Experiment 5		Experiment 6		Experiment 7		Experiment 8		Experiment 9	
Time (min.)	O.D.	Time (min.)	O.D.	Time (min.)	O.D.	Time (min.)	O.D.	Time (min.)	O.D.	Time (min.)	O.D.
7	1.801	6	1.762	7	1.838	7	1.712	8 1/2	1.818	5 1/2	1.682
22	1.770	15	1.698	22 1/2	1.728	14 1/2	1.598	17	1.758	14 1/2	1.460
43	1.735	30 1/2	1.624	39 1/2	1.680	23	1.502	27	1.600	24 1/2	1.270
69 1/2	1.682	53 1/2	1.535	56	1.608	31 1/2	1.398	37	1.528	34	1.125
94 1/2	1.630	73 1/2	1.452	71 1/2	1.548	40 1/2	1.300	57	1.382	42	1.018
116 1/2	1.591	93	1.380	87	1.487	54	1.195	77 1/2	1.278	57 1/2	0.888
174 1/2	1.495	122	1.285	113 1/2	1.410	74	1.042	95 1/2	1.160		
207 1/2	1.438	156	1.205	127	1.398			145 1/2	0.950		
281 1/2	1.372	213 1/2	1.080	196	1.225						
357	1.268			226	1.180						
415	1.215										
541	1.198										

Table 7. Rate constants for the ammoniation of cis-$[PtCl_2(NH_3)_2]$

Expt. no.	Temp. (^{o}C.)	NH_3 conc. (M.)	c-$[PtCl_2(NH_3)_2]$ (conc. x 10^3)	(O.D.)	$k_{cl} + k_{3a}$ (sec^{-1} x 10^4)	k_{cl} (sec^{-1} x 10^4)	k_{3a} (sec^{-1} x 10^4)	$\frac{k_{3a}}{[NH_3]}$ (M^{-1}sec^{-1} x 10^4)
4	15	.3369	1.348	.52	.282	.080	.202	.600
5	15	.9367	1.346	.457	.652	.080	.572	.611
								av. .606
6	25	.2093	1.375	.58	.648	.250	.398	1.90
7	25	.2039	1.350	.456	1.94	.250	1.69	1.87
								av. 1.89
8	35	.1936	1.423	.64	1.59	.72	.87	4.49
9	35	.582	1.323	.475	3.76	.72	3.04	5.22
								av. 4.85

Figure 11.   Typical plot of $\log(O.D. - O.D.)$ versus time for the determination of $k_{3,e}$; initial cis-$[PtCl_2(NH_3)_2]$ = 0.00135 M., $[NH_3]$ = 0.9039 M., 2 cm. cells, 25° C.
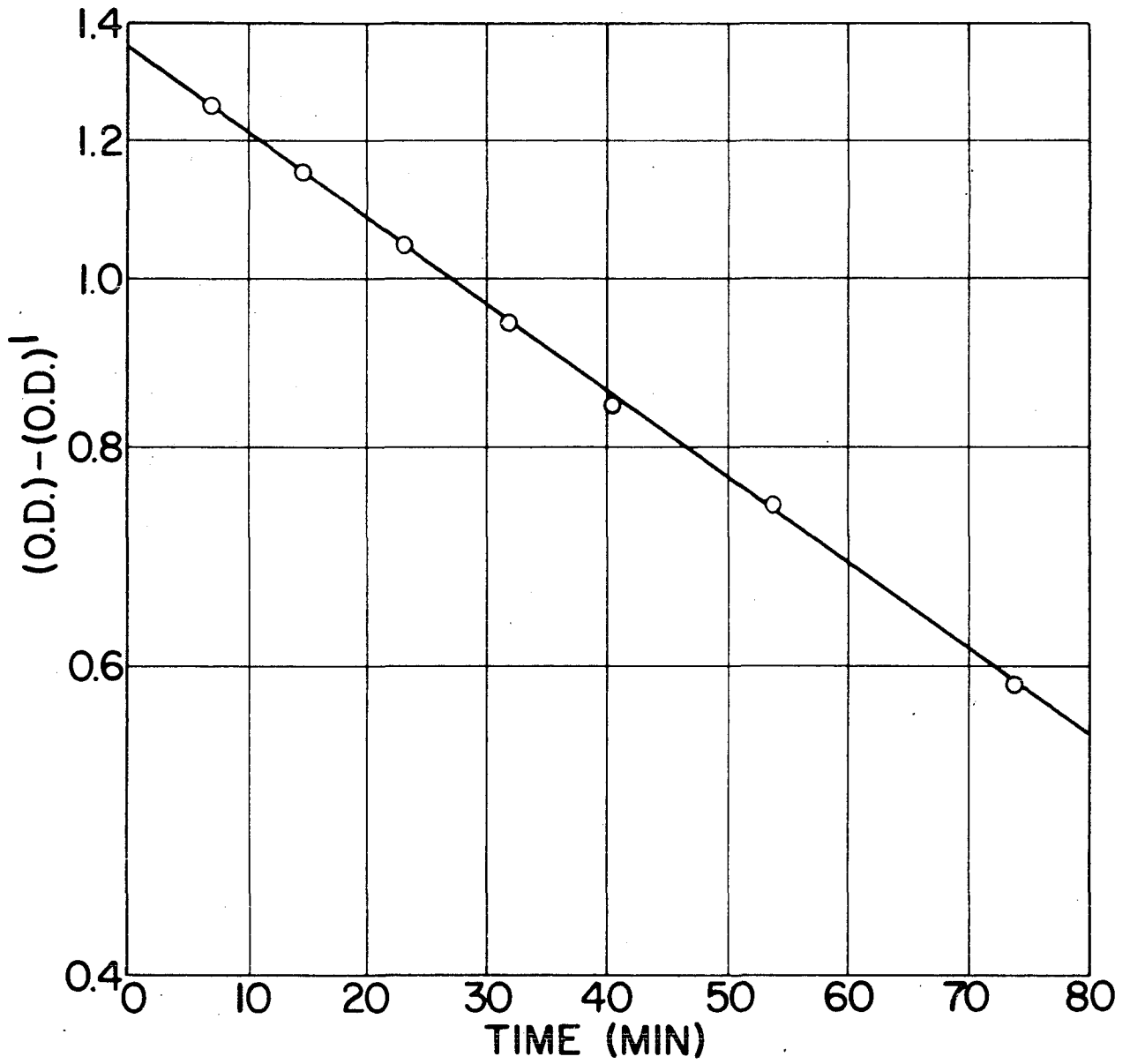
ultraviolet spectra of solutions of these species in aqueous
ammonia. Six to ten experiments with varying ammonia concen-
trations were made at each of the temperatures studied. The
rate constants were calculated by the use of the methods given
in section III. In contrast to the calculation of the base
hydrolysis rates, the method of plotting

$$\log\left[O.D._{390 \, m\mu} - 1/2(O.D._{375 \, m\mu} + O.D._{405 \, m\mu})\right]$$

versus time gives fairly good values for the rate constants
for the reaction of $[PtCl_4]^=$ with aqueous ammonia since, as
can be seen later, the rate constants determined in this way
agree reasonably well with other methods of calculation. It
can be concluded that the spectra of the ammoniation reaction
products are more nearly linear than are those from the base
hydrolysis reactions in this region. A typical plot of

$$\log\left[O.D._{390 \, m\mu} - 1/2(O.D._{375 \, m\mu} + O.D._{405 \, m\mu})\right]$$ versus time

is given in Figure 12. The total pseudo first order rate
constants were obtained from the initial slope of this curve.
The plot of the total pseudo first order rate constants versus
ammonia concentration is given in Figure 13. As can be seen,
a straight line may be drawn through these points at each of
the temperatures studied. Since the pseudo first order reac-
tion includes both the aquation and the reaction with ammonia,
it may be expected that the intercept at $NH_3 = 0$ on Figure 13
would again yield the first order base hydrolysis rate, $k_{a,1}$.
However due to the same reasons as encountered earlier in

Figure 12. Typical plot of $\log[O.D._{390\ m\mu} - 1/2(O.D._{375\ m\mu}$
$+ O.D._{405\ m\mu})]$ versus time for the determination
of $k_{1,a}$ (the short method of calculation);
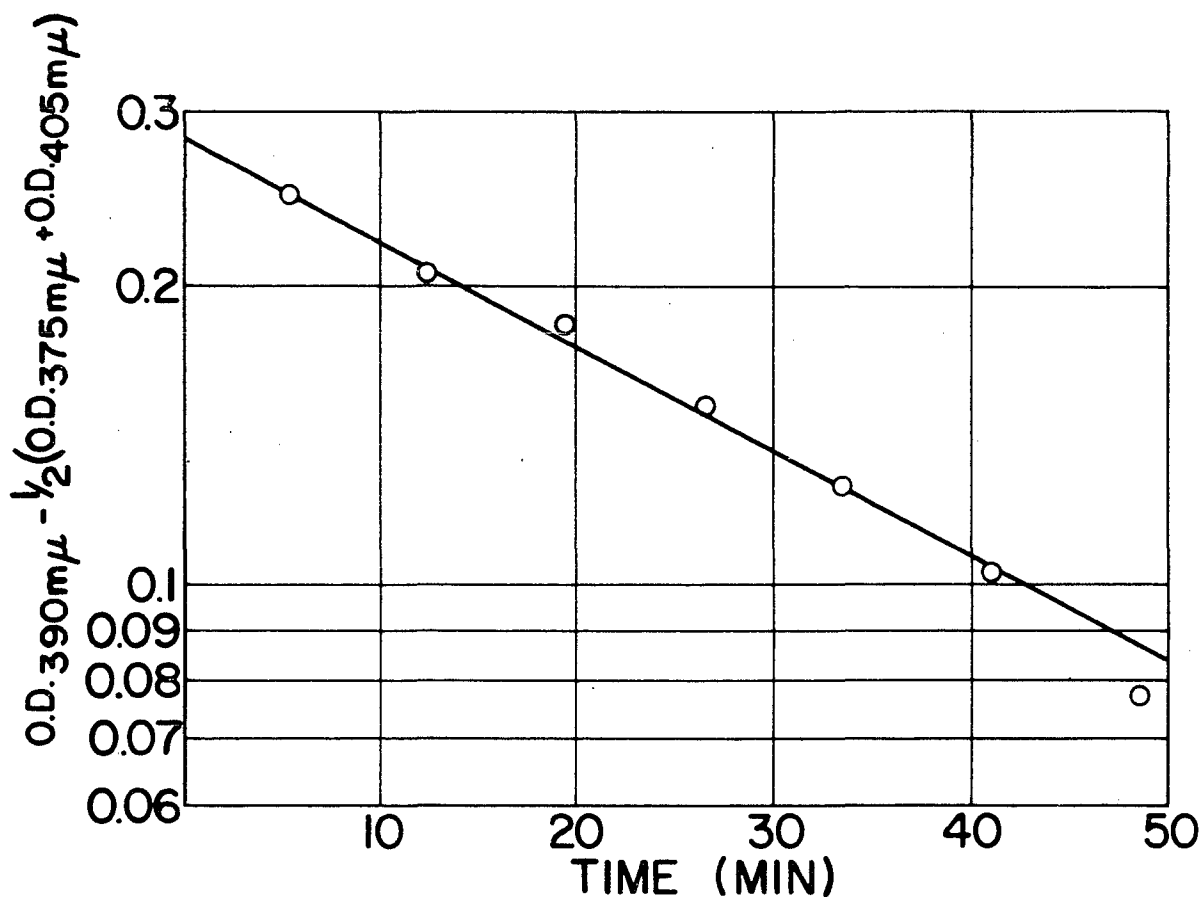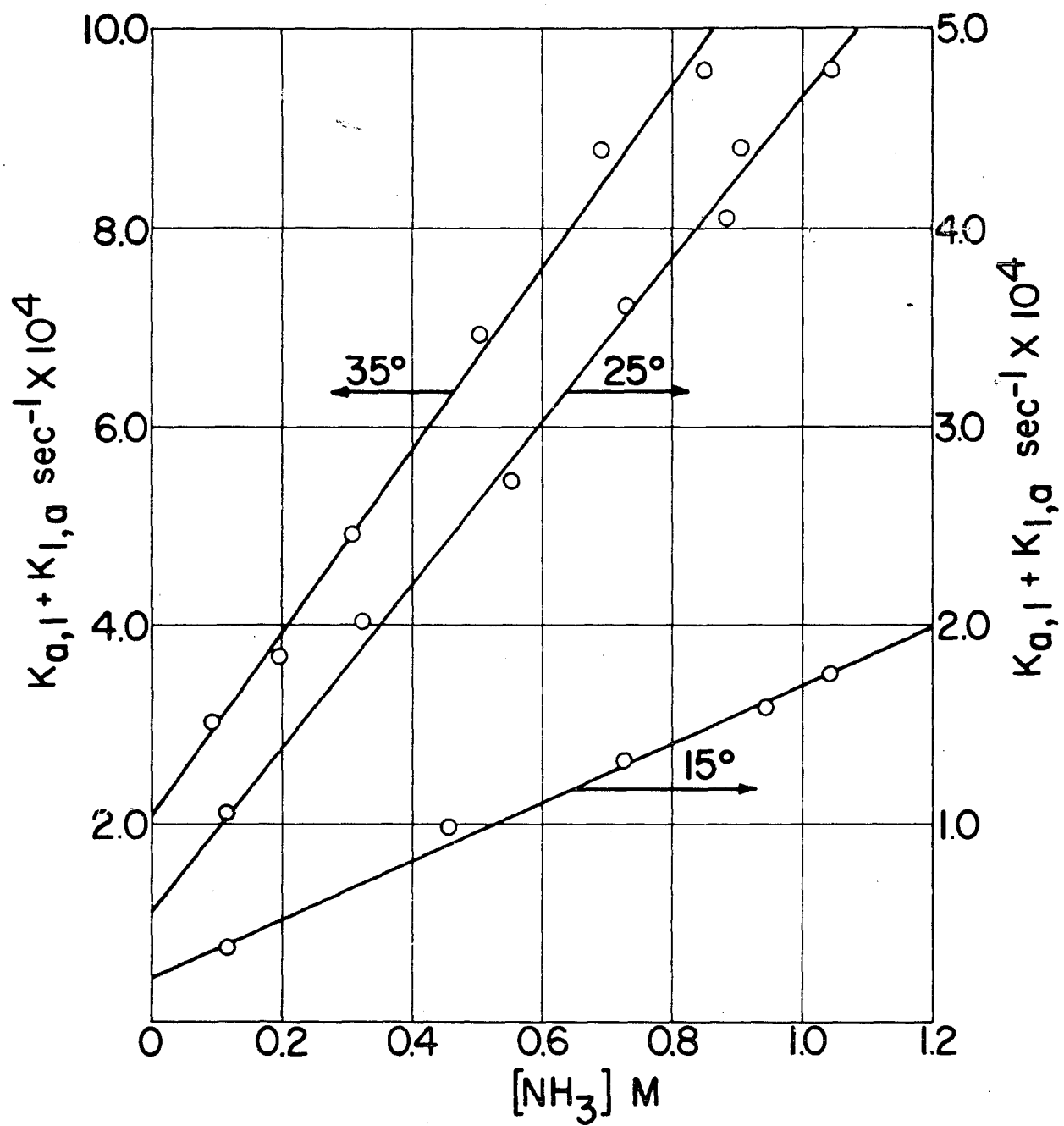initial $[PtCl_4]^= = 0.00986\ M.$, $[NH_3] = 0.8813\ M.$,
2 cm. cells, 25° C.

Figure 13. Plot of $k_{1a} + k_{a1}$ versus $[NH_3]$ concentration
as obtained from the short method of calculation;
plots for 15° C. and 25° C. refer to right hand
axis while the plot for 35° C. refers to the
left hand axis

the determination of the base hydrolysis constants, a high value is obtained due to the nonlinearity of the base hydrolysis reaction products. However the slope of the curve in Figure 13 should yield a reasonably good value for the second order rate constant for the ammoniation of $[PtCl_4]^=$ since at each concentration of ammonia this error should contribute an approximately constant value to the total pseudo first order rate constant. Thus the slope of the curve should be relatively unaffected. The values for the second order rate constants as determined in this manner are given in Table 8.

In order to refine the above rate constants and to determine values for the rate constants for the ammoniation of $[PtCl_3(NH_3)]^-$, more elaborate claculations were made with the aid of the computer. Using equations III.37-III.44, the concentrations of all the reaction products were calculated, and from these the resulting composite spectra were obtained for the times the experimental spectra were taken. Previously determined values were used for $k_{a,1}$, $k_{a,2}$, and $k_{a,3}$, while estimates were used for $k_{4,a}$, and $k_{1,b}$. The values for these latter two rate constants are not critical and even large errors in these constants would not make any appreciable change in the calculations. The values for $k_{1,a}$ and $k_{2,a}$ were varied until the best fit to the experimental data was obtained. These values are given in Table 8. Although reasonable agreement is obtained by the two methods of cal-

Table 8. Rate constants for the ammoniation of $[PtCl_4]^=$ and $[PtCl_3(NH_3)]^-$

Temp. (°C.)	$k_{1,a}/[NH_3]$ (as calc. from plot of O.D. in vicinity of 390 mμ) (M^{-1} sec^{-1} x 10^4)	$k_{1,a}/[NH_3]$ (as determined from best fit by computer) (M^{-1} sec^{-1} x 10^4)	$k_{1,a}/[NH_3]$ (as determined by Grinberg (29)) (M^{-1} sec^{-1} x 10^4)	$k_{2,a}/[NH_3]$ (M^{-1} sec^{-1} x 10^4)	$k_{2,a}/[NH_3]$ (as determined by Grinberg (29)) (M^{-1} sec^{-1} x 10^4)
15	1.47	1.50		3.7	
25	4.08	3.65	4.2	9.3	11.4
35	9.2	9.0	10.7	23.0	26.1

culation, it is expected that the computer gave the best values and they will be used in further calculations.

An example of the computer's fit to the experimental data is given in Figure 14. The best fit is found for the experiments at 25° C., while poorer agreement was obtained at 15° and 35° C. This was expected since the cell compartment of the spectrophotometer was not thermostated. Thus there was no temperature control for the sample for the approximately 5 minutes required to take a sample and obtain its spectrum. As could be expected the reactions at 35° appeared to be slower than expected, while the reverse was true of the reactions at 15° C. Since each sample of a given series of experiments was unthermostated for about the same length of time, each of these samples should be affected approximately equally. The first spectrum of a series appeared to be much slower or faster than expected, while the change in the spectrum, for each succeeding spectrum, was normal for the given increment of time. Thus an approximate correction could be made, and the error minimized, by making an appropriate change in the apparent zero time of the series of experiments. The error due to this source was least for the later spectra of a series, where the correction was only a small fraction of the total time. Even so these experiments were less accurate than those at 25° C. where the temperature was much closer to room temperature.

Figure 14. Typical comparison between experimental and calculated
spectra in the ammoniation of $[PtCl_4]^=$; curves refer
to experimental data while dots give calculated values:
initial $[PtCl_4]^=_0 = 0.00884$ M., $[NH_3] = 0.904$ M.,
2 cm. cells, 25° C.
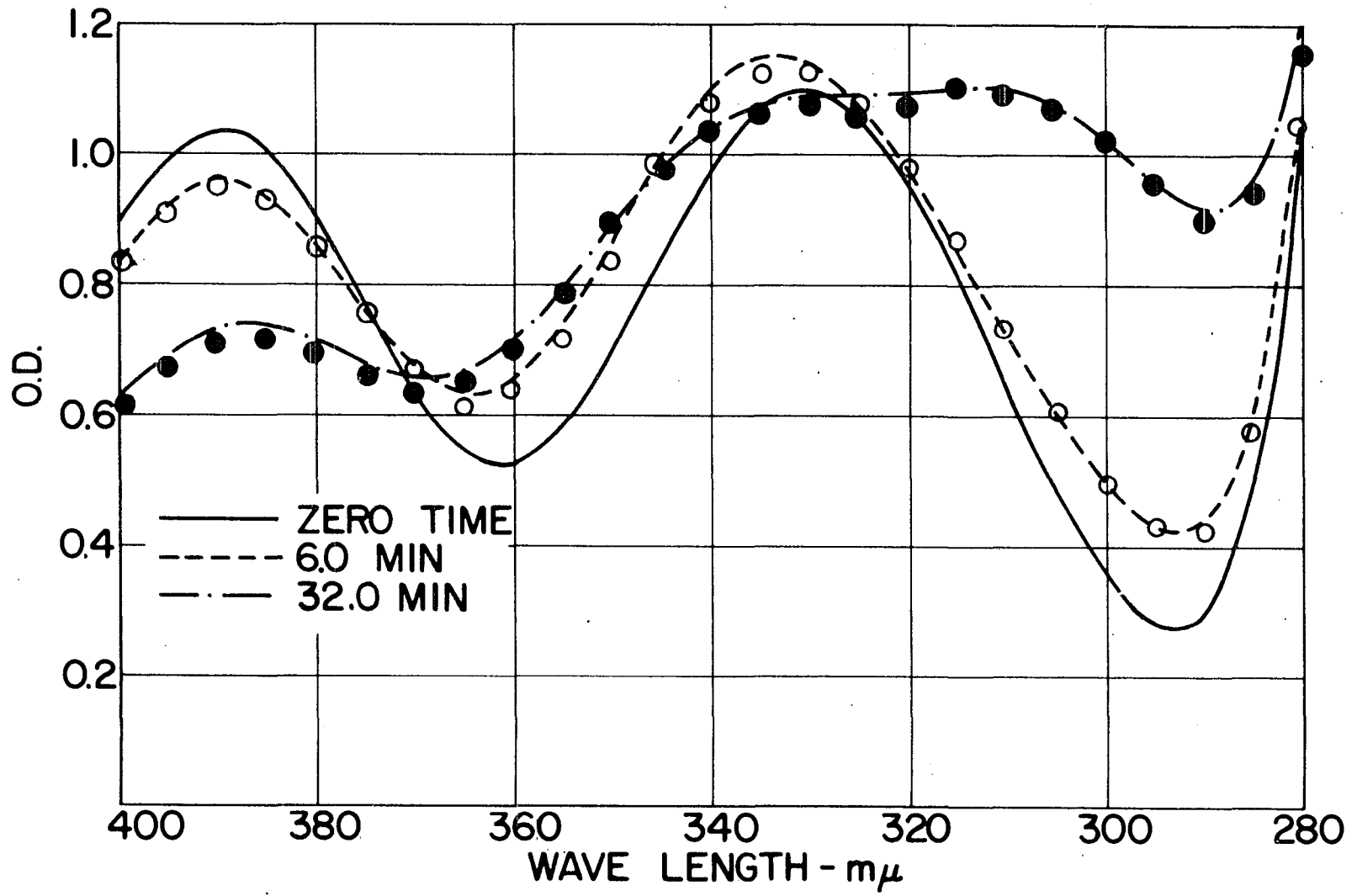
One preparation of K_2PtCl_4 yielded values for the rate constants significantly higher than those obtained from the many other preparations that had been made. Although the ultraviolet spectrum of the questioned preparation appeared to indicate pure $[PtCl_4]^=$, it was thought trace impurities might be present that would catalyze the reaction. To study the effect of catalysts on the reaction of $[PtCl_4]^=$ with ammonia, one experiment was made in which the reaction flask contained glass wool, while another experiment was made in which the reaction flask contained a platinum foil on which had been deposited active platinum black. No effect on the rates was noticed from these sources.

The effect of light on the reaction was studied by following two similar reaction mixtures of $[PtCl_4]^=$ in aqueous ammonia. One flask was exposed to a 100 watt tungsten light near the constant temperature bath, while the other flask was covered with black tape to prevent light from entering the reaction mixture except for the inevitable light due to the hydrogen lamp while obtaining a spectrum. Again no difference in reaction rates was observed.

A series of experiments was made in which the $[PtCl_4]^=$ concentration was varied between 0.002 M and 0.01 M, while the ammonia concentration was held constant. A first order dependence in $[PtCl_4]^=$ was found in the reaction rates.

One experiment was made in which the $[PtCl_4]^=$ was allowed

82

to age about one day in distilled water before ammonia was added to the solution. Under these conditions the $[PtCl_4]^=$ was in equilibrium with its aquo species before the ammonia was added. Significant concentrations of $[PtCl_3(OH)]^=$ were formed immediately and the reaction of this species with ammonia could be studied. Due to the uncertainties in the equilibrium constants, and in the hydroxo spectra, a completely quantitative treatment could not be made. However it appears that the reaction rate of $[PtCl_3(OH)]^=$ with ammonia is of the same order of magnitude as the rate of ammoniation of $[PtCl_4]^=$. Also it was observed that no larger quantity of $[PtCl_3(NH_3)]^-$ was formed than could be explained from the reaction of ammonia with the equilibrium concentration of $[PtCl_4]^=$ present at the time of addition of the ammonia. Thus it appears that the ammonia replaces the chloride ligand rather than the hydroxo ligand in its reaction with ammonia. This is also confirmed from previous experiments since in the reaction of ammonia with $[PtCl_4]^=$, the computer obtained a reasonably good fit to the experimental data without the necessity of using a term to indicate the possibility of the reaction of ammonia with $[PtCl_3(OH)]^=$ to form $[PtCl_3(NH_3)]^-$.

The enthalpies of activation and the entropies of activation were calculated from the temperature dependence of the rate constants for all the reactions studied. These results are tabulated in Table 9.

Table 9. Enthalpies and entropies of activation for reactions of various platinum species at 25° C.

| Platinum complex	Reactant	$\Delta H^{\pm}$ kcal.	$\Delta S^{\pm}$ eu.
$[PtCl_4]^=$	OH^-	18.2	-18
$[PtCl_3(OH)]^=$	OH^-	17.7	-20
$[PtCl_4]^=$	NH_3	15.1	-24
$[PtCl_3(NH_3)]^-$	NH_3	15.6	-20
$c-[PtCl_2(NH_3)_2]$	NH_3	17.6	-17

As can be seen from Table 8 reasonable agreement is found for the rate constants for the ammoniation of $[PtCl_4]^=$ and $[PtCl_3(NH_3)]^-$ between the present work and those obtained by A. A. Grinberg (29). Except for one series of experiments performed to confirm the first order dependence of the reaction on $[PtCl_4]^=$, all the experiments were made with an initial concentration of $[PtCl_4]^=$ of 0.01 M. Since Grinberg used 0.1 M $[PtCl_4]^=$ for the majority of his experiments, this agreement for the rate constant despite this difference in the concentration of the platinum complex is further proof of the first order dependence of $[PtCl_4]^=$ upon the reaction. A wider range of ammonia concentrations was used in the present work than that performed by Grinberg. The ammonia concentrations were varied over a range of 0.05 M to 1.05 M, while Grinberg did not use any concentrations above 0.4 M.

The agreement between Grinberg's experiments and the present work is also encouraging since different methods were used to follow the reaction. Grinberg used acid-base titrations to follow the ammonia concentration while the ultraviolet spectrum was used in the present work to follow the reaction.

V. CONCLUSIONS

It is interesting to compare the reactions which are characterized in Table 9. As can be seen, the activation energies are all in the range 16.5 ± 2 kcal. It thus appears that the heats of activation for the reaction of ammonia with these platinum complexes is independent of coulombic charge since the charge on the complex varies from zero in the case of $c-[PtCl_2(NH_3)_2]$ to -2 for $[PtCl_4]^=$. Before studying the mechanism of these ammoniation reactions, let us first look at the mechanisms that have been proposed for the reaction of water with platinum complexes. It is believed that the mechanism is similar to the acid hydrolysis mechanism (8), with an added fast removal of the acid proton of the water ligand to form the final product. Applying this mechanism to the base hydrolysis of $[PtCl_4]^=$ yields the following.
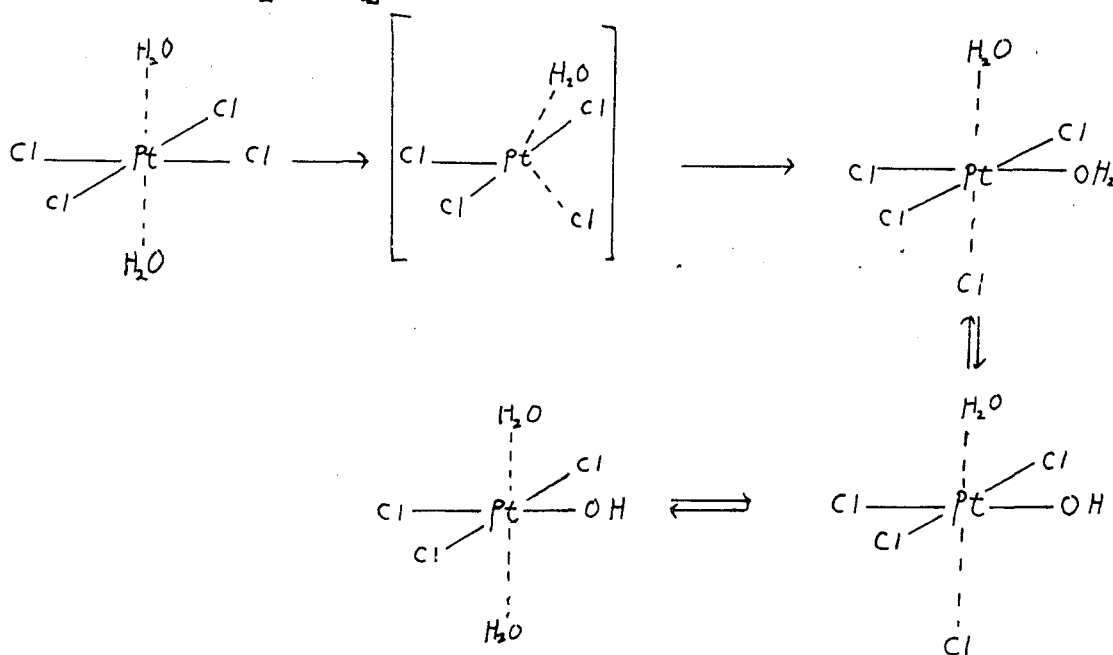
A similar reaction mechanism is proposed for the ammoni-ation reactions. To account for the observed first order dependence upon ammonia, an initial fast equilibrium reaction takes place in which the ammonia reversibly replaces a water molecule in the loosely bound axial position of the platinum complex. The equilibrium constant for this first reaction step must be small since the overall reaction had a simple first order dependence on ammonia throughout the range of concentrations used. Confirmation of this point comes from the fact that the ultraviolet spectrum of $[PtCl_4]^=$ is unaffected by even large concentrations of ammonia.

Following the addition of the ammonia to an axial position, the reaction proceeds in a similar manner to the base hydrolysis, except for the obvious elimination of the last step of the reaction, the removal of the acidic proton. This mechanism explains the fact that the activation energy is independent of the ionic charge on the platinum complex since the removal of the charged chloride ligand occurs through a stepwise process. A molecular rearrangement takes place in which the chloride ligand is transferred from the planar position to the loosely bound axial position from which it is later eliminated from the complex in a fast step. Thus in the rate determining step the platinum-chloride bond distance is not greatly elongated and coulombic forces should not have a great influence. It is true that the bond length for ligands

in the axial position is probably appreciably longer than the bond length for the same ligands in the plane, however it is the bond length for the platinum-chloride distance in the transition state that is important, and this may be nearly equal to the original bond distance. In any case it would have much less effect than removal of the chloride in a single step.

Since breaking of bonds is not significant in the reaction mechanism, the energy of activation should depend largely on the formation of the new platinum-ligand bonds. The activation energy of the ammoniation reactions and the base hydrolysis reactions listed in Table 9 are approximately equal in spite of the necessity of first replacing a water by an ammonia in the axial position of platinum complex as a first step in the ammoniation reactions. This implies a more stable platinum-ammonia bond as compared to a platinum-water bond in the transition state. It was previously noted that the equilibrium constant for the replacement of water by ammonia in the axial position of the platinum complex strongly favored the platinum complex containing water in the axial positions. The free energy change for taking water from the gas phase to the liquid phase is -2.4 kcal. (40) which is approximately equal to the free energy change of -2.1 kcal. for taking gaseous ammonia to an aqueous solution with a standard state of 1 molar. Thus the value of the equilibrium constant would

tend to indicate a stronger platinum-water bond than a
platinum-ammonia bond in the trigonal bipyramid transition
state. Also the ΔF^o of formation of the ammonia complexes
indicates that the platinum-ammonia bonds in the square plane
of the platinum complex are stronger than the corresponding
platinum-water bond.

In order to understand the shift in the relative order
of the platinum-water and the platinum-ammonia bonds, it is
necessary to consider the energy levels of the orbitals in-
volved as shown in Figure 15.

In the free atom, the energy levels of the electrons in
the outer shell of the platinum atom are arranged as indi-
cated. The energy levels of the p and d electrons are
degenerate in the free atom but this degeneracy is largely
removed in the crystal field of the square planar configura-
tion. If it is assumed that the ligands in the loosely bound
axial positions are at considerably greater distances than
the ligands in the plane, these levels will be as shown in
the middle portion of the diagram. The representations for
the orbitals are indicated on the diagram.

It is required that the orbitals which interact to form
molecular orbitals be of the same symmetry representation.
For maximum interaction it is also necessary that the orbitals
be of approximately equal energy. The energy levels of the
orbitals of the ammonia molecule are taken higher than the

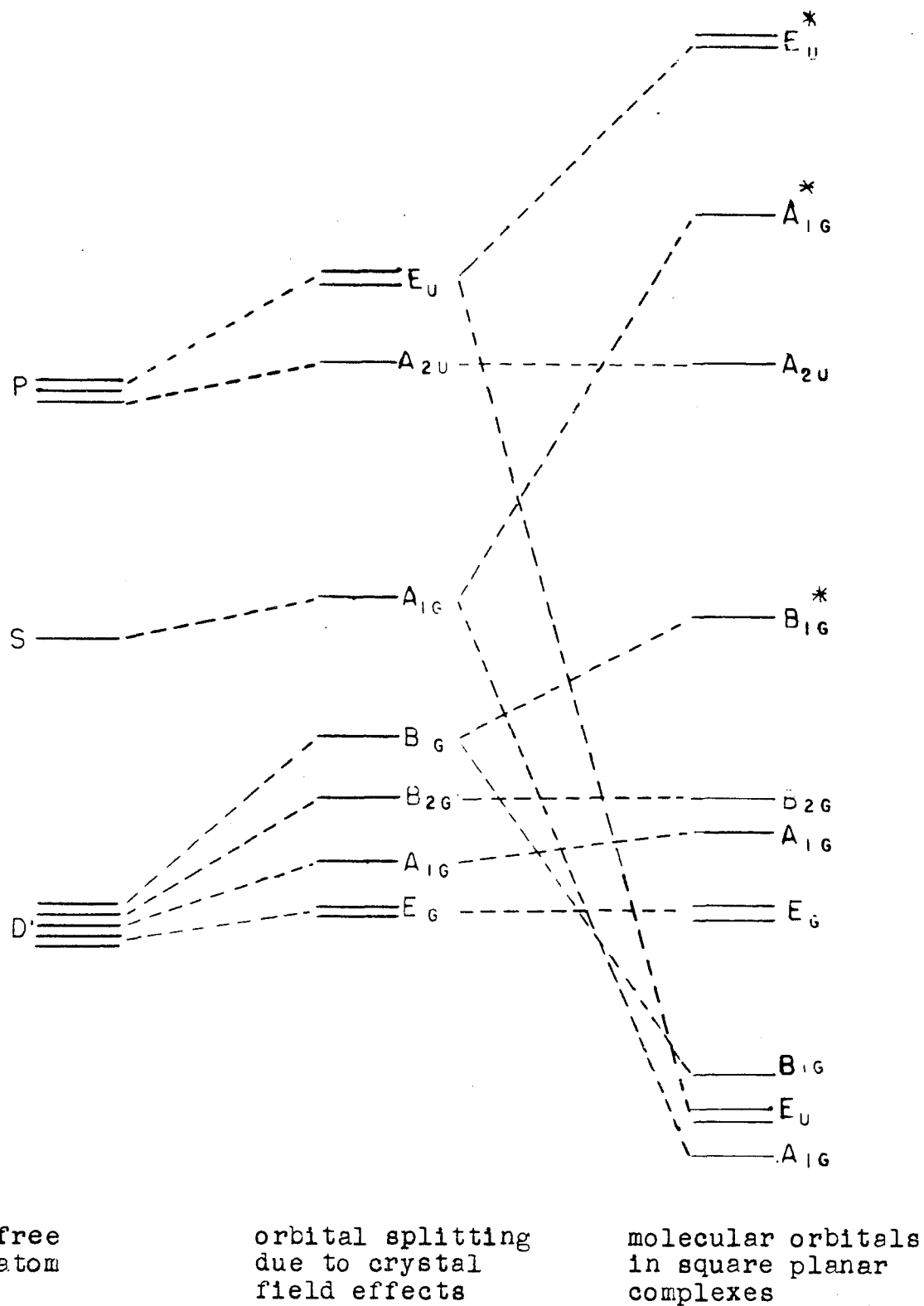| free atom | orbital splitting due to crystal field effects | molecular orbitals in square planar complexes |

Figure 15. Energy levels of platinum in square planar complexes

corresponding energy levels of the water molecule. However if the ammonia energy levels are nearly equal to the energy levels of the platinum atom which contribute to the bonding, a large degree of mixing will occur, with a resulting large decrease in the energy of the bonding orbital relative to the original orbitals. If it is not necessary to use also the corresponding antibonding orbital, a maximum stabilization will be obtained for the molecule relative to the original energies of the atoms. It is thus possible to account for the strong platinum-ammonia bonding in the plane of the complex if the assumption is made that the orbitals which are contributed to the bonding orbitals are of approximately equal energy.

If the energy levels of the water molecule are significantly lower than the energy levels of the platinum atom which are used for bonding, less interaction will be obtained in the construction of the molecular orbital. Thus the difference in energy levels can account for the difference in stabilization of the platinum-water and platinum-ammonia bonds in the plane of the complex.

In the axial position of the platinum complex, the bond distances are sufficiently great so that interaction of the electronic orbitals is smaller. The greater dipole moment of the water molecule may account for the greater stability of the platinum-water bond compared to the platinum-ammonia bond

in the axial positions. The shift in the relative order of stability of the water and ammonia ligands can thus be attributed to the ionic nature of the bonds in the axial position and to the covalent character in the planar positions. These qualitative considerations appear to be satisfactorily consistent with the observed rates and the enthalpies of activation.

VI. SUMMARY

(1) The spectra of $[PtCl_3(H_2O)]^-$, $[PtCl_2(H_2O)_2]$, $[PtCl_3(OH)]^=$, and $[PtCl_2(OH)_2]^=$ were determined. The positions of the peaks of these spectra agree closely with the calculations made by R. F. Fenske (7) based on crystal field considerations. The determination of these spectra made possible the following kinetic measurements, which were all followed by spectrophotometric methods.

(2) The rates for base hydrolysis of $[PtCl_4]^=$ were measured. The reaction rate was found to be independent of hydroxide concentration with first order rate constants of 1.25×10^{-5}, 3.81×10^{-5}, and 1.03×10^{-4} sec^{-1} at $15°$, $25°$, and $35°$ C. respectively. The indicated enthalpy and entropy of activation at $25°$ C. are 15.2 kcal. and -18 eu. respectively.

(3) The rates for base hydrolysis of $[PtCl_3(OH)]^=$ were measured. The reaction rate was again found to be independent of hydroxide concentration. The base hydrolysis of both $[PtCl_4]^=$ and $[PtCl_3(OH)]^=$ thus appears to follow an equation mechanism with an immediate fast neutralization of the acidic hydrogen of the aquo-complex. The first order rate constants for the base hydrolysis of $[PtCl_3(OH)]^=$ was found to be 1.0×10^{-5}, 3.5×10^{-5}, and 8.1×10^{-5} sec^{-1} at $15°$, $25°$, and $35°$ C. respectively. The indicated enthalpy and entropy of activation at $25°$ are 17.7 kcal. and -20 eu. respectively.

(4) The rates for the ammoniation of $[PtCl_4]^=$ were measured. The second order rate constants for the reaction of $[PtCl_4]^=$ with ammonia were found to be 1.50×10^{-4}, 3.65×10^{-4}, and 9.0×10^{-4} $M^{-1}sec^{-1}$ at 15°, 25°, and 35° C. respectively. The indicated enthalpy and entropy of activation at 25° C. are 15.1 kcal. and -24 eu. respectively.

(5) The rates for the ammoniation of $[PtCl_3(NH_3)]^-$ were measured. The second order rate constants for the reaction of $[PtCl_3(NH_3)]^-$ with ammonia were found to be 3.7×10^{-4}, 9.5×10^{-4}, and 23.0×10^{-4} $M^{-1}sec^{-1}$ at 15°, 25°, and 35° C. respectively. The indicated enthalpy and entropy of activation at 25° C. are 15.6 kcal. and -20 eu. respectively.

(6) The rates for the ammoniation of cis-$[PtCl_2(NH_3)_2]$ were measured. The second order rate constants for the reaction of cis-$[PtCl_2(NH_3)_2]$ were found to be 0.80×10^{-4}, 1.89×10^{-4}, and 4.85×10^{-4} $M^{-1}sec^{-1}$ at 15°, 25°, and 35° C. respectively. The indicated enthalpy and entropy of activation at 25° C. are 17.6 kcal. and -17 eu. respectively.

(7) The reaction of ammonia with $[PtCl_3(OH)]^=$ was studied qualitatively. The rate of ammoniation is of the same order of magnitude as the ammoniation of $[PtCl_4]^=$. The ammonia appeared to replace the chloride, and there was no evidence for the replacement of the hydroxo-group with any measurable rate.

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IX.   APPENDIX

In order to reduce the labor involved in the calculation of the rate constants for the ammoniation of $[PtCl_4]^=$, a program was written for the IBM 704 computer. The program was written in FORTRAN. This system acts as an intermediate language between the programmer and the basic machine language. The source program, in FORTRAN, is run on the computer and the output yields the program written in basic machine language. This program, together with any required data, is then rerun to obtain the desired computation. Since the computer was located at the University of Wisconsin, a method was required for the efficient operation of the machine while remaining in Ames, Iowa. An IBM 66 Printing Data Transciever permitted the two way exchange of information on standard IBM punched cards. These cards may then be introduced into the computer by an operator at the University of Wisconsin. A program named FRITO (Flexible, Remotely Instructed Tape Operator), as written by D. R. Fitzwater, G. Westland, and V. Pratt, was used to execute the desired program on the computer. The program to be run is included among many such programs on one of the tape inputs of the computer. Upon introducing a suitable punched card into the computer, the machine obtains the proper program from the tape input and turns control over to this program. Upon completion of the program, control may be returned to the card reader in order that other programs

may be run in a similar manner.

The computer was used to obtain the rate constants for the ammoniation of $[PtCl_4]^=$. Given a set of trial rate constants, the initial concentrations of $[PtCl_4]^=$, and the known spectra for all the species involved, the computer would calculate the ultraviolet spectra that would result from a set of reaction times. These computed spectra could then be compared to the observed spectra and the rate constants varied until the best fit was obtained. Equations III.35 through III.42 were used to calculate the concentrations of the species at any given time. Since a scanning rate of 60 mμ/ minute was used for the range of 250-400 mμ, it took 2 1/2 minutes to scan this range. Thus a different time should be used at every wave length. To reduce computer time, the concentration of all the species were calculated exactly at the times for the end points of the spectrum, 250 and 400 mμ, and the concentrations at intermediate points were calculated by interpolation. The computer then calculated the spectra that would be obtained for these rate constants at the given times, using this scanning rate. The resulting optical densities were printed out at intervals of 5 mμ .

The source program, in FORTRAN, is given below:

```
C       COLVIN SPEC
        DIMENSION RRA1(20), RR1A(20), RR1B(20), RRA2(20),
     RR2A(20),  RRB1(20), RR3A(20), RR4A(20), XT(10, 20),
     XX(10), AA1(25),  AA2(25), AA3(25), AA4(25), TT(25),
```

```
      HH1(25), HH2(25), AA1H1(25), G1(25), G2(25), SF(20),
      S(25), SA1(25), SA2(25), SA3(25), SA4(25), ST(25),
      SH1(25), SH2(25), SA1H1(25), CC(20)
100 FORMAT (30H COLVIN CHLOROPLATINATE SPECTRA)
101 FORMAT (1H0//4HRA1=F9.7, 6H  RA2=F9.7, 6H  R1A=F9.7,
      6H  R2A=F9.7, 6H  R3A=F9.7, 6H  R4A=F9.7, 6H  R1B=F9.7,
      6H  RB1=F9.7)
102 FORMAT (3H00=F7.5, 4H  X=F5.1, 4H  T=F7.5, 5H  H1=F7.5,
      5H  H2=F7.5, 5H  A1=F7.5, 5H  A2=F7.5, 5H  A3=F7.5,
      5H  A4=F7.5, 7H  A1H1=F7.5)
103 FORMAT (5H 280=F6.4, 6H  285=F6.4, 6H  290=F6.4,
      6H  295=F6.4, 6H  300=F6.4, 6H  305=F6.4, 6H  310=F6.4,
      6H  315=F6.4, 6H  320=F6.4, 6H  325=F6.4, 5H  330=F6.4,
      6H  335=F6.4, 6H  340=F6.4, 6H  345=F6.4, 6H  350=F6.4,
      6H  355=F6.4, 6H  360=F6.4, 6H  365=F6.4, 6H  370=F6.4,
      6H  375=F6.4, 5H  380=F6.4, 6H  385=F6.4, 6H  390=F6.4,
      6H  395=F6.4, 6H  400=F6.4)
104 FORMAT(I2)
105 FORMAT (9F6.6)
106  FORMAT (18F4.1)
107 FORMAT (14F5.2/11F5.2)
108 FORMAT (9F8.8/9F8.8/7F8.8)
150 READ 104, N
151 READ 105, (RRA1(M), RR1A(M), RR1B(M), RRA2(M), RR2A(M),
      RRB1(M), RR3A(M), RR4A(M), CC(M), M=1,N)
```

```
152 READ 106, ((XT(11,M), 11=1, 10), M=1,N)
153 READ 107,( SA1(L), L=1, 25)
154 READ 107,( SA2(L), L=1, 25)
155 READ 107,( SA3(L), L=1, 25)
156 READ 107,( SA4(L), L=1, 25)
157 READ 107,( ST(L), L=1, 25)
158 READ 107,( SH1(L), L=1, 25)
159 READ 107,( SH2(L), L=1, 25)
160 READ 107,( SA1H1(L), L=1, 25)
161 READ 108,( G1(K), K=1, 25)
162 READ 108,( G2(K), K=1, 25)
  1 WRITE OUTPUT TAPE 9, 100
  2 DO 87 I= 1,N
  3 RA1= RRA1(I)
  4 R1A= RR1A(I)
  5 R1B= RR1B(I)
  6 RA2= RRA2(I)
  7 R2A= RR2A(I)
  8 RB1= RRB1(I)
  9 R3A= RR3A(I)
 10 R4A= RR4A(I)
    C= CC(I)
 11 DO 12 J=1, 10
 12 XX(J)= XT(J,I)
```

```
14 WRITE OUTPUT TAPE 9,101, RA1, RA2, R1A, R2A, R3A, R4A,
   R1B, RB1
15 R1= RA1 + R1A
16 RH1= R1B + RA2
17 RA1T= R2A + RB1
19 CH11= RA1/(RH1-R1)
20 CH12= -CH11
21 CH21= CH12*RA2/R1
22 CH22= CH11*RA2/RH1
23 CH23= RA1*RA2/(R1*RH1)
24 CA11= R1A/(RA1T - R1)
25 CA12= -CA11
26 CA21= CA11*R2A/(R3A - R1)
27 CA22= CA12*R2A/(R3A - RA1T)
28 CA23= R1A*R2A/((R1 - R3A)*(RA1T - R3A))
29 CA31= CA21*R3A/(R4A - R1)
30 CA32= CA22*R3A/(R4A - RA1T)
31 CA33= CA23*R3A/(R4A - R3A)
32 CA34= R1A*R2A*R3A/((R1 - R4A)*(RA1T - R4A)*(R3A - R4A))
33 CA41= CA31*R4A/(-R1)
34 CA42= CA32*R4A/(-RA1T)
35 CA43= CA33*R4A/(-R3A)
36 CA44= -CA34
37 CA45= R1A*R2A/(R1*RA1T)
38 CA1H11= CA12*RB1/R1
```

39 CA1H12= CA11*RB1/RA1T

40 CA1H13= R1A*RB1/(R1*RA1T)

41 CA1H14= CH12*R1B/R1

42 CA1H15= CH11*R1B/RH1

43 CA1H16= RA1*R1B/(R1*RH1)

44 DO 86 M= 1, 10

45 X= XX(M)

46 IF (X) 47, 87, 47

47 E1= EXPF((-R1)*(X))

48 EH1= EXPF((-RH1)*(X))

49 EA1= EXPF((-RA1T)*(X))

50 E3A= EXPF((-R3A)*(X))

51 E4A= EXPF((-R4A)*(X))

52 E1P= EXPF((-R1)*(X + 2.5))

53 EH1P= EXPF((-RH1)*(X + 2.5))

54 EA1P= EXPF((-RA1T)*(X + 2.5))

55 E3AP= EXPF((-R3A)*(X + 2.5))

56 E4AP= EXPF((-R4A)*(X + 2.5))

57 T= E1

58 H1= CH11*E1 + CH12*EH1

59 H2= CH21*E1 + CH22*EH1 + CH23

60 A1= CA11*E1 + CA12*EA1

61 A2= CA21*E1 + CA22*EA1 + CA23*E3A

62 A3= CA31*E1 + CA32*EA1 + CA33*E3A + CA34*E4A

63 A4= CA41*E1 + CA42*EA1 + CA43*E3A + CA44*E4A + CA45

```
64 A1H1= CA1H11*E1 + CA1H12*EA2 + CA1H13 + CA1H14*E1
   + CA1H15*EH1 + CA1H16

65 TP= E1P

66 H1P= CH11*E1P + CH12*EH1P

67 H2P= CH21*E1P + CH22*EH1P + CH23

68 A1P= CA11*E1P + CA12*EA1P

69 A2P= CA21*E1P + CA22*EA1P + CA23*E3AP

70 A3P= CA31*E1P + CA32*EA1P + CA33*E3AP + CA34*E4AP

71 A4P= CA41*E1P + CA42*EA1P + CA43*E3AP + CA44*E4AP + CA45

72 A1H1P= CA1H11*E1P + CA1H12*EA1P + CA1H13 + CA1H14*E1P
   + CA1H15*EH1P + CA1H16

73 DO 81 K=1, 25

74 AA1(K)= (G1(K))*(A1) + (G2(K))*(A1P)

75 AA2(K)= (G1(K))*(A2) + (G2(K))*(A2P)

76 AA3(K)= (G1(K))*(A3) + (G2(K))*(A3P)

77 AA4(K)= (G1(K))*(A4) + (G2(K))*(A4P)

78 TT(K)= (G1(K))*(T) + (G2(K))*(TP)

79 HH1(K)= (G1(K))*(H1) + (G2(K))*(H1P)

80 HH2(K)= (G1(K))*(H2) + (G2(K))*(H2P)

81 AA1H1(K)= (G1(K))*(A1H1) + (G2(K))*(A1H1P)

82 DO 84 L= 1, 25

83 SP(L)= (AA1(L))*(SA1(L)) + (AA2(L))*(SA2(L))
   + (AA3(L))*(SA3(L)) + (AA4(L))*SA4(L)) + (TT(L))*ST(L))
   + (HH1(L))*(SH1(L)) + (HH2(L))*(SH2(L))
   + (AA1H1(L))*(SA1H1(L))
```

```
84 S(L)= (C)*(SP(L))

85 WRITE OUTPUT TAPE 9, 102, C,X,T,H1,H2,A1,A2,A3,A4,A1H1

86 WRITE OUTPUT TAPE 9, 103, (S(L), L= 1, 25)

87 CONTINUE

   REWIND 1

   CALL TAPE

   END(0,1,1,1,1)
```

To run the program, the above FORTRAN statements were placed in the computer, and the output yielded the program written in basic machine language. After placing this resulting program on the FRITO tape, the program was available for use in the following manner. The first card to be placed in the computer was a calling card, which instructed the computer to obtain the proper program from the tape and turn control over to this program. This card contained an * in column (2), a T in column (4), an E in column (6), and the name of the program, COLVIN SPEC, in columns 7-17. Following this card was placed a card containing in columns (1) and (2) the number of sets of rate constants to be used in the given run. The next cards contained the rate constants to be tried. These were punched one set to a card in the order $r_{a,1}$, $r_{1,a}$, $r_{1,b}$, $r_{a,3}$, $r_{2,a}$, $r_{b,1}$, $r_{3,a}$, $r_{4,a}$, and C, where C was the product of the initial concentration of $[PtCl_4]^=$ multiplied by the optical path length of the cell. These numbers were punched in groups of six columns extending from column (1)

through column (54). The next set of cards contained the reaction times for which the calculations were desired. Ten times were required for each set of rate constants; if a fewer number was required the excess was filled in with zeros. These times were punched in columns 1-72, groups of four columns being available for each time. It was not necessary to start a new card for each set of reaction times. The spectra for all the various species were punched in the next set of cards. The spectra were loaded in the following order: $[PtCl_3(NH_3)]^-$, cis-$[PtCl_2(NH_3)_2]$, $[PtCl(NH_3)_3]^+$, $[Pt(NH_3)_4]^{+2}$, $[PtCl_4]^=$, $[PtCl_3(OH)]^=$, $[PtCl_2(OH)_2]^=$, and $[PtCl_2(NH_3)(OH)]^-$. Two cards were allowed for the spectrum of each species, intervals of 5 mμ being used between 280 and 400 mμ. These spectra were punched in columns 1-70, five columns being allowed for the extinction coefficient at each wave length. The last set of cards in the data deck contained two series of numbers. The first series was the decimal equivalent of 24/30, 23/30, 22/30, ..., 0/30. The second series was the decimal equivalent of 6/30, 7/30, 8/30, ..., 30/30. Three cards were used for each series; columns 1-72 being used with eight columns being allowed for each number. A set of "impossible cards" was placed behind this deck to stop the computer in case of trouble with the program.