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EQUILIBRIUM AND KINETICS OF SOME SIMPLE
COMPLEXES OF PALLADIUM(II)

Richard A. Reinhardt
Kenneth J. Graham

July 1976

Final Report for Period July 1958 - June 1975

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Prepared for:

Chief of Naval Research, Arlington, Virginia 22217, and
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Palladium	Substitution Reactions									
Chemical Equilibrium	Ammine Complexes									
Chemical Kinetics	Chloro Complexes									
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)										
<p>Fifteen years of studies on Palladium(II) complexes of H_2O, NH_3, and Cl^- are summarized, including not only results from this laboratory but also from other laboratories, as have appeared in the chemical literature. More extensive report is given on several experiments not appearing elsewhere: the isomerism equilibria of $Pd(NH_3)_2Cl_2$ and the ammoniation kinetics of</p>										

cis-Pd(NH₃)₂Cl₂. Tables are given for all presently known equilibrium and kinetic data involving these complexes, and estimates are also provided for a number of reactions for which no data exist. Thirty-eight references are cited.

Block 19 (con):

cis-trans isomerism

Dichlorodiamminepalladium(II)

Aquo complexes

EQUILIBRIUM AND KINETICS OF SOME SIMPLE
COMPLEXES OF PALLADIUM(II)

by

Richard A. Reinhardt and Kenneth J. Graham

PREFACE

Since 1958, experimental studies have been pursued at this laboratory to investigate the chemistry of complexes of palladium(II) containing NH_3 , Cl^- , and H_2O as ligands. This report represents a summary of this work (through 1975) as well as of studies conducted at other laboratories which are germane to the general problem. We have included a compilation of the known equilibrium and kinetic data relating to this series of complexes, feeling that it will be of use to present this information in a single place and in uniform fashion. We have also attempted to demonstrate in a small way - by citing their names - our gratitude to the numerous collaborators, both military and civilian, who have assisted in these studies.

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DEFINITIONS

Concentrations are expressed in units of molarity, \underline{M} = moles of solute per liter (at 25°) of solution, or in decimal fractions thereof.

Ionic Strength, $\mu = \frac{1}{2}\sum C_i Z_i^2$, where C_i is the concentration in moles per liter and Z_i is the charge for each ion present in the solution.

Equilibrium constants (represented by capital K) are concentration constants, applicable at the specified ionic strength.

Rate constants are designated by lower case k, times being expressed in seconds. Subscripts f and r refer to forward and reverse reaction, respectively.

Activation enthalpy, ΔH^\ddagger is defined by the Eyring equation,

$$k_r = \frac{k_B T}{h} \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R)$$

I. INTRODUCTION

1. DESCRIPTIVE CHEMISTRY OF DIPOSITIVE PALLADIUM

Characteristic of d^8 species [1] Pd(II) forms complexes almost exclusively with coordination four in square-planar geometry. The chemistry is in many ways analogous to that of Pt(II), but with certain significant differences: (1) Oxidation to the +4 state is much more difficult with Pd than with Pt ($E^\circ = 0.7$ v for $\text{PtCl}_6^{2-} \rightarrow \text{PtCl}_4^{2-}$, 1.3 v for $\text{PdCl}_6^{2-} \rightarrow \text{PdCl}_4^{2-}$ [2]). (2) The aquated $\text{Pt}(\text{OH}_2)_4^{2+}$ appears to be incapable of existence, whereas solutions containing $\text{Pd}(\text{OH}_2)_4^{2+}$ can be prepared and stored [3]; this fact may indicate a considerably greater tendency for base hydrolysis with Pt(II) than with Pd(II). (3) Complexes of Pt(II) are in general substitution-inert, with substitution half-times typically of the order of 10^3 - 10^5 seconds and upward; the corresponding Pd(II) complexes are more reactive by a factor of 10^4 - 10^5 [4] and, in particular, the aquation-anation reactions are quite rapid [5].

Thus, among the ammineaquochloro complexes, all members of the series of Pt(II) complexes are in principle isolable, whereas with Pd(II) only the following appear capable of isolation (either as solids or in solution as predominant species): $\text{Pd}(\text{NH}_3)_4^{2+}$ and its salts; PdCl_4^{2-} and its salts, including $[\text{Pd}(\text{NH}_3)_4][\text{PdCl}_4]$; $\text{Pd}(\text{OH}_2)_4^{2+}$; cis- and trans- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. The last two must be formed under metastable conditions. It

appears [6] that pure solids can be obtained, but the nature of their aqueous solutions is an unresolved question to be discussed later in this report. In addition, it seems likely, based on the results of Poë and Vaughan [7], that solutions containing $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$ as predominant species can be prepared from cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2 + \text{aq HCl}$ and, though metastable, have useful lives of a few hours.

Table VI (in Section III) shows the entire array of possible complexes with NH_3 , H_2O , and Cl^- as ligands. H_2O ligands have been left out of the formulas, but are present to whatever extent is required to bring the coordination number to four. Complexes marked with asterisks exist as cis and trans isomers. Equilibrium data, given in Table VI as cumulative stability constants, are complete except for most of the cis-trans equilibria and except for any information dealing with either isomer of $\text{Pd}(\text{NH}_3)\text{Cl}(\text{OH}_2)_2^+$ or $\text{Pd}(\text{NH}_3)\text{Cl}_2(\text{OH}_2)$. Estimates for the latter are shown in parentheses. Kinetics data, summarized in Tables IX, X, and Xi, are largely limited to the complexes around the periphery of Table VI.

2. MECHANISTIC BEHAVIOR

Numerous review articles [8] have presented evidence regarding the mechanism of substitution reactions in square-planar complexes. These ideas will apply to the particular class of complexes being considered herein. The processes are associative, probably involving a five-coordinate intermediate.

For the reaction



the reaction rates depend on the nature of the leaving group, X (for the present system the effects are $H_2O > Cl^- \gg NH_3$), on the nucleophile Y ($NH_3 > Cl^- \approx H_2O$), on the ligand trans to X ($Cl^- > NH_3 > H_2O$), and on the ligands cis to X ($NH_3, H_2O > Cl^-$). The trans and cis effects indicated are those observed in the majority of cases so far studies; there are many irregularities, however.

The nucleophilicity of H_2O , though smaller than that of NH_3 or Cl^- , is still sufficient so that under some reaction conditions H_2O will compete appreciably. Considering reaction (1) as two-directional, then, for one direction or the other, this branched mechanism leads [9] to the two-term rate law considered typical of square-planar substitutions:

$$-d \ln [\text{Complex}]/dt = k_1 + k_2[X]$$

where X is the leaving group for the reaction in the direction considered. It then follows from the principle of microscopic reversibility [10] that for the reverse reaction

$$-d \ln [\text{Complex}']/dt = [Y](k_1'/[X] + k_2')$$

where the primes refer to the reverse reaction. This pattern has been observed in the system considered here for $X = Cl^-$, $Y = NH_3$ for both forward and reverse reactions [7,9,11]. In either direction, the k_2 term is associated with "direct"

substitution (addition of nucleophile followed by elimination of the leaving group) and the k_1 term with the indirect path involving first $ML_3(OH_2)$.

II. EXPERIMENTAL STUDIES

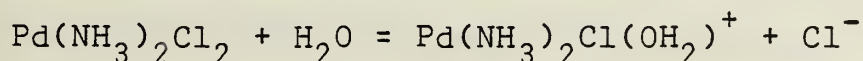
1. Trans-Pd(NH₃)₂Cl₂

Personnel: Mr. James Yax (1962-63)
Mrs. Carol Brown (1965)
Mrs. Lucille Smithson (1966)

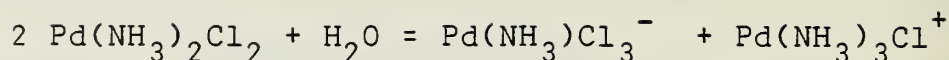
Publication: "The Solubility of Pd(NH₃)₂Cl₂ in Electrolyte Solutions" [12].

Early qualitative experiments (some of them arising from a previous research project [13] involving the separation of Ag from Pd) showed the sparing solubility of trans-Pd(NH₃)₂Cl₂ and the rather slow rate of its formation from Pd(NH₃)₄²⁺. The solubility study (R.A.R., 1958-62) was initiated primarily to set concentration limits which could be used for homogeneous equilibrium and kinetics studies. A by-product of these experiments was the identification as hydrous PdO of the ultimate product of the base hydrolysis occurring when Pd(NH₃)₂Cl₂ stands in contact with water in the absence of added electrolyte.

Solubilities were measured at 25° in a variety of electrolyte solutions. The observation that the solubility decreased with increasing concentration of Cl⁻ (approaching a limiting value, at high [Cl⁻], of 0.95 mM) was interpreted on the basis of the aquation equilibrium,

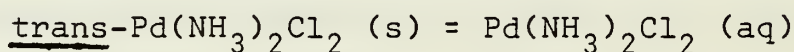


together with the phase equilibrium. Quantitatively, the analysis made at the time [12] failed to take into account the disproportionation equilibrium as well:



Correcting for this latter [14] it was estimated that in the saturated solution the concentration of the species $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ was 0.55 mM at 25°.

It is now possible to correlate this figure with the solubility at 10° given by Muromtsev [15], 0.21 mM in HCl solution. Assuming no disproportionation or deammonation at this lower temperature, because of the very slow rate (see Poë" and Vaughan [7]). we can estimate that for the equilibrium



$\Delta H^\circ \sim 11 \text{ kcal mol}^{-1}$ and $\Delta S^\circ \sim 20 \text{ cal mol}^{-1} \text{ K}^{-1}$.

Also supporting the half-millimolar "true" solubility at 25° are some rough rate of solution measurements at this temperature made by Mrs. Smithson in the laboratory (1966) which indicated that the concentration of dissolved trans-Pd(NH₃)₂Cl₂ rises to about 0.5 mM within 5 minutes after initial contact with the solvent (various concentrations of aqueous NaCl and NH₄Cl adjusted to unit ionic strength with NaNO₃), but thereafter rises quite slowly, requiring 24 to 36 hours to reach final equilibrium. For a considerable time, after this 0.5 mM value is reached, the rate of solution in any run is constant, the value decreasing with increasing [Cl⁻]. Zero-order rate constants found (chloride concentrations in parentheses) were: 4.4×10^{-8} (0.005), 1.4×10^{-8} (0.01), 0.8×10^{-8} (0.1); concentrations in M, time in seconds. It is presumed that 0.5 mM

represents phase equilibrium rather rapidly established with trans-Pd(NH₃)₂Cl₂ in solution and the slower stages represent establishment of the various solution equilibria. No explanation for the retarding effect of chloride can be offered.

Attempts were made by Yax (1962-63) to measure the concentration of Cl⁻ potentiometrically in solutions containing Pd(NH₃)₂Cl₂. This endeavor was unsuccessful, at least partly due to failure to appreciate the ease of ammoniation of the complex in the presence of NH₄⁺.

2. Cis-trans ISOMERISM IN Pd(NH₃)₂Cl₂

It has long been recognized [16] that solid cis-Pd(NH₃)₂Cl₂ is thermodynamically unstable with respect to the trans isomer. But it is not at all clear what the relative stabilities might be in solution. Analogous systems are not a satisfactory guide. Isomeric equilibria in a group of Pt and Pd complexes with Group V ligands lie heavily in favor of trans, [17] and more so with Pd than with Pt. Equilibrium between the isomers of Pt(NH₃)(OH₂)Cl₂ exists at about 90% trans [18]. Yet for the isomers of PtCl₂(OH₂)₂, about 45% cis is present at equilibrium [19] and for PdX₂(OH₂)₂ the ratio of cis:trans is 2 for X = Cl and 6 for X = Br [20]. In our analysis of structural effects in the reversible aquation of the Pd-ammine complexes [21] we estimated about 85% cis-Pd(NH₃)₂(OH₂)₂ at equilibrium, but this estimate is highly speculative.

As an incidental to his studies on the chloride anation of tetraamminepalladium(II), Sparkes [22] made some qualitative

observations suggesting the presence of at least some cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ in solution. From the appearance of the spectra it is clear that an aged solution of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is converted partly to $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$ on addition of HCl, whereas a freshly-prepared one (from the acidification of $\text{Pd}(\text{NH}_3)_4^{2+}$) is not. Also, if a solution of $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$ is carefully treated with NH_3 , to give a mixture of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2 + \text{Pd}(\text{NH}_3)_3\text{Cl}^+$, acidification of this also forms some $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$, presumably showing the presence of the cis form here also.

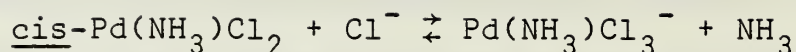
The suppositions are the following: $\text{Pd}(\text{NH}_3)_4^{2+}$ plus aq HCl yields initially pure trans- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$; the latter is slowly converted to the cis form, which reacts with additional HCl to produce $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$ much faster than does the trans. Addition of a little ammonia to $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$ forms cis rather than trans. All this kinetic behavior is parallel to that observed in the Pt(II) system, and is quite in accord with the trans effect. Further direct support comes from Poë" and Vaughan's experiments [7], showing that the rate of reaction of Cl^- with cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is two orders of magnitude greater than with trans.

Midas [23] found that his solutions of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ reacted rapidly with aq HCl, at the rate given by Poë" and Vaughan. The resulting solution, however, had an absorption maximum at 390 nm rather than the 430 nm reported by Poë" and Vaughan for $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$. This could signify that Midas's solutions contained appreciable trans- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ ($\lambda_{\text{max}} \sim 380$ nm) resulting from equilibration, whereas Poë" and Vaughan's did not.

A concerted effort was made in the laboratory in 1974 (R.A.R.) to devise an analytical method to distinguish the cis and trans isomers in solution on the basis of the rate of reaction with aq HCl and on the $\text{Pd}(\text{NH}_3)\text{Cl}_3^- - \text{PdCl}_4^{2-}$ isosbestic at 257 nm [7]. After adding HCl, the sample was divided into two halves. Part I was held at 25° and absorbance vs time followed until the conversion cis \rightarrow $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$ was complete (15-30 min). The increase in absorbance, $A_{\text{I}} - A_0 \propto [\text{cis}]$. Part II was held at 60° for 30 minutes, at the end of which period both isomers will have been converted to $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$, because of the elevated temperature. Thus, $A_{\text{II}} - A_{\text{I}} \propto [\text{trans}]$ and, assuming the absorbancies of the two isomers equal at this wavelength, $(A_{\text{II}} - A_{\text{I}})/(A_{\text{I}} - A_0) = [\text{trans}]/[\text{cis}]$.

The experiments proved that there is indeed considerable cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ in aged solutions prepared from either isomer initially. But the 60° sample often showed a decrease in absorbance after the 30 min heating period, whereas, $\epsilon_{\text{PdNH}_3\text{Cl}_3^-} > \epsilon_{\text{Pd}(\text{NH}_3)_2\text{Cl}_2}$. It appears that the isosbestic point may vary appreciably with the experimental conditions; or, conceivably, there is an additional species (perhaps polymeric) at the rather low acidity (0.01 M) used. In either case, the method could not be used except to provide evidence that both isomers are present in appreciable amounts at equilibrium.

More recently (R.A.R., 1975) an attempt was made to observe the reversibility of the chloride anation of the cis species:



by observing (spectrophotometrically at 260 nm) the rate in solutions buffered in NH_3 by the use of $\text{HOAc} - \text{OAc}^- - \text{NH}_4^+$ mixtures. Under the pseudo-first-order conditions used, the observed rate constant, k_{obs} , must equal the sum of the forward and reverse rate constants; thus k_r , and so also the equilibrium constant, could be found.

From the runs at nanomolar NH_3 , good first-order plots were obtained, with k_{obs} ranging from 0.00185 to 0.00197 sec^{-1} . This compares favorably with 0.00194 sec^{-1} found at high acidities by Poë" and Vaughan. For solutions around 1/2 micromolar NH_3 , a slower step was observed (whether Guggenheim plots [24] or infinite-time absorbance was used) with a rate constant of the order of $1 \times 10^{-3} \text{ sec}^{-1}$. It is true that k_{obs} for the faster step increases with increasing $[\text{NH}_3]$, and this increase could be interpreted as showing an equilibrium constant for the chloride anation of cis- $\text{Pd(NH}_3\text{)}_2\text{Cl}_2$ of about 10^{-6} . The latter value is about what should be expected if the cis-trans equilibrium corresponds to an appreciable concentration of both species. The slow step, however, corresponds to our estimates for none of the possibly observable reactions. Though it is of the expected magnitude for the ammoniation of trans- $\text{Pd(NH}_3\text{)}_2\text{Cl}_2$, that reaction should be extremely unfavorable, thermodynamically, in solutions of micromolar NH_3 [14].

3. EQUILIBRIA AMONG THE CHLOROAMMINE SPECIES

Personnel: LCDR Robert K. Sparkes, RCN (1966)
Mrs. Norma L. Brenner (1964-65)

Publication: "Equilibria Among the Chloroammine
Complexes of Palladium(II)" [14]

Thesis: "Substitution Reactions of the Ammine
Complexes of Palladium(II)" (in part) [22]

When trans-Pd(NH₃)₂Cl₂ is synthesized by the addition of insufficient aqueous HCl to Pd(NH₃)₄²⁺, the pH assumes an initially low value after a quantity of acid is added, increases, slowly at first, then more and more rapidly until close to equilibrium. (Rasmussen and Jørgensen [3] reported a similar surprise at this observation.) This is not an autocatalysis, but merely a result of the logarithmic nature of pH. The reaction is actually of zero order in hydrogen ion; that is, plots of [H⁺] vs t are linear over most of the range.

Based on the foregoing observation, and using conditions dictated by the solubility limitations, a series of experiments was designed and carried out to study the equilibrium and kinetics in this system, using pH and absorption spectrophotometry as monitors.

Most of the equilibrium measurements were carried out by Mrs. Brenner as potentiometric titrations with ammonia on a solution of Pd(NH₃)₂Cl₂ in NH₄NO₃ - NH₄Cl solution (at 25°, ionic strengths 0.5 and 1.0). Using the Bjerrum [25] analysis, values could be obtained for equilibrium quotients involving not only Pd(NH₃)₂Cl₂ (the equilibrium mixture of isomers), Pd(NH₃)Cl₃⁻, Pd(NH₃)₃Cl⁺, and Pd(NH₃)₄²⁺, but also some of the

aquated species: $\text{Pd}(\text{NH}_3)_2\text{Cl}(\text{OH}_2)^+$ and $\text{Pd}(\text{NH}_3)_3(\text{OH}_2)^{2+}$.

Absorbance - pH data (Sparkes) in 1M Cl^- at 25° and 30° permitted check determinations of the values involving the non-aquated species, as well as estimates of standard enthalpies and entropies of reaction. This technique also gave the basis for reconstructing the spectra of $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ and, especially, that of the unobtainable $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$ [14].

4. KINETICS OF CHLORIDE ANATION OF $\text{Pd}(\text{NH}_3)_4^{2+}$

Personnel: LCDR Robert K. Sparkes, RCN (1966)
Mrs. Lucille Smithson (1966-67)

Publications: "Kinetics of the Consecutive Substitutions of Ammonia by Chloride Ion in Tetraamminepalladium(II)" [11].

"Isosbestic Points and Consecutive Reaction Schemes. The Reaction of Tetra-amminepalladium(II) Ion with Chloride in Acid Solution" [26].

Thesis: "Substitution Reactions of the Ammine Complexes of Palladium(II) (in part) [22].

Kinetics experiments were carried out under pseudo-first-order conditions (Pd-limited) by the addition of excess aqueous HCl to solutions of $\text{Pd}(\text{NH}_3)_4^{2+}$ at varying concentrations of Cl^- . The reaction was followed using pH (Sparkes) at 25° and absorption spectrophotometry in the range 290-400 nm (Sparkes, Mrs. Smithson) at 20° - 30° .

Data were analyzed to obtain the two pseudo-first-order rate constants (designated k_A' and k_B') corresponding to the two consecutive steps leading to $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. In addition, using absorbance runs at the shortest wavelengths, a rough

estimate was made for the much slower third step leading to $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$; the validity of this estimate has since been demonstrated by the direct measurement of the rate made by Poë and Vaughan [7]. Though analysis of the pH data gave less precise results, it was valuable as providing uncontestable evidence that the second step was faster than the first ($k_B' > k_A'$). All steps showed the two-term pattern:

$$k_{\text{obs}} = k_1 + k_2[\text{Cl}^-]$$

Shortly after the publication of the foregoing [11], correspondence from J. S. Coe at Kings College, London, indicated quite similar experiments at their laboratory, but interpreted by them as showing $k_A' > k_B'$. These results were published a few months later [27]. A result of further discussions by mail was the resolution that the data from both laboratories could best be interpreted as indicating $k_B' > k_A'$ (using a detailed analysis of the absorbance-time data). This conclusion was published as a joint contribution from the two laboratories [26].

There also appeared about this time the very important paper by Poë and Vaughan [7] on the reaction of cis- and trans- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ with aqueous HCl to form $\text{Pd}(\text{NH}_3)\text{Cl}_3^-$ and PdCl_4^{2-} . This research thus completed the study of the chloride anation of $\text{Pd}(\text{NH}_3)_4^{2+}$.

5. KINETICS OF AMMONATION OF PdCl_4^{2-}

Personnel: LT W. W. Monk, USN (1968)

Mrs. Katherine Henry Collins (1968-69)

Publications: "The Kinetics of the Successive Ammoniation Reactions of Tetrachloropalladate(II) Ion" [9]

Thesis: "Kinetics of Ammonia Substitution into Tetrachloropalladate Ion" [28]

The ammoniation reactions are very fast ($k_f = k_r/K$ with $K \sim 10^5$ and the k_f , from the chloride anations, $\sim 10^{-3}$); thus, if they are to be studied using classical techniques, very low concentrations are required. This study by Monk and Mrs. Collins was conducted using solutions buffered in NH_3 as follows: An acetic acid-acetate ion buffer controlled the pH; then a high, fixed concentration of NH_4^+ served to hold NH_3 at a constant value of the order of 10 micromolar. Pd(II) , at 0.5 mM , was always the limiting reactant in these pseudo-first-order runs. The reaction was studied spectrophotometrically in the range 400-470 nm.

Again the data showed the appearance of two consecutive steps; each step shows dependence on chloride concentration as

$$k_{\text{obs}} = k_2[\text{NH}_3] + k_1[\text{NH}_3]/[\text{Cl}^-]$$

The faster step corresponds unambiguously to $\text{PdCl}_4^{2-} \rightarrow \text{Pd}(\text{NH}_3)\text{Cl}_3^-$. The slower step was tentatively assigned to the step cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2 \rightarrow \text{Pd}(\text{NH}_3)_3\text{Cl}^+$. Further discussion of this assumption will be made in a later section.

6. KINETICS OF AQUATION OF THE AMMINE COMPLEXES

Personnel: LT J. R. Funck, USN (1962)
ENS W. J. DeBerry, Jr., USN (1971)
K.J.G. (1970-72)

Publication: "Aquation Kinetics of the Aquoammine Complexes of Palladium(II)" [21]

Theses: "The Interaction of Hydrogen Ion with Tetraamminepalladium(II) Ion in the Presence of Nitrate and Chloride Ions" [29]

"The Kinetics of Successive Aquation Reactions of Tetraamminepalladium(II) Ion" [30]

Funck (1962) attempted to study deammonation kinetics in the absence of Cl^- (the chief anion was nitrate) from pH - time measurements under conditions of excess Pd(II). This study provided some useful qualitative information, but was unsuccessful quantitatively, largely because it was not possible to introduce a sample of acid small enough to give significant pH changes, yet large enough to avoid reverse-reaction complications.

A pH study of the equilibria in the system $\text{Pd}(\text{NH}_3)_x(\text{OH}_2)_{4-x}^{2+}$ was published by Rasmussen and Jørgensen in 1968 [3]. These authors, using the Bjerrum technique, measured the four equilibrium constants involved at 25° and unit ionic strength (their value for the first-step aquation constant of $\text{Pd}(\text{NH}_3)_4^{2+}$, is appreciably smaller than that found in our laboratory in a less direct measurement [14]). Rasmussen and Jørgensen were able to reconstruct absorption spectra for several of the intermediate species and also presented rough kinetic data from their pH - time curves for the first two steps of aquation of $\text{Pd}(\text{NH}_3)_4^{2+}$.

DeBerry (1971) studied the kinetics of the system in this laboratory. Excess aqueous perchloric acid was added to solutions of $\text{Pd}(\text{NH}_3)_4^{2+}$ (ClO_4^- was the only anion present). The reaction was followed spectrophotometrically in the range 300-

400 nm from 25° to 70 °C, $\mu = 1.0 \text{ M}$. Four consecutive steps occur in this process, leading ultimately to $\text{Pd}(\text{OH}_2)_4^{2+}$. Although there was no run in which reliable values of all four rate constants could be obtained, the Arrhenius plot showed the points as falling on four lines corresponding to those four steps, and thus values for the four rate constants could be found. Assignment of rate constants to mechanistic steps was based somewhat on Rassmussen and Jørgensen's preliminary results [3] but primarily on an analysis of intercepts in the $\log \Delta A$ vs t plots (where ΔA is the difference in absorbance at time t and at infinite time). It was in this way established that the rate constants decrease steadily from one step to the next.

7. AQUATION AND ANATION OF THE CHLORIDE COMPLEXES

Personnel: LT R. L. Burke, USN (1972)

K.J.G. (1972)

Thesis: "Stability Constants for the Chloride Complexes of Palladium(II)" [31].

A. SUMMARY

At the time this equilibrium study was undertaken, there existed only extremely divergent values for the various aquation constants of the chloropalladium species (Ref in [32]) with no guide to select reliable values. Burke based his method on that used by Srivasta and Newman [33] in their studies of the mixed halide complexes. By this technique, Burke was able to obtain reliable values for the aquation constants of PdCl_4^{2-} and

$\text{Pd}(\text{OH}_2)\text{Cl}_3^-$ which were to be in good agreement with those reported by Elding (vide infra). Unfortunately, the experiments intended to measure the remaining equilibria in the low-chloride range, were conducted under conditions where the equilibrium concentration of Cl^- was too small to be well defined. Further details of this research are given in Section B.

Simultaneous with the conclusion of Burke's studies was the publication of a paper by Elding [20], also on the stabilities of the halide complexes (bromide, as well as chloride). In this careful research, what must be considered definitive values for the equilibrium constants were obtained. The full set of results, as well as the kinetic data, published separately [5] are given in Section III. Elding's kinetic data are also largely in agreement with those of a less complete study by Pearson [34].

B. EXPERIMENTAL (Burke)

Solutions containing $\text{Pd}(\text{OH}_2)_4^{2+}$ were prepared by dissolving PdSO_4 [3] which had been synthesized by boiling $\text{Pd}(\text{NO}_3)_2$ in conc. H_2SO_4 . Solutions containing PdCl_4^{2-} were prepared from the sodium salt. Solutions low in chloride were prepared from Pd^{2+} (0.02 M), 1 M HClO_4 , and added chloride ranging from 2×10^{-4} to 0.02 M. Solutions high in chloride were prepared from PdCl_4^{2-} (0.003 M) with 1 M HCl and 1 M HClO_4 added to yield $[\text{Cl}^-]$ ranging from 0.01 M to 1.00 M. The ionic strength was 1.00 M for all solutions. Absorbances were measured on these

solutions (14 in all) using the Beckmann DK-1A scanning spectrophotometer over the range 350-550 nm.

The following analysis is restricted to systems at high $[\text{Cl}^-]$. When just two absorbers are present in these systems, the total absorbance A can be shown to be

$$A = \frac{A_0 + A_1 \beta_1 R}{1 + \beta_1 R}$$

(following the method and notation of Srivasta and Newman [33]) where A_0 is the absorbance due to the parent complex PdCl_4^{2-} , A_1 , that due to the second complex PdCl_3^- , β_1 is the equilibrium constant for formation of the second complex from the parent, and R is the "ligand ratio", which is $1/[\text{Cl}^-]$ for systems high in chloride.

Defining two new parameters, $\Delta = A_0 - A_1$ and $V = 1 + \beta_1 R$, it follows that $\Delta/V = A - A_1$ and $\log(V-1) = \log \beta_1$. By superimposing plots of A vs $\log R$ onto normalized plots of Δ/V vs $\log(V-1)$ to the best fit, $\log \beta_1$ is found from the translation in abscissa and A_1 from that in ordinate. These plots were done at each 5 nm over the range of utility. Table I gives the results of this fitting, for $\beta_1 = [\text{PdCl}_4^{2-}] / [\text{PdCl}_3^-][\text{Cl}^-]$.

When R is sufficiently large, the third complex, PdCl_2 (equilibrium mixture of cis and trans isomers) becomes significant. Absorbance is now represented by

$$A = \frac{A_0 + A_1 \beta_1 R + A_2 \beta_2 R^2}{1 + \beta_1 R + \beta_2 R^2}$$

TABLE I

AQUATION EQUILIBRIUM DATA FOR PdCl_4^{2-} AND $\text{PdCl}_3\text{OH}_2^-$ A. Data for determining β_1

λ	$A_{\text{PdCl}_3^-}$	$\log \beta_1$
420	0.730	1.450
425	0.758	1.400
430	0.790	1.450
435	0.725	1.400
440	0.760	1.500
445	0.667	1.320
450	0.630	1.380
455	0.650	1.510
460	0.580	1.440
470	0.425	1.560
475	0.420	1.380
480	0.335	1.500

B. Data for determining β_2

λ	A_{PdCl_2}	$\log \beta_1$	$\log \beta_2$
420	0	1.466	5.312
425	0	1.451	5.238
430	0.026	1.470	4.996
435	0.040	1.351	5.384
440	0.061	1.455	4.870
445	0.080	1.280	5.083
450	0.100	1.263	4.987
455	0.530	1.510	3.225
460	0.485	1.415	3.432
475	0.378	1.714	3.841

β_1 is the aquation constant for PdCl_4^{2-} and β_2 is the cumulative aquation constant for PdCl_4^{2-} to PdCl_2 . See accompanying text for details. Data are from [31].

or

$$\frac{(A-A_2)R^2}{A_0-A} = \frac{1}{\beta_2} + \frac{R(A_1-A)\beta_1}{A_0-A\beta_2}$$

where β_2 is the cumulative equilibrium constant for formation of PdCl_2 and A_2 the absorbance due to PdCl_2 . Previously found A_1 and an assumed A_2 were used to construct a plot of the variables of this last equation. The best correlation was used to evaluate β_2 and to yield a check value of β_1 . For the resulting determinations data are given in the second portion of Table I. For stepwise constants defined by $K_1 = \beta_1$ and $K_2 = \beta_2/\beta_1$, best values are $\log K_1 = 1.44 \pm 0.05$ and $\log K_2 = 2.42 \pm 0.05$. Results for K_3 and K_4 are not reported for the reason cited in Section A.

8. KINETICS OF AMMONIATION OF cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$

Personnel: LCDR M. T. Midas, Jr., USN (1969)
LT J. R. Atwill, Jr., USN (1973)
LCDR R. G. Hibler, USN (1974)
K.J.G. (1970-74)

Theses: "The Kinetics of Consecutive Substitution Reactions in cis-Dichlorodiamminepalladium(II)" [23]

"The Ammoniation of cis-Dichlorodiamminepalladium(II)" [35]

"Stopped-flow Kinetics of the Ammoniation of cis-Dichlorodiamminepalladium(II)" [36]

A. SUMMARY

The three studies considered under the present heading represent attempts to clarify Monk and Collins's experiments

(vide sup.) on the later steps in the ammonation of PdCl_4^{2-} by studying the reaction with solutions of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ as starting material. It was remarked in the earlier section that it was necessary to assume the slower step observed to be that for the conversion of the cis isomer to $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$. None of the experiments which started with the cis material has been able to give a definitive proof for this contention, although there are continued indications that that assignment is the correct one. The results are summarized briefly here and considered in more detail in Sections B, C, and D.

Midas, using substantially the same conditions as Monk and Collins, found two consecutive reactions of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ with ammonia of which the slower corresponded fairly well with the slower in the Monk-Collins experiments, not inconsistent with the assumption that either represents the ammonation of the cis isomer. The faster step could not be analyzed since at this low NH_3 concentration, subsequent reactions are extensively reversed.

Atwill measured the rates at higher ammonia concentrations (ca 0.5 mM) to avoid this complication of reversibility; but since classical mixing was being used, it was necessary to operate below room temperature to obtain rates in the measurable range. Qualitatively, Atwill's results were in accord with Midas's: there were observed two consecutive steps, each retarded by Cl^- . Quantitatively, his data when extrapolated to 25° are two to three times greater than Midas's at comparable concentrations - more difference than can be attributed to ionic strength

differences and in the opposite direction expected for elimination of the reverse reaction. Atwill's temperature and chloride-concentration dependences moreover showed anomalous behavior.

Hibler's stopped-flow data were obtained at ammonia concentrations up to 0.25 M and (in contrast to all the preceding studies) in the absence of ammonium ion. His rate constants are an order of magnitude less than those found previously and they showed very unusual dependence on ammonia concentration. It is proposed that the involvement of hydroxo-complexes is at least partly responsible for the differences seen.

B. EXPERIMENTS OF LCDR MIDAS

Following the synthetic method of Durig [6], cis-Pd-(NH₃)₂Cl₂ was prepared by mixing alcoholic solutions of (NH₄)₂-PdCl₄ and NH₄OAc at -15° C, maintaining the product in alcoholic HCl at -20° for 12 hours, and then washing with cold ethanol. The infrared spectrum showed the doublet at 484 and 463 cm⁻¹ characteristic of the cis isomer. On treatment with aq HCl at room temperature, the material reacted with a rate constant in excellent agreement with that reported by Poë and Vaughan [7].

Solutions for the kinetics runs were prepared as follows. The cis-Pd(NH₃)₂Cl₂ was stirred with a NaCl solution of desired concentration for 45 min; this solution was used for runs during the same day. To initiate a run, there was added a buffer solution, containing 0.02 M NaOAc, 0.04 M NaOAc and sufficient NH₄ClO₄ and NaClO₄ to give the desired ammonium-ion

concentration and an ionic strength of 0.8 M. Data were obtained for the ranges 0.4 to 0.7 M Cl^- and 0.06 to 0.23 M NH_4^+ , corresponding to NH_3 concentrations from 2 to 9 μM . Absorbance-time data were obtained on a Beckmann DU spectrophotometer at 400 nm, 25°C.

Two steps of reaction were observed in most of the runs, and the data were analyzed by the method previously described [11], by first evaluating the slow step from the long-time data and then subtracting this to obtain the rate of the fast step. Results are given in Table II. Agreement with reciprocal $[\text{Cl}^-]$ plots is also indicated by the computed values shown in columns 4 and 6 of the Table. These correspond to $k_{\text{obs}} = [\text{NH}_3](k_2 + k_1/[\text{Cl}^-])$, where for the slow step $k_2 = 5.1 \text{ M}^{-1} \text{ sec}^{-1}$, $k_1 = 8.9 \text{ sec}^{-1}$ and for the fast step, $k_2 = 64 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_1 = 135 \text{ sec}^{-1}$, all at 25°, $\mu = 0.8 \text{ M}$.

C. EXPERIMENTS OF LT ATWILL

a. Synthesis of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$. Coe and Lyons [37] reported a synthesis of this material based on the fact that the two-step aquation of $\text{Pd}(\text{NH}_3)_4^{2+}$ leads exclusively (or nearly so - see [21]) to cis- $\text{Pd}(\text{NH}_3)_2(\text{OH}_2)_2^{2+}$. Thus, about 2½ moles of acid per mole of Pd were added to the tetraammine solution and the system was allowed to stand for a time, whereupon chloride was added to precipitate the desired product by the nearly instantaneous anation. Coe and Lyons recommended an overnight period before adding Cl^- . It is easy to show, however, that a shorter time will result in improved yield, since unavoidably appreciable $\text{Pd}(\text{NH}_3)_3(\text{OH}_2)^{2+}$ forms.

TABLE II
 KINETICS DATA FOR THE AMMONATION OF cis-Pd(NH₃)₂Cl₂
 (Midas [19], 25⁰, μ = 0.8)

[Cl ⁻], <u>M</u>	[NH ₃], <u>μM</u>	10 ⁴ k _s , sec ⁻¹		10 ⁴ k _f , sec ⁻¹	
		<u>obs</u>	<u>calc</u> ^a	<u>obs</u>	<u>calc</u> ^b
0.36 ^c	8.75	2.62	2.61	39.1	38.4
		2.62		37.7	
0.48 ^d	8.75	2.17	2.06	29.9	30.2
		1.99		29.2	
0.71	8.75	1.55	1.54	23.7	22.2
		1.38		20.5	
0.36	4.34	1.33	1.29	-	
		1.40			
0.36	2.17	0.625	0.65	-	
		0.800			

^aCalculated from 8.9[NH₃]/[Cl⁻] + 5.1[NH₃]

^bCalculated from 135[NH₃]/[Cl⁻] + 64[NH₃]

^cRuns at 0.305 mM Pd except as noted.

^d0.203 mM Pd.

Insufficient time, however, results in the presence of some $\text{Pd}(\text{NH}_3)_3(\text{OH}_2)^{2+}$, and when Cl^- is added, this latter will form trans- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ preferentially. Computations based on DeBerry's [21] kinetic data (neglecting reverse reactions) show that the maximum yield of the cis product occurs after about 10 min at room temperature, but the material would contain about 10% trans isomer due to the residual triammine. After 4 hours the contamination from this source has fallen to a few tenths of a percent and the yield of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ is still acceptable.

Thus 3 mmoles of $\text{Pd}(\text{NH}_3)_4^{2+}$ were treated with 7.3 mmoles of HClO_4 in about 50 cc. After 4 hours excess concentrated NaCl is added and the crystals of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ are collected promptly.

Samples so prepared gave the characteristic infrared spectrum [6] and a positive KI - acetone test [16].

b. Kinetics runs

Rates were observed by following absorbance at 235 nm, data being obtained on the recording Beckmann DK-1A spectrophotometer. Final reaction mixtures were 0.05 mM in Pd, 0.5 mM in NH_3 (added as free base) and 0.05 to 0.5 M in Cl^- . All solutions were 1.0 M in NH_4^+ , maintaining ionic strength at 1.0. Measurements were performed in the range $10^\circ - 22^\circ$. Runs were initiated by injecting the ammonia solutions into the Pd solutions from a hypodermic syringe. Internal consistency suggests that mixing was complete within 3 seconds.

The combination of reduced temperature and rapid injection made possible these runs at higher ammonia concentrations than could be used heretofore. It was necessary to maintain much lower Pd concentrations so that pseudo-first-order conditions could be approximated in these unbuffered systems (a small correction was, in fact, applied for depletion of NH_3 during a run), which explains the use of the far-ultra-violet spectral region where molar absorbances are much greater.

c. Results

Data were analyzed into two rate constants per run, corresponding to two consecutive steps, just as described for Midas's research in Section B. Results are given in Table III.

Arrhenius plots for each of the three chloride concentrations show considerable scatter. Nonetheless, best values can be given for the three nominal temperatures 10° , 15° , and 20° . These are shown in Table IV as $k_{\text{obs}}/[\text{NH}_3]$.

At each temperature, the data were then fitted to the two-term rate law

$$\frac{k_{\text{obs}}}{[\text{NH}_3]} = \frac{k_1}{[\text{Cl}^-]} + k_2$$

for both slow and fast steps. It was found that the most reasonable fit was obtained with k_2 independent of temperature for both steps. (It is true that a better fit to the data could have been obtained with each k_2 having a negative temperature coefficient, but this is totally inconsistent with the concept that the second-order term corresponds to direct one-step reaction of complex with nucleophile). The resulting k_1 and the

TABLE III
 KINETICS OF THE AMMONATION OF cis-Pd(NH₃)₂Cl₂
 (Atwill [35], $\mu = 1$)

[Cl ⁻], <u>M</u>	[NH ₃] _{1/2} , <u>mM</u> ^a	t, °C (±0.1 ⁰)	k _{obs} , sec ⁻¹	
			fast	slow
0.50	0.435	19.6	0.237	0.0221
"	"	20.6	0.225	0.0221
"	"	20.6	0.212	0.0234
"	"	19.9	0.216	0.0213
"	"	21.0	0.254	0.0258
"	"	21.3	0.270	0.0255
"	"	15.7	0.178	0.0171
"	"	16.6	0.197	0.0211
"	"	16.0	0.220	0.0214
"	"	16.2	0.157	0.0159
"	0.460	10.7	0.174	0.0145
"	"	10.6	0.175	0.0163
"	"	10.6	0.178	0.0147
0.050	"	10.3	0.382	0.0531
"	"	10.3	0.394	0.0555
"	"	10.3	0.50	0.0594
"	"	10.3	0.460	0.0552
"	"	14.6	0.708	0.0829
"	"	14.5	0.819	0.0970
"	0.445	14.6	0.739	0.0882
"	"	14.0	0.648	0.0743
"	"	12.3	0.546	0.0670
0.40	"	11.2	0.192	0.0149
"	"	10.6	0.202	0.0147
"	"	12.7	0.210	0.0166
"	"	14.8	0.217	0.0189
"	"	16.6	0.243	0.0225
"	"	19.3	0.226	0.0216
"	"	20.2	0.277	0.0263

^aConcentration of NH₃ at 50% reaction.

TABLE IV

SUMMARY OF RATE CONSTANTS FROM TABLE III^a

t, °C	$k_{\text{obs}}/[\text{NH}_3], \text{M}^{-1}\text{sec}^{-1}$			k_1, sec^{-1}	$k_2, \text{M}^{-1}\text{sec}^{-1}$	ΔH_1^\ddagger kcal mol ⁻¹
	0.05M Cl ⁻	0.4M Cl ⁻	0.5M Cl ⁻			
10	115(110)	32(31)	32(29)	4.5	20	
15	197(200)	43(43)	40(38)	9	20	
20	-	59(60)	52(52)	16	20	
25 ^b				[29]	20	9.9
10	920(850)	430(325)	375(310)	30	250	
15	1700(1750)	500(440)	440(400)	75	250	
20	-	610(650)	540(570)	160	250	
25 ^b				[360]	250	13.1

^aData in parentheses are computed from k_1 and k_2 (see text). k_2 independent of temperature was assumed, as shown.

^bValues at 25° are by extrapolation from Arrhenius plots.

corresponding activation enthalpies are given in Table IV. Also seen in this table are, in parentheses, the values of $k_{\text{obs}}/[\text{NH}_3]$ computed from the appropriate k_1 and k_2 , for comparison with the experimental values.

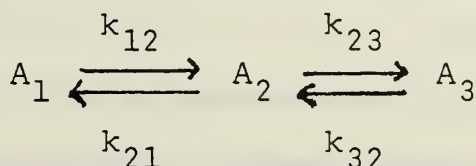
It must be emphasized that even the poor fit (especially for the fast step) requires using second-order constants which are invariant with temperature. This behavior is totally unlike that of similar reactions with other chloroamines of Pd(II) (See Table XII).

D. DISCUSSION OF THE NON-FLOW EXPERIMENTS

Assuming that the slow step of Midas's [23], Atwill's [35], and Monk's [9] experiments all represent the same process, i.e., the ammoniation of $\text{cis-Pd}(\text{NH}_3)_2\text{Cl}_2$, it becomes of interest to compare these:

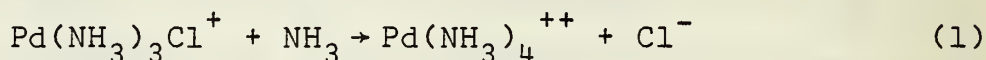
	<u>k_1 (sec⁻¹)</u>	<u>k_2 (M⁻¹sec⁻¹)</u>
Monk ($\mu = 1$)	14	12
Midas ($\mu = 0.8$)	9	5
Atwill (extrapolated, $\mu = 1$)	29	20

Now, ammonia concentrations were such that whereas Monk's and Midas's conditions led to equilibrium mixtures of diammine and triammine species, Atwill's led solely to $\text{Pd}(\text{NH}_3)_4^{2+}$. Thus the earlier studies dealt with a reaction scheme

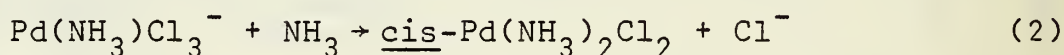


wherein A_1 and A_3 are the cis and trans species, respectively, and A_2 is $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$. It can be shown (see the treatment in Frost and Pearson [10], e.g.) that if $k_{23} \sim k_{32} > k_{12} \sim k_{21}$, as appears to be the case here, the observed rate constants will be approximately $\lambda_1 \sim k_{12} + \frac{1}{2}k_{21}$ and $\lambda_2 \sim k_{23} + k_{32}$. Thus we should expect Midas's or Monk's data to give $k_{12} + \frac{1}{2}k_{21}$, where Atwill's should be k_{12} alone, and thus be smaller, not larger as is observed. Again if, as suggested below, A_2 rather than A_1 represents cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$, Atwill's data give k_{23} and the earlier measurements, $k_{23} + k_{32}$.

The fast step in Midas's or Atwill's study cannot be identified. In addition to the obvious choice:



a real alternative possibility is



inasmuch as disproportionation of cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2$ into triammine plus trichloro species can be presumed to have taken place (by analogy with solutions of the trans isomer). Estimates of reaction rates for various steps in a reasonable mechanism for this disproportionation indicate equilibrium should be reached in a few hours in solutions of cis material in 1 M chloride, a typical stock solution for any of these studies.

Values for the rate constants of the fast step are compared with estimates, computed for reaction (1) from rate and

equilibrium data for the reverse reaction [11,14] and for (2) [7] also assuming equal concentrations of cis and trans at equilibrium:

	<u>k_1 (sec⁻¹)</u>	<u>k_2 (M⁻¹sec⁻¹)</u>
Midas, $\mu = 0.8$	135	64
Atwill, extrapolated	360°	250
Step (1), computed	20	140
Step (2), computed	120	370

It is felt that no conclusion can be drawn regarding the identity of the fast step.

E. STOPPED-FLOW EXPERIMENTS OF LCDR HIBLER

The reaction of cis-Pd(NH₃)₂Cl₂ (prepared by Atwill's method [35]) with ammonia was observed by following the change in absorbance with time at a wavelength of 380 nm, all at unit ionic strength, 25°. In each run the stopped-flow apparatus [38] mixed equal volumes of mM complex with the appropriate ammonia solution. Concentrations of chloride were varied from 0.1 to 1.0 M, those of ammonia from 0.025 to 0.25 M. Data were recorded either on a strip-chart recorder at chart speeds up to 2 in/sec, or, for the faster runs, by photographing the trace of a Techtronix 434 storage oscilloscope with a Polaroid camera.

Each stopped-flow record could be analyzed into a slow and fast step, using the technique described in Sections B and C. Results are given in Table V. Also shown in the table are

TABLE V
 STOPPED-FLOW KINETICS FOR THE AMMONIATION OF cis-Pd(NH₃)₂Cl₂
 (Hibler, [36], 24.5⁰ ± 0.5⁰, μ = 1)

[NH ₃], <u>M</u>	[Cl ⁻], <u>M</u>	k _s , sec ⁻¹	k _f , sec ⁻¹
0.125	0.1	0.34(0.35)	7.0(7.4)
"	0.5	0.92	8.8
"	0.625	0.49	7.0
"	0.75	0.60	3.4
"	1.0	0.17(0.17)	0.80(1.4)
0.05	1.0	0.04(0.04)	0.39(0.36)
0.25	1.0	0.49(0.49)	4.2(4.0)
0.05	0.1	0.22(0.22)	5.0(4.7)
0.25	0.1	0.72(0.50)	9.8(10.5)
0.025	0.1	0.15(0.16)	3.5(3.3)

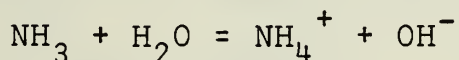
Values in parentheses are computed from the empirical expressions given in the text.

values computed from the purely empirical representations:

$$k_s = 1.0 [\text{NH}_3]^{1/2} \text{ and } k_f = 21 [\text{NH}_3]^{1/2} \text{ in } 0.1 \text{ M } \underline{\text{Cl}^-}$$

$$k_s = 3.9 [\text{NH}_3]^{3/2} \text{ and } k_f = 32 [\text{NH}_3]^{3/2} \text{ in } 1.0 \text{ M } \underline{\text{Cl}^-}$$

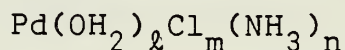
The half-order dependence on $[\text{NH}_3]$ could be the result of involvement of hydroxide ion (leading to hydroxo complexes) resulting in these unbuffered solutions, from



since, if $[\text{NH}_4^+] = [\text{OH}^-]$, then each = $(K_b[\text{NH}_3])^{1/2}$. Actually, as reaction proceeds, ammonium ion concentration must exceed that of OH^- , so that an exact half-order dependence could not be expected. The change in $[\text{NH}_3]$ dependence from low to high chloride concentrations cannot be explained at all, and no empirical relations could be found to account for the dependence on $[\text{Cl}^-]$ at constant $[\text{NH}_3]$.

III. PRESENTATION OF EQUILIBRIUM AND KINETICS DATA

To clarify the discussion of the treatment of the various equilibrium and rate data, a special notation will be used in this section. Any of the complexes may be denoted:



Its cumulative stability constant (or formation constant) is:

$$\beta_{mn} = \frac{[\text{Pd}(\text{OH}_2)_l \text{Cl}_m (\text{NH}_3)_n]}{[\text{Pd}(\text{OH}_2)_4^{2+}][\text{NH}_3]^n[\text{Cl}^-]^m}$$

which are the quantities given in Table VI.

The stepwise equilibrium constant for the formation of this complex by substitution of H_2O by Cl^- is designated $K_{mn}(\text{Cl})$; for substitution of H_2O by NH_3 , $K_{mn}(\text{NH}_3)$; and for substitution of NH_3 by Cl^- , $K_{mn}(\text{NH}_3\text{-Cl})$. Forward rate constants will be labelled in the same way using lower case k . Reverse rate constants are defined by:

$$k_{-mn}(\text{Cl}) = k_{mn}(\text{Cl})/K_{mn}(\text{Cl})$$

and the other two types mutatis mutandis. Note that reverse rate constants thus refer to rate of reaction of the complex (whereas forward rate constants refer to its rate of formation). Data considered are those at 25°C, unit ionic strength.

In Table VII the sources for the bulk of the data of Table VI are given. The result of calculating β_{13} from either

TABLE VI
THE CHLOROAMMINES OF PALLADIUM(II) AND THEIR
CUMULATIVE STABILITY CONSTANTS (25⁰, $\mu = 1$)

Pd^{2+}	PdCl^+	PdCl_2^*	PdCl_3^-	PdCl_4^{2-}
1.0	2.17×10^4	4.19×10^7	1.10×10^{10}	2.22×10^{11}
$\text{Pd}(\text{NH}_3)^{2+}$	$\text{Pd}(\text{NH}_3)\text{Cl}^+*$	$\text{Pd}(\text{NH}_3)\text{Cl}_2^*$	$\text{Pd}(\text{NH}_3)\text{Cl}_3^-$	
4.15×10^9	(4×10^{13})	(4×10^{16})	3.17×10^{18}	
$\text{Pd}(\text{NH}_3)_2^{2+*}$	$\text{Pd}(\text{NH}_3)_2\text{Cl}^+*$	$\text{Pd}(\text{NH}_3)_2\text{Cl}_2^*$		
3.30×10^{18}	7.85×10^{21}	1.67×10^{24}		
$\text{Pd}(\text{NH}_3)_3^{2+}$	$\text{Pd}(\text{NH}_3)_3\text{Cl}^+$			
1.04×10^{26}	1.04×10^{29}			
$\text{Pd}(\text{NH}_3)_4^{2+}$				
1.06×10^{33}				

Notes :

H_2O has been omitted from the formulas.

cis and trans isomers are possible for the complexes marked with an asterisk.

Stability constants are computed from data in references [3], [7], [9], [14], [20], and [21]. See Section IV for further discussion.

Values in parentheses have been roughly estimated.

TABLE VII
SOURCES FOR THE DATA OF TABLE VI

$\beta_{10}, \beta_{20}, \beta_{30}, \beta_{40}$ computed from kinetics data in Elding [5].^a

$\beta_{01}, \beta_{02}, \beta_{03}$ from Rasmussen and Jørgensen [3].

$$\beta_{31} = \beta_{40} \times k_{31}(\text{NH}_3\text{-Cl}) [9]/k_{-31}(\text{NH}_3\text{-Cl}) [7].$$

$$\beta_{22} = \beta_{31} \times K_{22}(\text{NH}_3\text{-Cl}) [14].$$

$$\beta_{12} = \beta_{22} \times K_{12}(\text{Cl}) [14].$$

$$\beta_{13} = \beta_{22} \times K_{13}(\text{NH}_3\text{-Cl}) [14]. = 1.04 \times 10^{29}$$

or $\beta_{13} = \beta_{03} \times K_{13}(\text{Cl}) [14]^b = 1.04 \times 10^{29}$

$$\beta_{04} = \beta_{03} \times K_{04}(\text{NH}_3) [3] = 6.56 \times 10^{32}$$

or $\beta_{04} = \beta_{13} \times K_{04}(\text{NH}_3\text{-Cl}) [14]^b = 17.0 \times 10^{32}$

Notes:

^aComputing equilibrium constants from the kinetics data thus gives values consistent with those in Table IX. Equilibrium data from reference [20] differ somewhat. β_{20} is computed for the equilibrium mixture of isomers ($\text{cis/trans} = 2.1$); thus $K_{20}(\text{Cl}) = K_{\text{cis}} + K_{\text{trans}}$ and $K_{30}(\text{Cl}) = (1/K_{\text{cis}} + 1/K_{\text{trans}})^{-1}$.

^bSee text

$\beta_{22}K_{13}(\text{NH}_3\text{-Cl})$ or $\beta_{03}K_{13}(\text{Cl})$ is the same: 1.04×10^{29} -- an agreement much closer than is warranted by the precision of the data, but which reinforces our confidence as to the internal consistency. The disagreement for β_{04} was already noted by Rasmussen and Jørgensen [3]. We have selected the geometric mean for inclusion in Table VI.

It is noted that no attempt is made in Table VI to indicate precision of the data.

Values of β for $\text{Pd}(\text{NH}_3)\text{Cl}^+$ and $\text{Pd}(\text{NH}_3)\text{Cl}_2$ are enclosed in parentheses to indicate that they are estimates only. These estimates were obtained by the following consideration. In Table VIII are given three sets of stepwise equilibrium constants, so chosen that the range of values in each column is rather small. (Thus the $K(\text{Cl})$ for constant m show an overall range of a factor of 20 for the +1 ions, whereas a comparison based on constant n would show a range of a factor of 10^3 for $n = 0$). It will be noted in Table VIII that the values in parentheses, those for $\text{Pd}(\text{NH}_3)\text{Cl}^+$ and $\text{Pd}(\text{NH}_3)\text{Cl}_2$, all lie between those of their neighbors in each vertical column. The estimated β values were selected so as to meet this criterion. No attempt has been made to find structural correlations for the equilibrium data.

The kinetics data of Tables IX and X are from the sources therein noted.

In Table XI the values given for cis- $\text{Pd}(\text{NH}_3)_2\text{Cl}_2 + \text{NH}_3 \rightarrow \text{Pd}(\text{NH}_3)_3\text{Cl}^+$ ($k_{-22}(\text{NH}_3\text{-Cl})$) are based on the assumption that the slower step in the studies of Monk [9], Midas [23], and

Atwill [35] is this reaction and a rough average of their results is given. As noted above (Section II 8 D) the faster step observed by each of them could be for the ammonation of either $\text{Pd}(\text{NH}_3)_3\text{Cl}^+$ or (with rather closer agreement to expectation) of $\text{PdNH}_3\text{Cl}_3^-$ (formed by disproportionation of the starting material before the experimental runs began).

Asterisks are used in Table XI to indicate the assumption of equal concentrations of cis and trans at equilibrium.

Activation enthalpies for some steps appear in Tables IX and X, and in Table XII, which gives such data for the processes of Table XI. A few enthalpies of reaction (ΔH°) are given in Tables IX and XII.

TABLE VIII

STEPWISE EQUILIBRIUM CONSTANTS (25°, μ = 1)

Log K(Cl) for constant m (charge)		
$\underline{m = 1}$	$\underline{m = 2}$	$\underline{m = 3}$
PdCl^+	PdCl_2	PdCl_3^-
4.336	3.286	2.420
$\text{Pd}(\text{NH}_3)\text{Cl}^+$	$\text{Pd}(\text{NH}_3)\text{Cl}_2$	$\text{Pd}(\text{NH}_3)\text{Cl}_3^-$
(4.0)	(3.0)	(1.9)
$\text{Pd}(\text{NH}_3)_2\text{Cl}^+$	$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	
3.377	2.326	
$\text{Pd}(\text{NH}_3)_3\text{Cl}^+$		
3.000		
Log K(NH ₃) for constant n		
$\underline{n = 1}$	$\underline{n = 2}$	$\underline{n = 3}$
$\text{Pd}(\text{NH}_3)^{2+}$	$\text{Pd}(\text{NH}_3)_2^{2+}$	$\text{Pd}(\text{NH}_3)_3^{2+}$
9.618	8.900	7.498
$\text{Pd}(\text{NH}_3)\text{Cl}^+$	$\text{Pd}(\text{NH}_3)_2\text{Cl}^+$	$\text{Pd}(\text{NH}_3)_3\text{Cl}^+$
(9.3)	(8.3)	7.121
$\text{Pd}(\text{NH}_3)\text{Cl}_2^-$	$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$	
8.459	(7.6)	
$\text{Pd}(\text{NH}_3)_3\text{Cl}_3^-$		
Log K(NH ₃ -Cl) for constant m		
$\underline{m = 0}$	$\underline{m = 1}$	$\underline{m = 2}$
$\text{Pd}(\text{NH}_3)^{2+}$	$\text{Pd}(\text{NH}_3)\text{Cl}^+$	$\text{Pd}(\text{NH}_3)\text{Cl}_2$
5.281	(6.0)	(6.6)
$\text{Pd}(\text{NH}_3)_2^{2+}$	$\text{Pd}(\text{NH}_3)_2\text{Cl}^+$	$\text{Pd}(\text{NH}_3)_2\text{Cl}_2$
(4.9)	(5.3)	5.722
$\text{Pd}(\text{NH}_3)_3^{2+}$	$\text{Pd}(\text{NH}_3)_3\text{Cl}^+$	
4.121	4.794	
$\text{Pd}(\text{NH}_3)_4^{2+}$		
		$\text{Pd}(\text{NH}_3)\text{Cl}_3^-$
		7.155

TABLE IX

KINETICS OF SUBSTITUTION OF H_2O BY Cl^- AND REVERSE (25° , $\mu = 1$) [31].

Reaction	ΔH°		Forward		Reverse	
	kcal mol^{-1}	$\text{M}^{-1}\text{sec}^{-1}$	kcal mol^{-1}	sec^{-1}	kcal mol^{-1}	kcal mol^{-1}
$\text{Pd}^{2+} + \text{Cl}^- = \text{PdCl}^+$	-3.0	1.8×10^4	10	0.83	14	
$\text{PdCl}^+ + \text{Cl}^- = \text{trans-PdCl}_2$		3.5×10^4		5.6	12	
$\text{PdCl}^+ + \text{Cl}^- = \text{cis-PdCl}_2$		510		0.37		
$\text{trans-PdCl}_2 + \text{Cl}^- = \text{PdCl}_3^-$		22	13	0.027		
$\text{cis-PdCl}_2 + \text{Cl}^- = \text{PdCl}_3^-$		5400	10			
$\text{PdCl}_3 + \text{Cl}^- = \text{PdCl}_4^{2-}$	-3.4	180	10	8.9	12	

TABLE X

KINETICS OF SUBSTITUTION OF NH_3 BY H_2O AND REVERSE (25° , $\mu = 1$)^a

Reaction	k_f, sec^{-1}	$k_r, \text{M}^{-1} \text{sec}^{-1}$
$\text{Pd}(\text{NH}_3)_4^{2+} \rightarrow \text{Pd}(\text{NH}_3)_3(\text{OH}_2)^{2+}$	1.12×10^{-3}	$1.8 \times 10^4 (7.1 \times 10^3)^b$
$\text{Pd}(\text{NH}_3)_3(\text{OH}_2)^{2+} \rightarrow \text{Pd}(\text{NH}_3)_2(\text{OH}_2)_2^{2+}$	4.6×10^{-4}	1.46×10^4 c
$\text{Pd}(\text{NH}_3)_2(\text{OH}_2)_2^{2+} \rightarrow \text{Pd}(\text{NH}_3)(\text{OH}_2)_3^{2+}$	8×10^{-5}	6×10^4 c
$\text{Pd}(\text{NH}_3)(\text{OH}_2)_3^{2+} \rightarrow \text{Pd}(\text{OH}_2)_4^{2+}$	ca. 2×10^{-5} d	8×10^4

F 5

Notes:

^aKinetics data for the forward reaction are from [21]; those for the reverse are computed using equilibrium data from [3] except as noted. Activation enthalpies for the forward reactions are [21], in order: 23, 21, 22 and 24 kcal mol⁻¹.

^bThe selected value is computed from the equilibrium data in [14]; that in parentheses is from [3].

^cIt is believed [3,21] that $\text{Pd}(\text{NH}_3)_2(\text{OH}_2)_2^{2+}$ occurs predominantly in the cis form in both kinetics and equilibrium experiments.

^dExtrapolated from data obtained at 50° and above.

TABLE XI

KINETICS OF SUBSTITUTION OF NH₃ BY Cl⁻ AND REVERSE (25°, μ = 1)

<u>Reaction</u>	<u>Forward</u>		<u>Reverse</u>	
	k_1	k_2	k_1	k_2
(1) Pd(NH ₃) ₄ ²⁺ → Pd(NH ₃) ₃ Cl ⁺	.0011	.0071	[11]	[70]
(2) Pd(NH ₃) ₃ Cl ⁺ → <u>trans</u> -Pd(NH ₃) ₂ Cl ₂	9x10 ⁻⁴	.030	[112*]	[3750*]
(3) Pd(NH ₃) ₃ Cl ⁺ → <u>cis</u> -Pd(NH ₃) ₂ Cl ₂	[(1x10 ⁻⁴ *)]	[(1x10 ⁻⁴ *)]	(15±5)	(15±5)
(4) <u>trans</u> -Pd(NH ₃) ₂ Cl ₂ → Pd(NH ₃)Cl ₃ ⁻	3.7x10 ⁻⁶	6.9x10 ⁻⁶	[1.0*]	[1.8*]
(5) <u>cis</u> -Pd(NH ₃) ₂ Cl ₂ → Pd(NH ₃)Cl ₃ ⁻	.00048	.00140	[120*]	[370*]
(6) Pd(NH ₃)Cl ₃ ⁻ → PdCl ₄ ²⁻	[2.1x10 ⁻⁶]	2.3x10 ⁻⁶	30	33

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Notes:

First-order rate constants (k_1) are given in units of sec⁻¹; second-order (k_2) in M⁻¹sec⁻¹.

Values in square brackets [] are computed from the equilibrium data of Table VI and kinetics data for reaction in the opposite direction.

Values in parentheses are estimates based on the assumed assignment of the reaction step as discussed in Ref [7] and in Section II, 8, above.

Asterisk indicates the additional assumption of equal cis and trans species at equilibrium.

Data are taken from Ref [7], [9], [11], [21], [23], [35]. See text for further discussion.

TABLE XII
 ACTIVATION ENTHALPIES AND REACTION ENTHALPIES
 FOR THE REACTIONS OF TABLE XI

<u>Reaction</u>	kcal mol ⁻¹		<u>ΔH⁰</u>
	<u>ΔH[‡]</u> 1st order	<u>ΔH[‡]</u> 2nd order	
(1) Forward	13	18.5	10
(2) Forward	16	14	10
(3) Reverse	~10?	0?	
(4) Forward	22	22	
(5) Forward	18	18	
(6) Forward	--	23	13(computed)
(6) Reverse	--	10	

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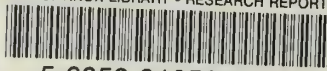
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