United States
Naval Postgraduate School

THESIS

THE KINETICS OF SUCCESSIVE AQUATION REACTIONS OF TETRAAMMINEPALLADIUM(II) ION

by

William Jennings DeBerry, Jr.

Thesis Advisor: R. A. Reinhardt

June 1971

Approved for public release; distribution unlimited.

91

The Kinetics of Successive Aquation Reactions
of
Tetraamminepalladium(II) Ion

by

William Jennings DeBerry, Jr.
Ensign, United States Naval Reserve
B.A., Southern Connecticut State College, 1970

Submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the
NAVAL POSTGRADUATE SCHOOL
June 1971

Author William J. DeBerry Jr.

Approved by: Richard A. Reinhardt
Thesis Advisor

John W. Dutkin
Chairman, Department of Chemistry

Milton U. Clauser
Academic Dean

ABSTRACT

Solutions of tetraamminepalladium(II) perchlorate were made up and analyzed.

The following acid hydrolysis reactions of tetraammine-palladium(II) ion were studied by ultraviolet spectroscopy. First order rate constants were evaluated for each step of the reaction series at various temperatures. Activation parameters were determined.

$$\mathrm{Pd(NH_3)_4^{2+}} \xrightarrow{k_1} \mathrm{Pd(NH_3)_3OH_2^{2+}} \xrightarrow{k_2} \underline{\text{cis}}\text{-}\mathrm{Pd(NH_3)_2(OH_2)_2^{2+}} \xrightarrow{k_3}$$

$$\mathrm{Pd(OH_2)_3NH_3^{2+}} \xrightarrow{k_4} \mathrm{Pd(OH_2)_4^{2+}}$$

At $T = 25°\mathrm{C}$, $\mu = 1M$: $k_1 = 11.0\mathrm{x}10^{-4}$ sec^{-1}, $k_2 = 5.6\mathrm{x}10^{-4}$ sec^{-1}, $k_3 = 0.58\mathrm{x}10^{-4}$ sec^{-1}, $k_4 = 0.10\mathrm{x}10^{-4}$ sec^{-1}

Mechanisms for the consecutive reactions are proposed, and cis and trans effects are discussed.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

Figure

ACKNOWLEDGEMENT

The author wishes to acknowledge the analog computer staff of the Electrical Engineering Department for their help with the analog computer simulations. Also the author wishes to express his appreciation to Ken Graham for his help during the course of this research; to the typist, M. Wright, for her kindness; to Dr. Richard A. Reinhardt for much patience, understanding, and guidance; and especially to his wife, Susanne, for her contribution to the preparation of this work and her continuous loving encouragement.

I. INTRODUCTION

A. GENERAL

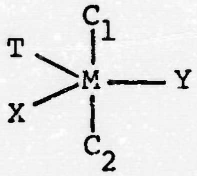
Palladium(II) is one of a group of metals with low spin, d^8 electronic configuration (others being Pt(II), Ni(II), Au (III), Rh(I) and Ir(I)) which form square planar coordination complexes [Ref. 1]. The idea that the square planar configuration was the form of such complexes was that of Werner [Ref. 1] who could not account for isomeric forms of dichlorodiammineplatinum(II) with a tetrahedral structure. Further evidence for a square planar configuration was the result of x-ray studies by Dickenson [Ref. 2] and dipole moment studies by Jensen [Ref. 2], along with much other experimental evidence regarding isomers.

The reactions of the square planar platinum complexes have been extensively studied [Ref. 3], and most conclusions for square planar reactions have been based on the studies of the platinum complexes. It has been observed in the platinum studies [Ref. 1] that bimolecular substitution reactions predominate. The rate law for such reactions has been determined to be:

$$\text{Rate} = -d\,[\text{substrate}]/dt = (k_1 + k_2[Y])[\text{substrate}]$$

where k_2 is the second order rate constant and refers to the bimolecular attack of Y on the substrate [Ref. 4].

The generally accepted transition state for the platinum reactions involves an associative type mechanism where the metal temporarily takes on five bonds in a trigonal bipyramid structure such as:



where T, X and Y are in one plane with the C_1-C_2 axis perpendicular to it.

These same conclusions have been found to apply to the other square planar d^8 systems, Palladium(II) in particular [Ref. 4]. It has been found that platinum complexes are substitution inert, that is their reactions are quite slow. Pearson and Johnson [Ref. 5] have concluded in their studies of $Pd(acac)_2$ (acac = acetylacetonate) that there are basic similarities in the reactions of palladium and platinum complexes. Basolo, Grey and Pearson have found that the reactions of palladium complexes are about 10^5 times faster than those of platinum [Ref. 6].

B. TETRAAMMINEPALLADIUM(II)

The preparation of tetraamminepalladium(II) chloride by H. Müller is described in Mellor's Comprehensive Treatise On Inorganic and Theoretical Chemistry [Ref. 7] where the physical properties of the monohydrate crystal are discussed.

In previous work it has been determined that tetraamminepalladium(II) will undergo consecutive substitution reactions in the presence of excess acid. If a nucleophilic reagent is available, such as chloride ion, the two term rate law is observed to hold as it does for most other square planar complexes, rate = -d[substrate]/dt = $(k_1 + k_2[Y])$[substrate] where Y is the substituting reagent. Results of the reactions of tetraamminepalladium(II) with chloride are found in the literature [Refs. 8, 9].

There has also been some work done on the reaction of tetraamminepalladium(II) with excess acid in the absence of any nucleophilic reagent other than the solvent. Reference is made specifically to the works of Coe et al and Rasmussen and Jφrgensen [Refs. 9, 10]. Both of these works report that the reaction is a consecutive reaction of at least two steps. The values of the rate constants for the first two steps are evaluated by Rasmussen and Jφrgensen by pH titration methods. Coe et al determined the rate constant for the first step by initial absorbance gradient techniques. The applicable rate law was found to be, rate = -d[substrate]/dt = k_1[substrate], where k_1 should be equal to the k_1 in the two term rate law for the first step in the reaction involving a nucleophilic reagent. Coe et al report spectral changes of a reacting mixture of 0.001M tetraamminepalladium(II) perchlorate with 0.01M perchloric acid, over a time scale of ninety minutes. These scans agree with scans taken by this author of a reacting mixture of 0.005M tetraamminepalladium(II) perchlorate with 1M perchloric acid in a one-cm cell, except that Coe et al report that the infinite time spectrum resembles the spectrum of diaquodiamminepalladium(II), whereas the infinite time spectrum taken by this author resembles that of tetraaquopalladium(II) [Ref. 10]. Additional evidence of the reaction going to the tetraaquo ion is that about two weeks after a run, the reaction solution had minute traces of a brown precipitate in it. This observation compares with that of Rasmussen and Jørgensen regarding solutions of tetraaquopalladium(II) ion [Ref. 10].

The objective of this present study was the investigation of the stepwise interaction of tetraamminepalladium(II) ion with excess acid for the purpose of evaluating rate constants and activation parameters. The reactions were followed spectrophotometrically and the rate constants were evaluated from absorbance data.

In this work it was found at 25°C that, in most cases, the kinetic runs revealed three rate constants, the largest of which was on the order of the rate constants determined by Coe et al and assigned by Rasmussen and Jørgensen to be the rate of the first step, and the next largest on the order of the rate constant determined by Rasmussen and Jørgensen, to be the rate of the second step in the substitution series. The smallest values obtained from these kinetic runs was evidently the result of an additional replacement step. When the reaction was carried out at 50°C, the reaction was found to go completely to the tetraaquo ion. However, at this temperature, the largest constant that was extracted from the data was determined to be that for the second step in the replacement sequence. It was found that at any given temperature, at most three rate constants could be extracted. All the rate constants evaluated in this study are listed in Table II and specific values of these rate constants at various temperatures along with activation parameters are given in Table IV.

II. EXPERIMENTAL

A. MATERIALS

All materials in this research, except the palladium complexes, were reagent grade and used without further purification. Sodium tetrachloropalladate was obtained from Alpha Inorganics Pd108 lot 02218.

Solutions of tetraamminepalladium(II) perchlorate were formed from the corresponding solutions of tetraamminepalladium(II) chloride by adding the equivalent amount of silver perchlorate to remove chloride from the system. The tetramminepalladium(II) chloride solution was prepared in essentially the same manner described by Reinhardt et al [Ref. 11]. Sodium tetrachloropalladate was dissolved in excess aqueous ammonia forming a solution of tetraamminepalladium(II) chloride which was purified by precipitation as trans-dichlorodiamminepalladium(II). This precipitate was then dissolved in excess aqueous ammonia and tetramminepalladium (II) chloride monohydrate was crystallized out by evaporation. Solutions of tetraamminepalladium(II) chloride were prepared from these crystals. Details of the synthesis follow.

1. Preparation of trans-Dichlorodiamminepalladium(II)

Approximately 2.5 grams of Na_2PdCl_4 were dissolved in distilled water. Concentrated aqueous ammonia was added to this solution until the pink salts (presumably Vauquelin's salt, $[Pd(NH_3)_4]$ $[PdCl_4]$) which were formed, redissolved. The solution was then placed in an ice bath and concentrated hydrochloric acid was added slowly until the solution was slightly acidic, at which point a yellow precipitate was formed. This precipitate (trans-dichlorodiamminepalladium (II)) was separated, washed in ice water and ethanol, and allowed to air dry.

2. Preparation of Tetraamminepalladium(II) Chloride Monohydrate

The trans-dichlorodiamminepalladium(II) was dissolved in concentrated aqueous ammonia and left to evaporate at room temperature. Long colorless needles ($Pd(NH_3)_4Cl_2.H_2O$) interspersed with a fine yellow crystalline material (presumably trans-dichlorodiammine) remained. About 1.3 grams of these crystals were dissolved in 100ml of water, and the resulting tetraamminepalladium(II) chloride solution was filtered to remove any insoluble impurities.

3. Preparation of Aqueous Tetraamminepalladium(II) Perchlorate Solutions

Since the kinetics were to be investigated in the absence of chloride, the chloride had to be removed. This was done by the addition of an equivalent amount of silver perchlorate to the solution, which precipitated silver chloride. The equivalent amount of silver perchlorate was determined as follows: An approximately 0.1M solution of silver perchlorate was made up and was titrated against four 5ml aliquots of the tetraamminepalladium(II) chloride solution using Fajans method [Ref. 12]. The equivalent amount of silver perchlorate was calculated and added to the remaining tetraamminepalladium(II) chloride solution which was then filtered repeatedly to remove all of the silver chloride and diluted to a total volume of 250ml. To a small amount of this solution ($Pd(NH_3)_4(ClO_4)_2$) some silver perchlorate was added to test for the presence of chloride. This test was negative.

B. ANALYSIS OF TETRAAMMINEPALLADIUM(II) PERCHLORATE SOLUTION

For the determination of palladium in a solution of roughly 0.015M $Pd(NH_3)_4(ClO_4)_2$, the precipitation of palladium as a salt of dimethylglyoxime was used essentially as outlined in Treadwell and Hall [Ref. 13]. Four ml of this solution were pipetted into a beaker and three ml of 1% dimethylglyoxime in 95% ethanol were added to this. The solution was diluted to about 75ml with water, and acetic acid was added to precipitate bis(dimethylglyoximato)palladium(II). This precipitate was collected, dried at 110°C, and weighed. From this the concentration of palladium(II) in solution was determined.

Ammonia in the solution was analyzed by the Kjeldahl method [Ref. 12]. A solution which gave a palladium analysis by the dimethylglyoxime method of 0.0151M was determined to contain 0.0602M ammonia (corresponding to 0.0150M Pd).

C. EQUIPMENT

Spectral scans were taken on a Beckman model DB recording spectrophotometer, utilizing both four- and one-cm silica cells. No provisions were made for thermostatting the cell compartment. Spectrophotometric kinetic data were taken on a Beckman model DU spectrophotometer equipped with a thermostatted cell holder. Fused silica ten-cm cells were used initially for 25°C runs. For runs of higher temperatures, one-cm silica cells were used and the spectrophotometer was adapted with a one-cm cell holder and Beckman thermospacers. The temperature was monitored by a copper-constantan thermocouple with an ice bath cold junction, placed on the cell holder. A Varian G-4000 millivolt recorder was used to record the temperature throughout a run. Kinetic data were also taken on a Beckman model DK 1A recording spectrophotometer equipped with a Beckman electrically controlled thermostatted cell holder. To maintain the temperature more precisely, a hot water bath, was used to circulate hot water through the cell holder. The temperature was monitored by a copper-constantan thermocouple with an ice bath cold junction in conjunction with the Varian G-4000 millivolt recorder. IR spectra were run on Perkin-Elmer 337 and 621 grating spectrophotometers with samples in KBr disc form. Analog computer data were obtained using a Comcor CI 5000 computer.

D. KINETIC RUNS

The kinetics of the acid hydrolysis reaction of tetraamminepalladium(II) ion were studied by observing the change in absorbance with time. All runs were done at constant ionic strength of $\mu=1$ maintained with perchloric acid. For preliminary kinetic scans on the DB spectrophotometer, 10ml of 0.051M $Pd(NH_3)_4(ClO_4)_2$ were mixed with 100ml of 1.1M $HClO_4$ at ambient temperature. At various intervals an aliquot of the reacting solution was removed, scanned and the spectral changes observed. For later runs, the reaction was run in a thermostatted water bath and aliquots were quenched in an ice bath before being scanned.

For most of the DU kinetic runs at 25°C, ten-cm fused silica cells were used for the reaction. Into both the sample and reference cells were pipetted 26ml of 1.040M perchloric acid. After thermal equilibrium was established, one ml of 0.012M $Pd(NH_3)_4^{2+}$ solution was injected into the cell with a one ml hypodermic syringe fitted with a small hypodermic needle. The palladium solution was forcefully injected into the perchloric acid solution over a time span of less than two seconds. Complete mixing was almost instantaneous when using one-cm cells and was less than thirty seconds when using ten-cm cells. A timer was started as soon as the syringe was emptied, and the first absorbance reading was made as quickly as possible. Most of the other absorbance readings were taken at intervals of 50 or 100 seconds.

Higher temperature runs were made with one-cm silica cells by pipetting two-ml of 1.50 M perchloric acid into both the sample and reference cells. One ml of water was added to the reference cell. After thermal equilibrium had been obtained, one ml of 0.015M $Pd(NH_3)_4^{2+}$ solution (which was kept at the temperature of the reaction) was injected into the perchloric acid in the sample cell. Absorbance readings were then taken at certain intervals. An identical procedure was used for DK 1A runs except that it was not necessary to take absorbance readings, since the change in absorbance was continuously recorded.

III. TREATMENT OF DATA AND RESULTS

A. DETERMINATION OF RATE CONSTANTS

1. Preliminary Investigations

Initial investigations of the change in spectral scans of a reaction mixture with time indicate that the reaction does not follow simple first order kinetics, but that the acid hydrolysis is probably a stepwise consecutive reaction of the following type:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D \xrightarrow{k_4} E$$

The complete scheme would be followed if each ammonia ligand is consecutively replaced by a water molecule:

$$Pd(NH_3)_4^{2+} \xrightarrow{k_1} Pd(OH_2)(NH_3)_3^{2+} \xrightarrow{k_2} Pd(OH_2)_2(NH_3)_2^{2+} \xrightarrow{k_3}$$

$$Pd(OH_2)_3(NH_3)^{2+} \xrightarrow{k_4} Pd(OH_2)_4^{2+}$$

In general, it was found that at 25°C the kinetic runs revealed three rate constants, presumably those for the first three steps in the overall reaction scheme. Likewise at higher temperatures, three rate constants were also generally observed, presumably those for the last three steps in the reaction scheme. These observations were due to the fact that at low temperatures, the slowest step had a half life much greater than the time over which the run was carried out, and at higher temperatures the fastest step had a half life on the same order of magnitude as the sampling period.

2. General Kinetic Considerations

Based on the previous observations it is possible to consider at any given temperature, the above consecutive reaction occurring via three steps,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} D$$

For such a reaction the system of differential equations may be given for each species as follows [Ref. 14]:

$$(1) \quad \frac{-dA}{dt} = k_1 A$$

$$(2) \quad \frac{dB}{dt} = k_1 A - k_2 B$$

$$(3) \quad \frac{dC}{dt} = k_2 B - k_3 C$$

$$(4) \quad \frac{dD}{dt} = k_3 C$$

Solving equations (1) - (3) for concentration of each species, one obtains:

$$(5) \quad A = A_o e^{-k_1 t}$$

$$(6) \quad B = \frac{A_o k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t})$$

$$(7) \quad C = \frac{k_1 k_2 A_o}{k_2 - k_1} \left[\frac{e^{-k_1 t} - e^{-k_3 t}}{k_3 - k_1} + \frac{e^{-k_3 t} - e^{-k_2 t}}{k_3 - k_2} \right]$$

Making the following identifications [Ref. 14]

$$(8) \quad a = e^{-k_1 t}$$

$$(9) \quad b = X(e^{-k_1 t} - e^{-k_2 t})$$

$$(10) \quad c = XY\left[(k_3-k_2)e^{-k_1t} - (k_3-k_1)e^{-k_2t} + (k_2-k_1)e^{-k_3t}\right]$$

$$(11) \quad d = 1-a-b-c$$

where

$a = A/A_o$

$b = B/A_o$

$c = C/A_o$

$X = \dfrac{k_1}{k_2-k_1}$

$Y = \dfrac{k_2}{(k_3-k_1)(k_3-k_2)}$

and

$$(12) \quad \bar{e} = e_Aa + e_Bb + e_Cc + e_\infty d$$

where

$\bar{e}$ = absorbance per cm divided by total concentration

e_i = molar absorptivity of the ith species

e_∞ = molar absorptivity at infinite time.

One obtains by substitution of equations (8)-(11) into equation (12):

$$(13) \quad \bar{e}-e_\infty = I_1e^{-k_1t} + I_2e^{-k_2t} + I_3e^{-k_3t}$$

where

$I_1 = [(e_A-e_\infty) + (e_B-e_\infty)X + (e_C-e_\infty)(k_3-k_2)XY]$

$I_2 = -[(e_B-e_\infty)X + (e_C-e_\infty)(k_3-k_1)XY]$

$I_3 = [(e_C-e_\infty)(k_2-k_1)XY]$

If k_3 is arbitrarily chosen as the rate constant for the slowest step, the following is obtained:

$$(14) \quad \ln(\bar{e}-e_\infty) = \ln I_3 - k_3 t + \ln\left[1 + \frac{I_2}{I_3} e^{-(k_2-k_3)t} + \frac{I_1}{I_3} e^{-(k_1-k_3)t}\right]$$

At long times, the last terms on the right hand side of equation (14) become negligible and a plot of $\ln(\bar{e}-e_\infty)$ versus time should be linear with slope of $-k_3$ and intercept $\ln I_3$. The rate constants k_2 and k_1 could be extracted from this equation by following the method used by Ashley and Hamm [Ref. 15] of extrapolating the linear portion to zero time, and plotting the difference between the extrapolated line and the nonlinear experimental points. This results again in a linear and nonlinear portion. The linear portion has slope $-k_2$ and intercept $\ln I_2$. The same procedure is repeated, yielding $-k_1$ and $\ln I_1$. Figure (1) is an example of this plot.

The Guggenheim method of analysis [Ref. 14] was used in some cases where infinity readings were difficult to obtain. For these cases, $\ln \bar{e}-\bar{e}_{t+\Delta}$ was plotted versus time where Δ is a fixed interval of time usually greater than twice the half life of the step in question. The rest of the analysis follows the same method previously outlined.

For a few runs, a computer program [Ref. 16] based on a nonlinear least squares fit was used to determine rate constants from the raw data. In this program, which utilized a Wang 700 computer, absorbance and time data as well as estimates of the rate constants and infinite absorbance, if

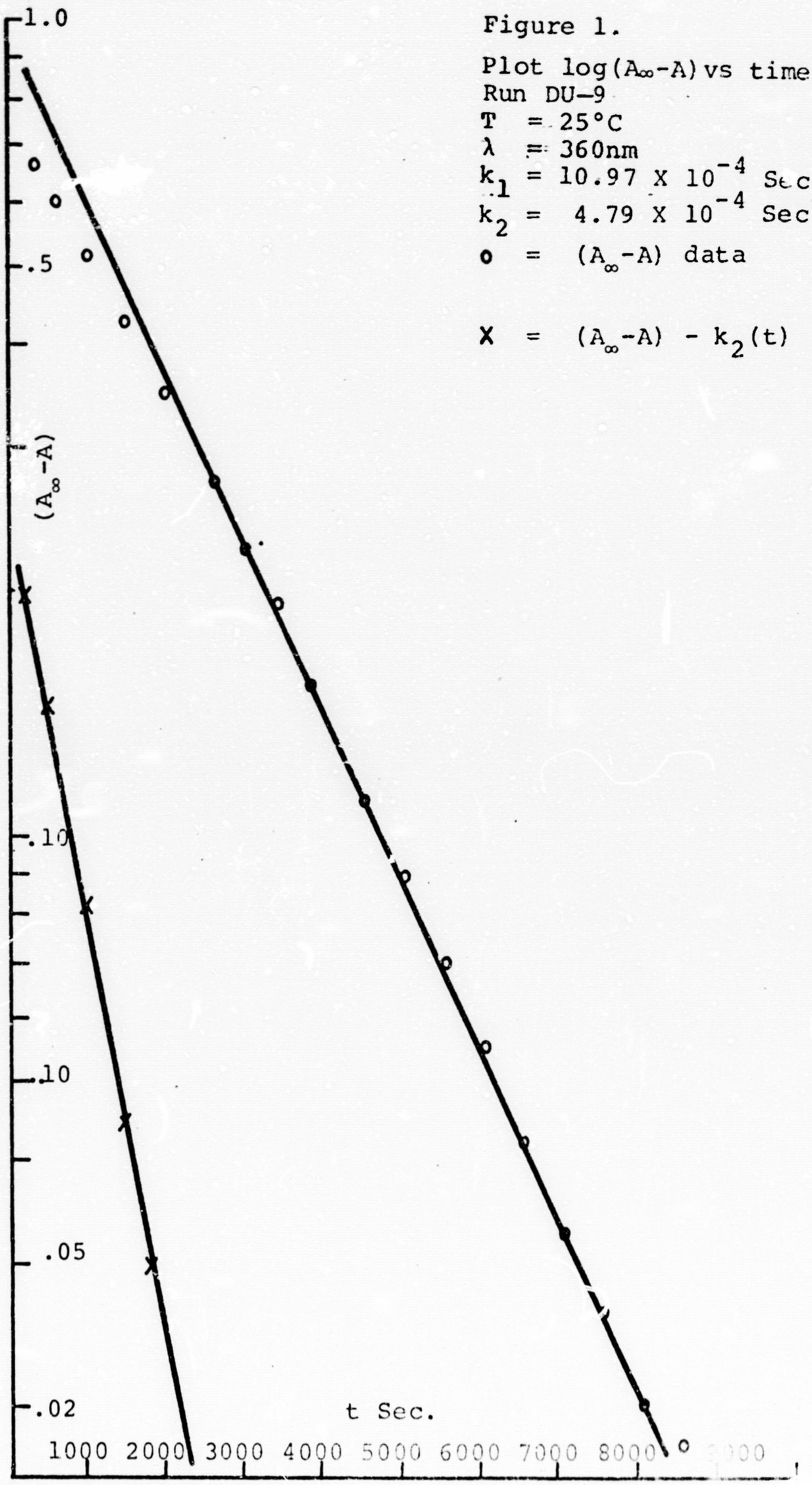


Figure 1.

Plot $\log(A_\infty - A)$ vs time
Run DU–9
$T = 25°C$
$\lambda = 360nm$
$k_1 = 10.97 \times 10^{-4}$ Sec^{-1}
$k_2 = 4.79 \times 10^{-4}$ Sec^{-1}
o = $(A_\infty - A)$ data

X = $(A_\infty - A) - k_2(t)$

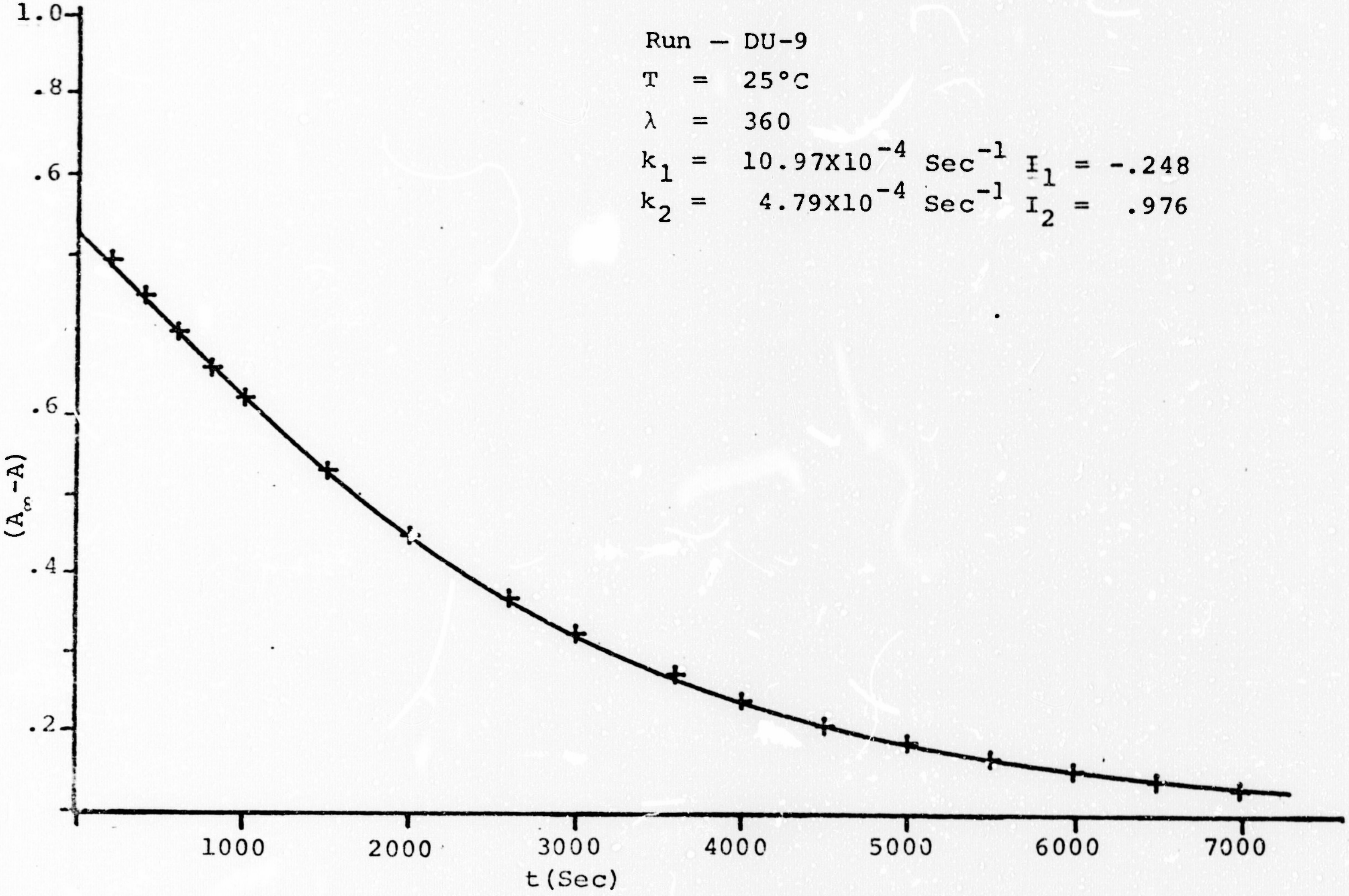
available, were entered into the program. Based on these estimates of the rate constants, the program calculated the root mean square deviation of equation (13) from the data points. The faster rate constant was then varied with the others held constant and the value of the rate constant which yielded the least deviation was established. The next faster rate constant was now varied to try to obtain the least deviation. With this value fixed, the faster rate constant was again varied to try to find a value which would yield an even smaller deviation. If this yielded a different value for the faster constant, this value was held constant and the process was repeated until the changes in the rate constants were less than experimental error. The slowest rate constant was then varied with the others fixed to give the least deviation. With the best value for this constant the other rate constants were varied to obtain the least deviation. This process was repeated until the value of all rate constants gave the least deviation from the experimental points. These rate constants were then considered the best ones for a given set of data.

B. METHODS USED TO CHECK AND ASSIGN RATE CONSTANTS

After rate constants were determined by the previously outlined methods, it was desirable to check the accuracy of these rate constants. One method used was a computer program [Ref. 16] which involved the use of a Hewlett Packard desk calculator model 9120A and plotter package. This program plotted the data points and utilized the rate constants and intercepts derived from the rate plots to plot a curve, based on equation (13), where I is to be identified with the intercept for a given step. For this analysis, $\bar{e}$ was the absorbance at time t, e_∞ was the assumed absorbance at infinite time or the equivalent in Guggenheim analysis $\bar{e}_{t+\Delta}$. Since the data points $\bar{e}-e_\infty$ or $\bar{e}-\bar{e}_{t+\Delta}$ were plotted on the same graph as the curve based on the derived constants, it was possible to determine, at least qualitatively, the accuracy of the derived constants in terms of the data for a given kinetic run. The interdependence of the intercepts on the rate constants and the rate constants on each other made "curve fitting" impractical by this method. However, if there was a discrepancy in the fit, it was possible to reanalyze the rate plot in terms of the observed discrepancy. Figure (2) is an example of these plots.

The methods used to determine the rate constants yielded them in order from the slower rates through the faster ones. These methods did not allow one to assign a particular rate constant to a particular step in the overall reaction scheme. Because of this, a method was needed that would enable one logically to assign the rate constants to the reaction steps. The initial gradient method of analysis used by Coe <u>et al</u> [Ref. 9] for the aquation of tetraamminepalladium(II) is generally regarded as best being able to determine the first rate constant in a series reaction. In addition, Reinhardt <u>et al</u> determined through careful analysis of isosbestic conditions [Refs. 8, 17] the rate constant for the chloride independent path of the reaction of tetraamminepalladium(II) chloride

Figure 2. Plot of Experimental $(A_\infty - A)$ (+) and Equation (13) (Solid Line)



with hydrochloric acid. The fastest rate constant observed by this author agreed substantially with those values for the first step as determined independently by Coe et al, and Reinhardt, et al.

From equation (13) and the expression for I_3 ($I_3=(e_c-e_\infty)(k_2-k_1)XY$) it may be seen that at a wavelength where $e_c=e_\infty$, the entire coefficient I_3 is equal to zero, and equation I_3 reduces to

$$\bar{e} - e_\infty = I_1e^{-k_1t} + I_2e^{-k_2t}$$

A comparison at a given temperature of kinetic runs at the wavelength where the above isosbestic condition holds and some other wavelength should enable one to determine which rate constant to associate with the step involving the isosbestic condition. The problem of assigning the two remaining constants was solved by simulating the reaction scheme on an analog computer [Ref. 8]. The diagram for the analog simulation circuit is given in Fig. (3). The rate constants were assigned to particular reaction steps in the analog computer circuit where they were simulated by potentiometer settings. Five outputs from the circuit, which were recorded simultaneously, represented the change in concentration of species A, B, C, D and E in the reaction scheme given in Section III, A-1 with respect to time. Since the absorbance of the i^{th} species is given by:

$$A_i = e_iC_id$$

where e_i is the molar absorptivity of the i^{th} species at a given wavelength, C is the molar concentration and d is the

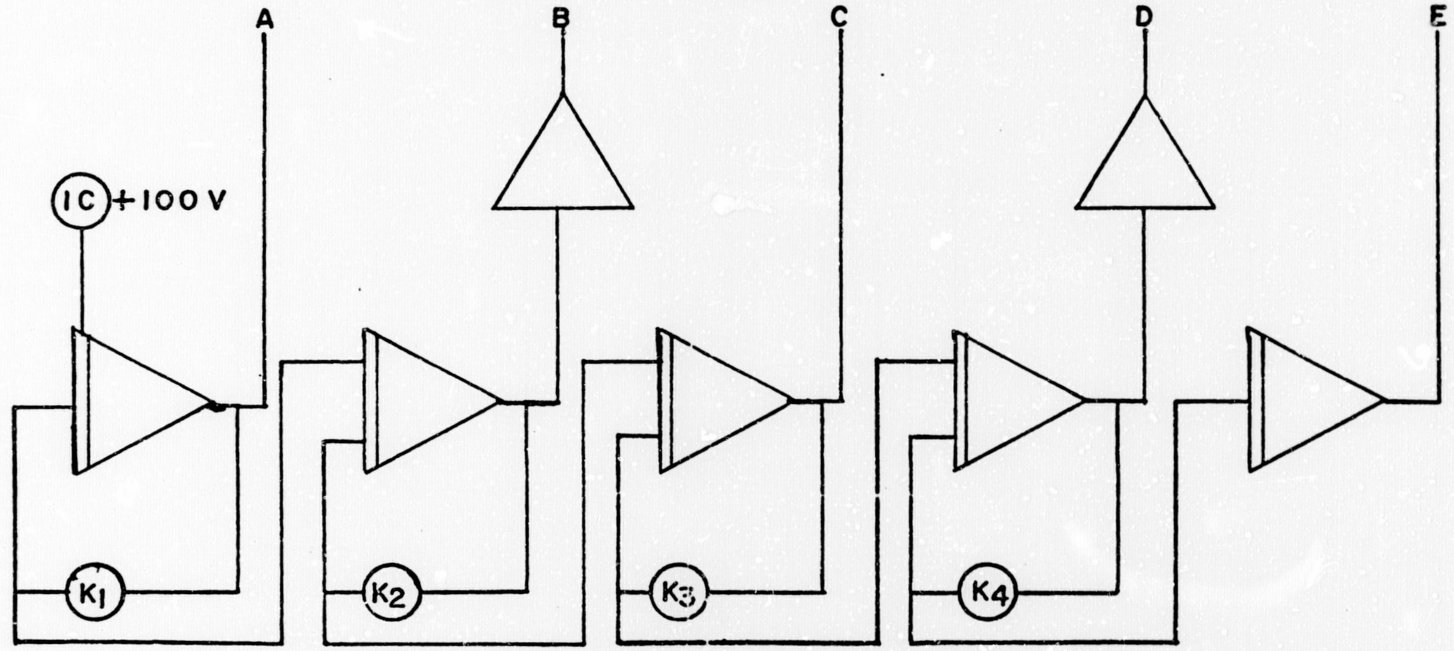


Figure 3. Analog Computer Circuit for Simulation of Consecutive Reactions

path length; it is possible to calculate the absorbance at a given wavelength, knowing the molar absorptivity and concentration and assuming d=1. Also, the average absorbance $\bar{A}$ at a given wavelength is given by [Ref. 17]:

$$\bar{A} = C_A e_A + C_B e_B + C_C e_C + C_D e_D + C_E e_E$$

The molar absorptivities for the species, $Pd(NH_3)_4^{2+}$, $Pd(OH_2)_2(NH_3)_2^{2+}$, $Pd(OH_2)_3NH_3^{2+}$, and $Pd(OH_2)_4^{2+}$ were published by Rasmussen and Jϕrgensen [Ref. 10], over wavelengths from about 280nm to 400nm. Missing from the data by Rasmussen and Jϕrgensen are the molar absorptivities for $Pd(NH_3)_3OH_2^{2+}$. Since the wavelength for the absorbance maximum for this species is given, this author arbitrarily chose the molar absorptivity of this species to be 210 at 320nm. The absorptivities at other wavelengths were found by interpolating between this maximum and the curve in Rasmussen and Jϕrgensen's Fig. 4 [Ref. 10] labeled $\bar{n}$ = 2.95. The values of this interpolation along with the rest of the data used are given in Table I. Using the data given in Table I along with the analog computer concentration data, the average absorbance data of the reacting species were calculated over the range of wavelengths from 280nm to 400nm for several different times. A Fortran IV program, written by this author, was used to calculate this information on an IBM 360 computer. A plot of this information resulted in scans over the range of wavelengths for different times. These calculated scans were compared with actual scans of the reaction from the DB spectrophotometer

TABLE I

MOLAR ABSORPTIVITIES OF PALLADIUM COMPOUNDS

	Molar Absorptivities[a] of				
λ nm	$Pd(NH_3)_4^{2+}$	$Pd(OH_2)(NH_3)_3^{2+}$	$Pd(OH_2)_2(NH_3)_2^{2+}$	$Pd(OH_2)_3NH_3^{2+}$	$Pd(OH_2)_4^{2+}$
400	1	20	41	70	70
390	2	30	61	93	77
380	10	47	90	115	78
370	11	60	125	127	75
360	11	85	153	130	68
350	18	110[b]	206	122	55
340	33	147[b]	215	108	41
330	58	188[b]	198	87	27
320	100	210[b]	160	60	15
310	155	190[b]	120	40	11
300	196	150[b]	76	29	9
290	196	108[b]	45	22	8
280	148	66	22	20	9

Given in units of absorbance per cm divided by concentration

[a] [Ref. 10].

[b] [Ref. 10] values obtained by assuming maximum absorptivity of $Pd(OH_2)(NH_3)_3^{2+}$ occurs between that of $Pd(NH_3)_4^{2+}$ and $Pd(OH_2)_2(NH_3)_2^{2+}$

and the assignment of rate constants was based on their comparison.

As an additional check of the proper assignment of rate constants, the concentration of $Pd(OH_2)_2(NH_3)_2^{2+}$ was roughly determined at various times during the course of the reaction. This was accomplished by adding chloride ion to a reacting solution 0.057M in palladium and 1M in perchloric acid (at 37° C). The chloride ion should react with any species in the reacting solution as follows: (Rate constants are $10^4 M^{-1} sec^{-1}$).

1. $Pd(NH_3)_4^{2+} + Cl^- \xrightarrow{8.3^a} Pd(NH_3)_3Cl^+, + Cl^- \xrightarrow{30.8^a}$ <u>trans</u>-$Pd(NH_3)_2(Cl_2)$

2. $Pd(OH_2)(NH_3)_3^{2+} + Cl^- \xrightarrow{fast} Pd(NH_3)_3Cl^+, + Cl^- \xrightarrow{30.8}$ <u>trans</u>-$Pd(NH_3)_2Cl_2$

3. <u>cis</u>-$Pd(OH_2)_2(NH_3)_2^{2+} + 2Cl^- \xrightarrow{fast}$ <u>cis</u>-$Pd(NH_3)_2Cl_2$

[a] [Ref. 8].

The anation of the aquo species in reactions 2 and 3 is considered to be quite fast. Aprile and Martin [Ref. 19] give the corresponding rate of anation of $Pt(NH_3)_3(OH_2)^{2+}$ by Cl^- as $2.6x10^{-5}sec^{-1}$ at 25°C. Considering that the relative reactivities of Pd to Pt is about 10^5 [Ref. 6], the corresponding rate of anation for the palladium case should be about $2.6sec^{-1}$ at 25°C. Thus it can be seen that the overall rate of reaction 3 is greater than the rate of reaction 2 is greater than reaction 1. Also, reactions 1 and 2 yield <u>trans</u> isomers while reaction 3 yields <u>cis</u> isomer.

The addition of chloride should yield a precipitate [Ref. 20]. If this precipitate is filtered off immediately after it is formed it should be a rough measure of the concentration of $Pd(OH_2)_2(NH_3)_2^{2+}$. Actually, according to equations 1, 2, and 3, above, and the discussion of the rates of these reactions, any immediate precipitate should be due to equation 3 and the product should be cis-$Pd(NH_3)_2Cl_2$, while another precipitation should occur at a later time and should be trans-$Pd(NH_3)_2Cl_2$. It was anticipated that the actual yield of cis-$Pd(NH_3)_2Cl_2$ would be less than the concentration of cis-$Pd(OH_2)_2(NH_3)_2^{2+}$, since the reaction of cis-$Pd(NH_3)_2Cl_2$ with chloride ion in acid is substantial [Ref. 21]. The approximate concentration of cis-$Pd(OH_2)_2(NH_3)_2^{2+}$ determined by this method may be compared with the concentrations using a particular assignment for the rate constants. A favorable comparison would indicate the proper choice for the assignment of k_2 and k_3. (This analysis would not determine anything about rate constants k_1 and k_2, however since interchanging these two constants has no effect on the concentration of diaquodiammine.)

An experiment designed to determine the relative abundance of trans impurities in the cis-dichlorodiammine precipitate was attempted, based on the differential rates of reaction of cis and trans species in HCl. The findings however, were inconclusive.

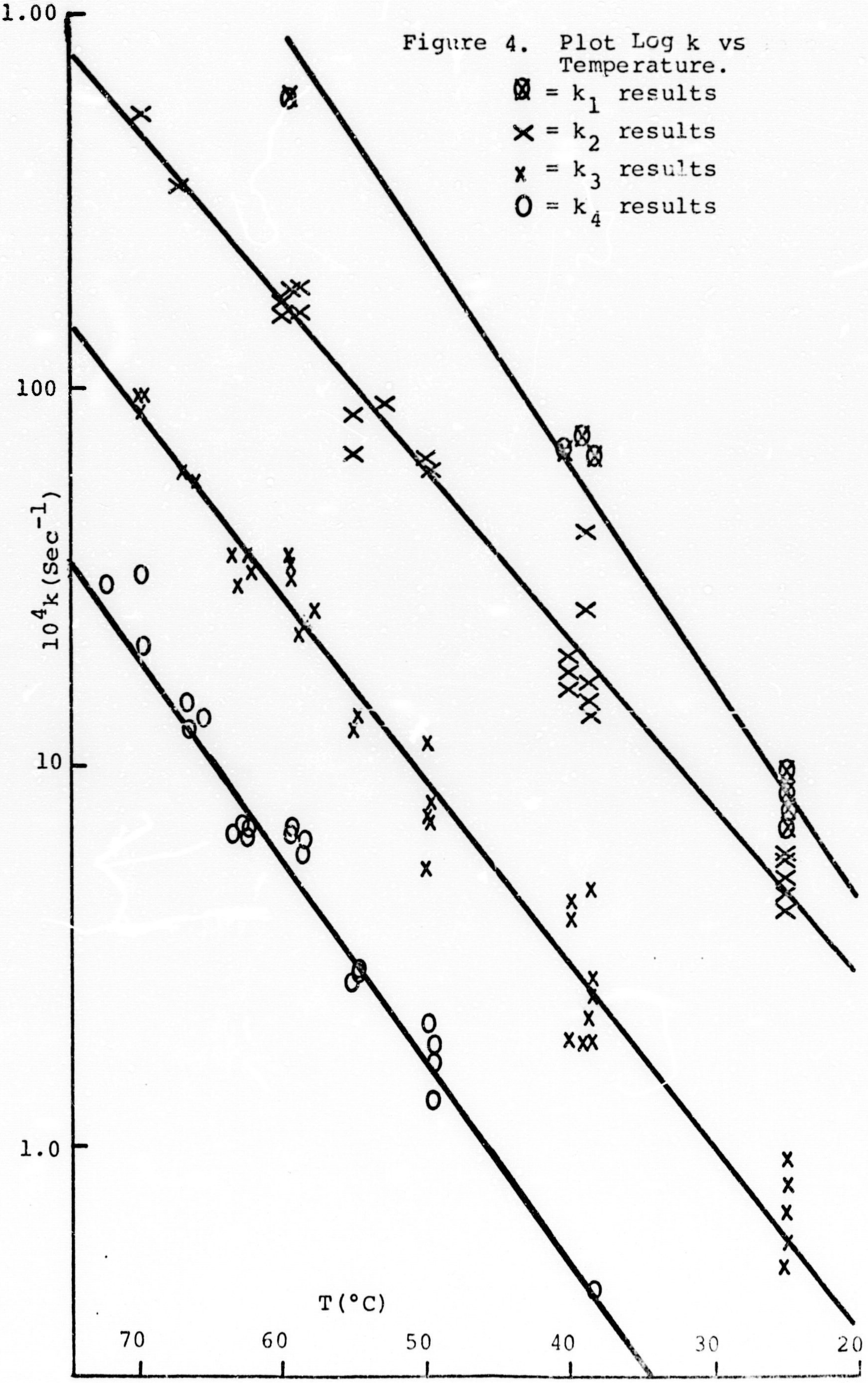


Figure 4. Plot Log k vs Temperature.

C. KINETIC RESULTS

1. Rate Constants

Table II summarizes the results of the kinetic runs done on the DU and DK 1A spectrophotometers and analyzed as outlined previously in Section III, A2. The results are also plotted in Fig. (4) to show the temperature dependence of ln k. The plot of ln k vs 1/T yielded the Arrhenius activation energy, which was used to estimate the activation parameters.

2. Assignment of Rate Constants to Reaction Steps

As indicated previously in Section III, B, the largest rate constant was assigned to the first step in the reaction on the basis of previous results. From the dependence of rates on wavelength the smallest constant was assigned to the last step. From Fig. 4 in Rasmussen and Jφrgensen [Ref. 10] it was seen that $e_C = e_\infty$ at about 396nm where e_C represents the molar absorptivity of $Pd(OH_2)_3(NH_3)^{2+}$, and e_C represents the absorbance at infinite time, which corresponds to the molar absorbtivity of $Pd(NH_3)_4^{2+}$. Thus at this wavelength, the rate constant for the reaction step $Pd(OH_2)_3NH_3^{2+} \rightarrow Pd(OH_2)_4^{2+}$ should not be seen, as explained in Section III, B. By comparing runs at this wavelength with runs at other wavelengths, it was found that this step corresponded to the smallest constant.

The results of adding chloride ion to a reacting solution of $Pd(NH_3)_4^{2+}$ and $HClO_4$ are shown in Fig. [5]. The $Pd(NH_3)_2Cl_2$ filtered out was found to be the cis-isomer by the characteristic IR absorbtion band at 1260 cm^{-1} which is

TABLE II

KINETIC RUNS

All k x 10^{+4} sec. $^{-1}$

70°C runs ± .25 with electrically heated thermostat

Run No.	T±.1°C	λ(nm)	Analysis[a]	k_1	k_2	k_3	k_4
DU 2	25	300	Δ=10,000	10.96	5.75	.78	
DU 2	25	300	Δ=5,000	11.5	5.35	1.09	
DU 3	25	300	Δ=5,000	9.72	4.43		
DU 5	25	305	Δ=2,500	9.8	6.5	.89	
DU 7	25	310	A_∞		7.08	.55	
DU 6	25	310	Δ=2,500	9.28	6.63	.64	
DU 9	25	360	A_∞	10.97	4.79		
DU 10	50	310	A_∞		76.1	9.37	2.32
DU 11	50	320	A_∞			6.14	1.82
DU 11	50	320	Δ=5,000		70.8	8.65	1.99
DU 15	55	323	Δ=5,000			15.4	3.15
DU 13	55	340	Δ=5,000		76.8	14.57	2.97
DU 14	55	350	Δ=5,000		98	15.5	2.89
DU 14	55	350	A_∞				2.89
DU 16	62.8	325	A_∞			37.75	7.49
DU 17	62.8	325	A_∞			41.87	8.01
DU 18	63.1	350	Δ=2,000			41.50	7.43
DU 19	63.2	350	A_∞			34.63	7.41
DK 1A 22	38.8	310	Wang		18.83	2.11	
DK 1A 22	38.8	310	A_∞	83.44	18.27	2.11	
DK 1A 21	38.8	330	A_∞		48.5	2.52	.481
DK 1A 23	38.8	396	A_∞	76.7	29.4	5.26	
DK 1A 24	38.8	400	A_∞		17.1	3.2	
DK 1A 24	38.8	400	Wang		15.46	2.8	
DK 1A 25	40	310	A_∞	83.5	18.3	2.11	
DK 1A 26	40	396	A_∞		22.83	4.74	
DK 1A 26	40	396	Wang		19.7	4.57	

---

[a] Δ Refers to delta in Guggenheim analysis.

A_∞ Indicates plot of log $A-A_\infty$ vs t.

Wang Indicates the nonlinear least square program analysis.

TABLE II--Continued

All k x 10^{+4} sec.$^{-1}$

70°C runs ± .25 with electrically heated thermostat

Run No.	$T \pm .1$°C	λ(nm)	Analysis[a]	k_1	k_2	k_3	k_4
DK 1A 27	50	328	A_∞			7.84	1.47
DK 1A 28	50	396	A_∞		68.8	13.3	
DK 1A 29	58.5	300	A_∞		213.2	27.4	6.8
DK 1A 29	58.5	300	Wang		190.0	25.2	7.0
DK 1A 30	59.7	360	A_∞	660.	194.8		8.39
DK 1A 31	59.7	380	A_∞		214.0	38.0	
DK 1A 32	59.7	400	A_∞		171.3	39.9	
DK 1A 33	59.8	420	A_∞			40.4	8.6
DK 1A 34	66.4	325	A_∞			65.1	15.1
DK 1A 35	67.6	310	A_∞		384	71.0	17.28
DK 1A 36	70	310	A_∞				37.2
DK 1A 37	70	320	A_∞		640	112.5	24.7
DK 1A 38	70	396	A_∞			111.6	

absent in the <u>trans</u> isomer [Ref. 20]. A precipitate formed in the filtrate of the solution and this was determined to be the <u>trans</u>-isomer. At each time, 3ml of reacting solution were removed for determination. Figure (5) shows that the concentration of <u>cis</u>-dichlorodiammine is less than the concentration of <u>cis</u>-diaquodiammine, as would be expected. Also, the curve based on the assignment of k_2 is greater than k_3 best approximates the experimental concentration data.

The rate constants at 25°C as determined by the plot of ln k vs. temperature were used in the analog computer to obtain concentrations as functions of time. These data together with the molar absorptivity data from Rasmussen and Jφrgensen [Ref. 10] listed in Table I, were used to plot absorbance vs. wavelength scans at various times. The assignments of the rate constants were permuted in a logical manner and the scans for these permutations were calculated. As can be seen from Table III, the assignment of the rate constants as follows, is in best agreement with the actual scan at 25°C:

$$Pd(NH_3)_4^{2+} \xrightarrow{k_1=11.0\times10^{-4}} Pd(OH_2)(NH_3)_3^{2+} \xrightarrow{k_2=5.6\times10^{-4}}$$

$$\underline{cis}\ Pd(OH_2)_2(NH_3)_2^{2+} \xrightarrow{k_3=0.58\times10^{-4}} Pd(OH_2)_3NH_3^{2+} \xrightarrow{k_4=0.10\times10^{-4}}$$

$$Pd(OH_2)_4^{2+}.$$

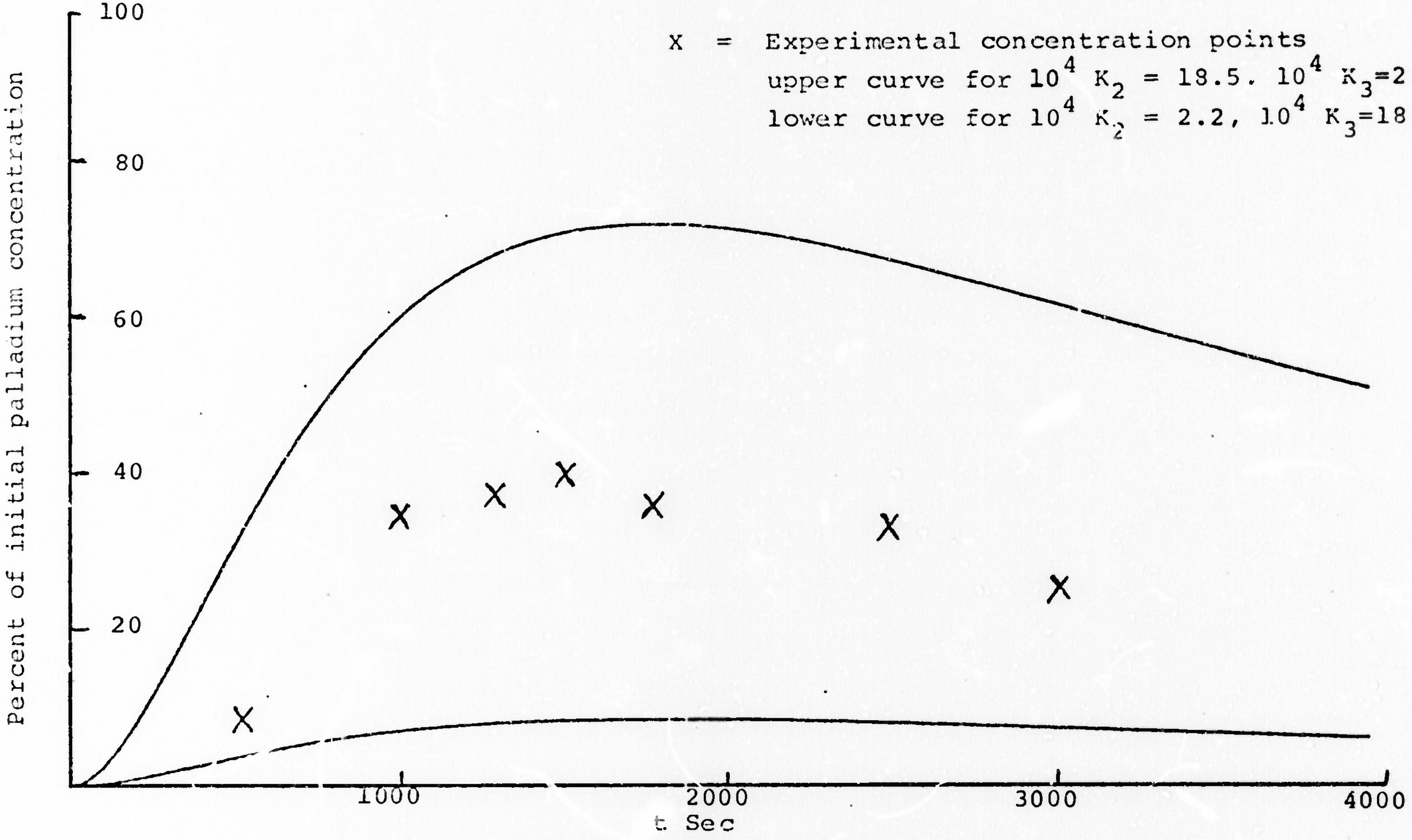


Figure 5. Concentration of $Pd(OH_2)_2(NH_3)_2$ vs time T = 37°C.

X = Experimental concentration points

upper curve for 10^4 K_2 = 18.5. 10^4 K_3=2.2

lower curve for 10^4 K_2 = 2.2, 10^4 K_3=18.5

TABLE III

WAVELENGTH FOR OCCURRENCE OF ABSORPTION MAXIMA FOR EXPERIMENTAL AND CALCULATED RATE SCANS

T = 25°C μ=1

Time Sec.	Experimental DB Scans	Order 1[a]	Order 2[a]	Order 3[a]	Order 4[a]
500	305	302	300	300	300
1000	314	313	307	310	305
2000	325	326	317	317	318
3000	336	333	328	320	335
4000	340	338	330	320	338
5000	344	340	336	320	340
10,000	348	344	340	322	342
15,000	350	347	340	324	345
20,000		348	340	325	346
30,000		352	340	331	346
40,000		358	340	335	350
50,000		359	344	348	350
60,000	360	360	344	355	350
80,000	366	366	344	358	360
100,000	368	368	344	362	363

[a]Order	$10^4 k_1 \sec^{-1}$	$10^4 k_2 \sec^{-1}$	$10^4 k_3 \sec^{-1}$	$10^4 k_4 \sec^{-1}$
1	11.0	5.6	0.58	0.1
2	11.0	5.6	0.1	0.58
3	11.0	0.58	5.6	0.1
4	05.6	11.0	0.58	0.1

TABLE IV

RATE CONSTANTS AND ACTIVATION PARAMETERS

T°C	10^4k_1sec^{-1}	10^4k_2sec^{-1}	10^4k_3sec^{-1}	10^4k_4sec^{-1}
15	4.8[b]			
20	5.5[a]			
	7.7[b]	3.3[a]		
	4.0[c]	1.7[c]		
25	11.0	5.6	0.58	0.10[a]
	11.0[d]	4.0[c]		
	13.7[b]			
	7.8[c]			
40	80	21	3.4	0.56
ΔH* kcal./mol	24.2	19.5	22.2	22.2
ΔS* eu	+8	-9	-4	-8

---

[a] Values extrapolated from Fig. (4).

[b] Reference [9].

[c] Reference [10].

[d] Reference [8].

IV. DISCUSSION

A. GENERAL CONSIDERATIONS

It may be noticed from Table II for the kinetic runs and Fig. (4) the plot of the kinetic results vs temperature that there are really very few data for k_1. Also, the results presented for this first step are probably the least reliable of the four rate constants determined in this research. This arises primarily from the fact that all of the faster rate constants are based on values of the slower rate constants. In the method of analysis employed, (Section IIIA,2) the linear portion of the log $(A-A_\infty)$ vs time plot was extrapolated to zero time. This linear portion represented the slowest step. In the case of the fastest step, if the reaction was run at a temperature high enough to yield a good value for the slowest step, the fastest step was so fast that its half life was of the same order as the sampling period, and, therefore, was indetectable. Likewise, as a lower temperature, the half life of the slowest step was so long that to follow the reaction that length of time was impractical. For these reasons, there are fewer data in this report for the fastest step than for the others; and except for the results at 25°C which agree fairly well with published values, the temperature dependence of this first step remains uncertain.

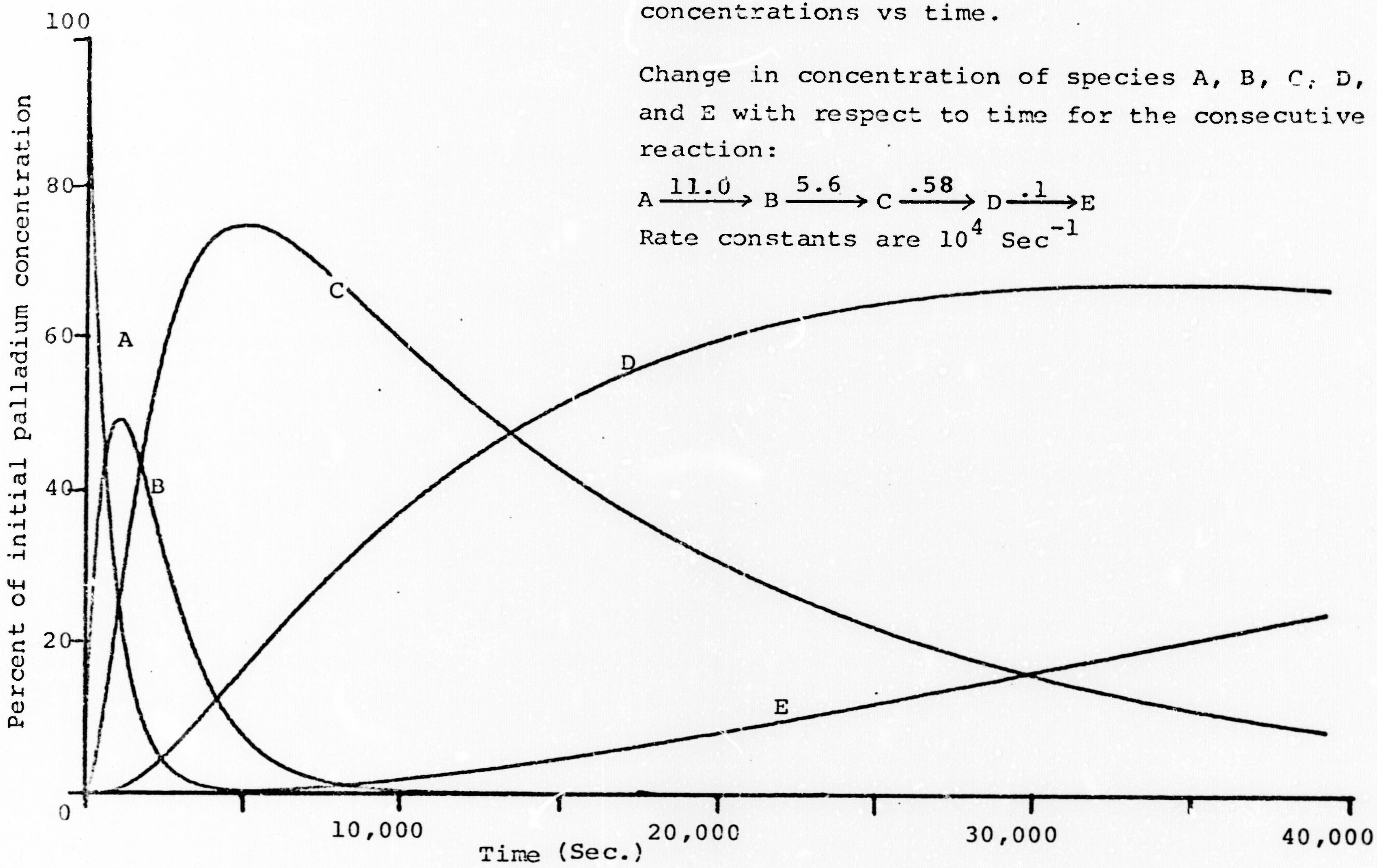
It should be pointed out that the peculiar value for the activation entropy, which for the first step is positive, is

Figure 6. Analog computer plot of consecutive reaction concentrations vs time.

Change in concentration of species A, B, C, D, and E with respect to time for the consecutive reaction:

$A \xrightarrow{11.0} B \xrightarrow{5.6} C \xrightarrow{.58} D \xrightarrow{.1} E$

Rate constants are 10^4 Sec^{-1}



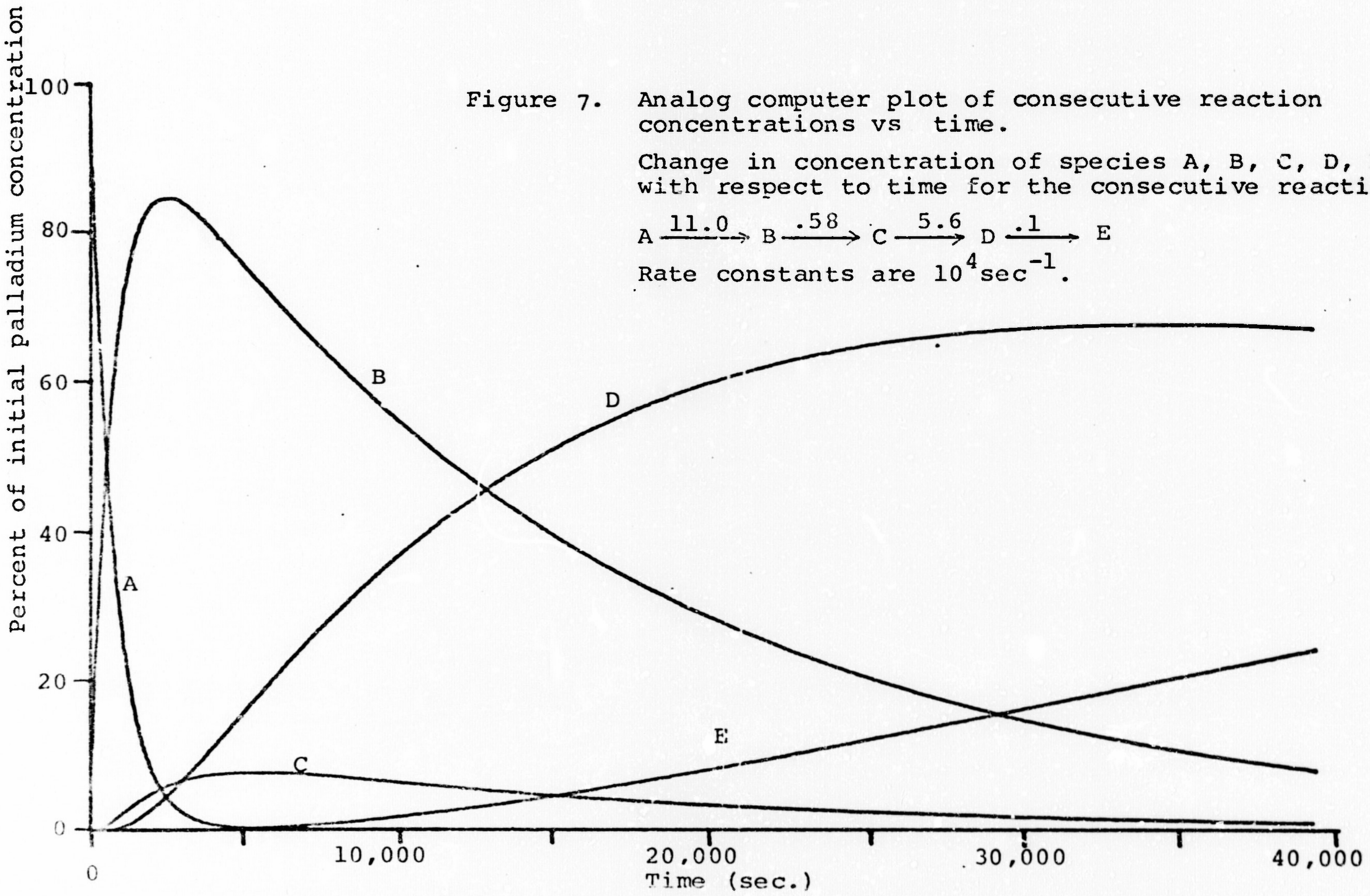


Figure 7. Analog computer plot of consecutive reaction concentrations vs time.

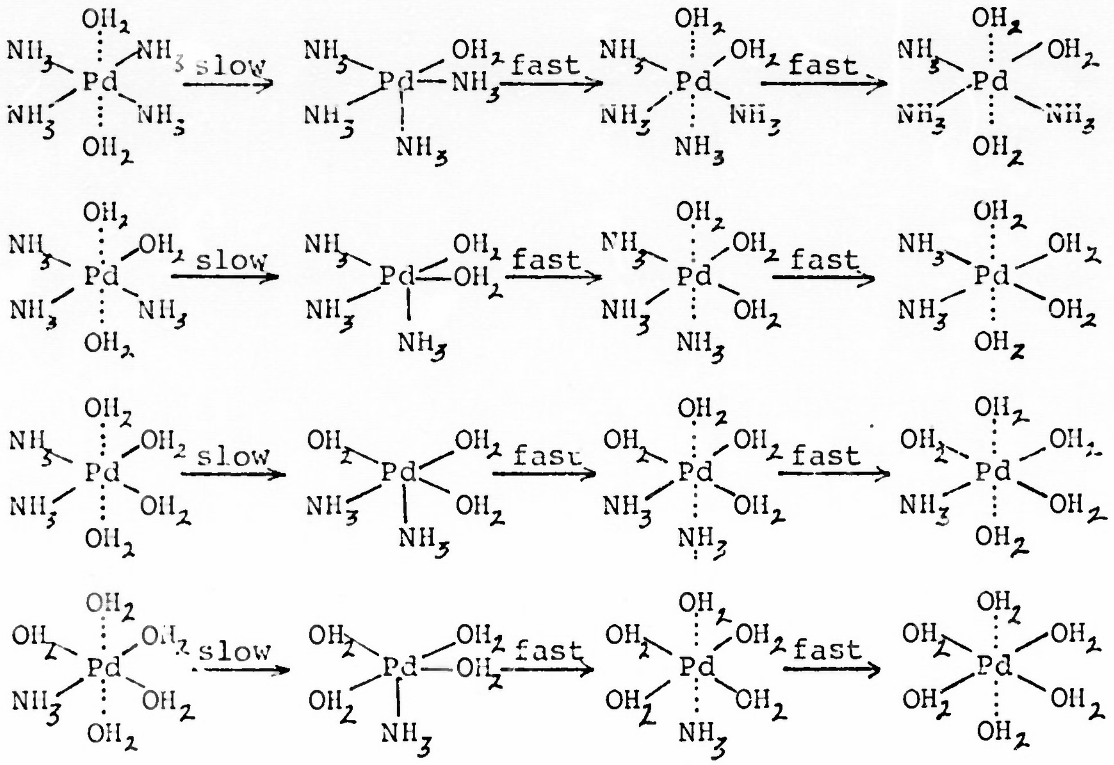
Change in concentration of species A, B, C, D, E with respect to time for the consecutive reaction

$A \xrightarrow{11.0} B \xrightarrow{.58} C \xrightarrow{5.6} D \xrightarrow{.1} E$

Rate constants are $10^4 sec^{-1}$.

an indication of a problem, since all the other activation entropies are negative, and an associative mechanism predicts a negative activation entropy. The positive activation entropy for this step is undoubtably due to the use of a too high activation enthalpy.

The following mechanism is not inconsistent with the rate data and activation parameters observed for this reaction series, except perhaps for the activation parameters of the first step which are uncertain. One may consider the square planar configuration to be a tetragonally distorted octehedron with solvent molecules loosely held in the axial positions. The process may proceed as follows:



B. STRUCTURAL CONSIDERATIONS

In the reaction series with tetraamminepalladium(II) in perchloric acid, it has been demonstrated that the diaquodiamminepalladium(II), formed as an intermediate, exists predominantly in the cis configuration [Ref. 20]. This is shown by adding chloride ion to the reacting solution in which the diaquodiammine species is present. The chloride immediately replaces the water in the complex and precipitates out as a bright yellow solid. Infrared studies reveal the characteristic absorbtion bands of the cis isomer.

It is interesting to note that in the reaction of tetraamminepalladium(II) with hydrochloric acid, in which the ammonia ligands are replaced by chloride ions, the configuration of dichlorodiamminepalladium(II) exists as the more stable trans isomer [Ref. 8]. The question naturally arises as to what causes these differences. It is known from the studies of platinum(II) that there are certain ligands which tend to labilize the ligand trans to it. This is known as the "trans effect" [Ref. 1]. From the generally accepted order of trans labilizing ligands, Cl^- is greater than NH_3 which is greater than H_2O. The results that the aquation of tetraamminepalladium(II) yields a cis intermediate, and chloride substitution yield a trans intermediate seem consistent with the accepted trans effect order.

To try to correlate the rate data for a particular set of related reactions and try to make some generalizations is an important goal of the research chemist. For example, the previously noted "trans effect" order resulted from the correlation of much rate data on the reactions of platinum complexes. Comparisons of rates of different reactions with some features in common give rise to generalizations. Of continuing interest is the testing of these generalizations by new rate data. Of particular interest to those working with square planar complexes is the effect on rate of the substituents cis as well as trans to a leaving group.

It may be appropriate to compare the structural effects on the rate of a solvent path of a reaction. All the rate constants derived in this work refer to the solvent path. Consider Table V, the summary of solvent step rate constants, where n is the number of equivalent NH_3 leaving groups, and the rates are given as 10^4k. It should be noticed that there are several reactions listed which have the same cis neighbors. For these reactions one may compare the different rate effects of the trans neighbors. Likewise for reactions with the same trans neighbors, the effect of different cis neighbors may be compared.

For reactions 1 and 2 the relative trans effect of Cl^- vs. NH_3 is about 3.3. Comparing reactions 3 and 4, one notices a trans effect of Cl^- vs. NH_3 of about 1.3, using the rate constant given by Poe and Vaughan [Ref. 21] for this step at 25°C $\mu=5$. One may also compare reactions 6 and 7 for the relative trans effect of NH_3 vs. H_2O and obtain a factor of 9.7. Thus for a trans effect, the relative order Cl^- greater than NH_3 greater than H_2O is again observed.

A *cis* effect may be observed for several reactions. Considering first reactions 2 and 8 it can be seen that one *cis* Cl^- deactivates the reaction relative to one *cis* NH_3 ligand by a factor of about 3.8, whereas in reactions 3 and 8 for the same ligands one finds a factor of 100. In reactions 1 and 4 one observes a *cis* deactivation of two Cl^- vs. two NH_3 of about 150. If one compares reactions 2 and 3 one will observe the *cis* deactivation of two *cis* Cl^- vs two *cis* NH_3 of 400. It may also be determined that in reactions 5 and 7, an H_2O ligand *cis* to the leaving group deactivates the reaction relative to an NH_3 group *cis* by about 3. Whereas the comparison of equations 1 and 6 indicates a *cis* deactivation of H_2O vs NH_3 of 1, i.e., no *cis* effect. Thus these results would seem to indicate a *cis* group deactivation order of $Cl^- > H_2O > NH_3$. However, there seems to be quite a range of values for the deactivation by *cis* ligands, for example, the observed values for *cis* deactivation of Cl^- vs NH_3 of 3.8 in one case and 100 in another. This could indicate that this may not really be an adequate basis for determining *cis* effects, or that some of the rate constants may be in error.

To attempt to systematize the relative *trans* and *cis* effects of various ligands in the substitution of Cl^- in the chloroammineplatinum(II) series, Tucker, Colvin and Martin [Ref. 22] have used the empirical relationship $k/n=X(Y)^m(Z)^p$ where n is the number of equivalent leaving groups, m is the number of NH_3 ligands *trans* to the leaving group, p is the

TABLE V

SUMMARY OF SOLVENT STEP RATE CONSTANTS

No.	Reaction	n	$10^4k/n$	Group trans	Group cis
1.	$Pd(NH_3)_4^{2+} + H_2O \xrightarrow{11.0}$ $Pd(NH_3)_3OH_2^{2+}$	4	2.75	NH_3	NH_3-NH_3
2.	$Pd(NH_3)_3Cl^+ + H_2O \xrightarrow{9.0^a}$ *trans*-$Pd(NH_3)_2OH_2Cl^+$	1	9.0	Cl^-	NH_3-NH_3
3.	$Pd(NH_3)Cl_3^- + H_2O \xrightarrow{.023}$ $Pd(OH_2)Cl_3^-$	1	.023	Cl^-	Cl-Cl
4.	*trans*-$Pd(NH_3)_2Cl_2 + H_2O \xrightarrow{.037^b}$ *trans*-$Pd(NH_3)(OH_2)Cl_2$	2	.018	NH_3	Cl-Cl
5.	$Pd(NH_3)(OH_2)_3^{2+} + H_2O \xrightarrow{.1}$ $Pd(OH_2)_4^{2+}$	1	.1	H_2O	H_2O-H_2O
6.	$Pd(NH_3)_3OH_2^{2+} + H_2O \xrightarrow{5.6}$ *cis*-$Pd(NH_3)_2OH_2^{2+}$	2	2.8	NH_3	H_2O-NH_3
7.	*cis*-$Pd(NH_3)_2(OH_2)_2^{2+} + H_2O \xrightarrow{.58}$ $Pd(NH_3)(OH_2)_3^{2+}$	2	.29	H_2O	H_2O-NH_3

---

[a] Reference [5].

[b] Reference [18].

TABLE V--Continued

No.	Reaction	n	$10^4k/n$	Group trans	Group cis
8.	*cis*-$Pd(NH_3)_2Cl_2 + H_2O \xrightarrow{4.8^b}$ $Pd(NH_3)Cl_2OH_2$	2	2.4	Cl^-	Cl-NH_3

number of NH_3 ligands cis to the leaving group and X, Y, and Z are empirical constants. Reinhardt and Monk [Ref. 23] have used a similar equation for the cis and trans effects in reactions of the chloroammine series of palladium(II). A similar equation may be used to try to correlate the rates of the reactions in Table V.

Such an equation may be given as:

$$k/n = 0.03\text{x}10^{-4}(0.5)^m(15)^p(0.05)^o(10)^q,$$

where n is the number of equivalent NH_3 leaving groups, m is the number of NH_3 groups trans to the leaving group; p, the number of NH_3 groups cis to the leaving group; o, the number of H_2O groups trans to the leaving groups and q the number of H_2O groups cis to the leaving group. All of the rate constants fit this equation to within about 20% except that given in reaction 8, for which this equation predicts $0.45\text{x}10^{-4}$.

Thus it may be seen that in reactions involving chloride ion there is a profound cis effect, whereas in reactions not involving chloride ion there is less of an effect due to the cis neighbor, and the trans effect predominates. This information indicates that perhaps the cis effect is the result of a charge on the cis neighbor. All the reactions in Table V not involving chloride ion should exhibit no charge effect, whereas reactions involving chloride ion may exhibit such an effect. Cis and trans effects are summarized in Table VI.

Further information in this area could be obtained from looking at the reverse series of reactions, starting with tetraaquopalladium(II) ion and determining the rate constants

TABLE VI

SUMMARY OF CIS AND TRANS EFFECTS

trans Effect

Reaction Pair -Table V	Groups Involved	Activation Factor
1,2	Cl^- vs NH_3	3.3
3,4	Cl^- vs NH_3	1.3
6,7	NH_3 vs H_2O	9.7

cis Effect

Reaction Pair -Table V	Groups Involved	Deactivation Factor
2,8	$1Cl^-$ vs $1NH_3$	3.8
3,8	$1Cl^-$ vs $1NH_3$	100
1,4	$2Cl^-$ vs $2NH_3$	150
2,3	$2Cl^-$ vs $2NH_3$	400
5,7	$1H_2O$ vs $1NH_3$	3
1,6	$1H_2O$ vs $1NH_3$	1

of successive ammonation. It would be anticipated that these rates would depend on the ammonia concentration and follow the usual two term rate law. Insight could also be gained as to relative cis and trans effects.

APPENDIX A

ABSORBANCE DATA

This Appendix contains all absorbance versus time data taken during the course of this research. Times for DU data are in seconds, while for DK 1A data times are in minutes. The data pertains to the following reaction:

$$Pd(NH_3)_4^{2+} \xrightarrow{k_1} Pd(OH_2)(NH_3)_3^{2+} \xrightarrow{k_2} Pd(OH_2)_2(NH_3)_2^{2+} \xrightarrow{k_3}$$

$$Pd(OH_2)_3(NH_3)^{2+} \xrightarrow{k_4} Pd(OH_2)_4^{2+}$$

DU Run -1

All times in seconds

T = 25.0°C

Pd = .445mM

λ = 300nm

H^+ = 1.0M cell = 10cm

Time	Abs	Time	Abs	Time	Abs	Time	Abs
80	.7	2900	.489	6100	.310	9100	.2555
100	.71	3000	.478	6200	.307	9200	.254
200	.705	3100	.471	6300	.304	9300	.252
300	.841	3200	.464	6400	.301	9400	.250
400	.822	3400	.450	6500	.299	9500	.248
500	.870	3500	.440	6600	.295	9600	.247
600	.785	3600	.435	6700	.295	9700	.247
700	.765	3700	.431	6800	.293	9900	.246
800	.749	3800	.419	6900	.291	10,000	.244
900	.741	3900	.419	7000	.290	10,100	.243
1000	.721	4000	.408	7100	.287	10,200	.242
1100	.700	4100	.404	7200	.286	10,500	.238
1200	.691	4300	.390	7300	.283	10,800	.236
1300	.675	4400	.387	7400	.282	10,900	.235
1400	.658	4600	.376	7500	.279	11,000	.235
1500	.645	4700	.375	7600	.277	11,500	.230
1600	.635	4800	.362	7700	.276	A_∞	.087
1700	.620	4900	.357	7800	.275		
1800	.607	5000	.356	7900	.273		
1900	.596	5100	.350	8000	.269		
2000*	.586	5200*	.347	8100*	.267		

*Continued on following page.

Time	Abs	Time	Abs	Time	Abs	Time	Abs
2100	.571	5300	.341	8200	.267		
2200	.560	5400	.340	8300	.266		
2300	.550	5500	.334	8400	.264		
2400	.536	5600	.334	8500	.262		
2500	.525	5700	.321	8600	.261		
2600	.516	5800	.322	8700	.260		
2700	.507	5900	.313	8900	.256		
2800	.499	6000	.310	9000	.256		

DU Run-2

T = 25.0° C λ = 300nm

Pd = .445mM H^+ = 1.0M cell = 10cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.800	3700	.411	7400	.2735
100	.795	3800	.406	7500	.271
200	.780	3900	.398	7700	.268
300	.770	4000	.392	7800	.265
400	.755	4100	.386	7900	.266
500	.741	4200	.381	8000	.266
600	.730	4300	.376	8500	.260
700	.711	4400	.371	9000	.255
800	.700	4500	.366	9500	.249
900	.688	4600	.361	10,000	.245
1000	.673	4700	.362	10,500	.240
1100	.661	4800	.352	11,000	.236
1200	.645	4900	.349	11,500	.232
1300	.635	5000	.345	12,000	.228
1400	.622	5100	.430	12,500	.225
1500	.610	5200	.337	13,000	.221
1600	.600	5300	.333	13,500	.217
1700	.590	5400	.330	14,000	.215
1800	.576	5500	.325	14,500	.213
1900	.566	5600	.323	15,000	.209
2000	.555	5700	320	15,500	.206
2100	.545	5800	.321	16,000	.2035
2200	.532	5900	.313	16,500	.2015
2300	.521	6000	.311	17,000	.2000
2400	.511	6100	.308	17,500	.1975
2500	.501	6200	.305	18,000	.1945
2600	.493	6300	.302	18,500	.1925
2700	.485	6400	.300	19,000	.1900
2800	.475	6500	.297	19,500	.1870
2900	.467	6600	.295	20,000	.1840
3000	.460	6700	.2935	20,500	.1810
3100	.451	6800	.2902	21,000	.1780
3200	.443	6900	.287	21,500	.1710
3300	.438	7000	.282	22,000	.1680
3400	.431	7100	.282	22,500	.1650
3500	.424	7200	.277	A	.0940
3600	.418	7300	.275		

DU Run-3

T = 25.0° C λ = 300nm

Pd = 5.33mM H^+ = 1.0M cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.760	4800	.357	9600	.245
100	.759	4900	.353	9700	.244
200	.754	5000	.346	9800	.243
300	.748	5100	.342	9900	.242
400	.736	5200	.339	10,000	.242
500	.729	5300	.335	10,100	.240
600	.716	5400	.331	10,500	.236
700	.709	5500	.328	11,000	.231
800	.696	5600	.325	11,500	.227
900	.684	5700	.321	12,000	.223
1000	.671	5800	.318	12,500	.219
1100	.659	5900	.315	13,000	.215
1200	.648	6000	.312	13,500	.209
1300	.634	6100	.308	14,000	.207
1400	.621	6200	.305	14,500	.206
1500	.610	6300	.303		
1600	.600	6400	.301	4100	.390
1700	.589	6500	.297	4200	.385
1800	.576	6600	.295	4300	.380
1900	.569	6700	.293	4400	.375
2000	.556	6800	.291	4500	.370
2100	.545	6900	.288	4600	.366
2200	.534	7000	.286	4700	.362
2300	.524	7100	.284		
2400	.516	7200	.282	8900	.255
2500	.505	7300	.280	9000	.254
2600	.496	7400	.277	9100	.253
2700	.488	7500	.275	9200	.251
2800	.479	7600	.274	9300	.250
2900	.471	7700	.273	9400	.248
3000	.463	7800	.272	9500	.247
3100	.458	7900	.270		
3200	.449	8000	.267		
3300	.441	8100	.266		
3400	.434	8200	.265		
3500	.429	8300	.263		
3600	.422	8400	.261		
3700	.416	8500	.260		
3800	.409	8600	.259		
3900	.403	8700	.258		
4000	.396	8800	.256		

DU RUN-4

T = 25.0° C λ = 300nm

Pd = .445mM H^+ = 1.0M cell = 10cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
35	.895	1600	.630	3200	.468
100	.875	1700	.618	3300	.460
200	.860	1800	.608	3400	.453
300	.839	1900	.595	3500	.445
400	.820	2000	.581	3600	.439
500	.800	2100	.570	3700	.432
600	.785	2200	.560	3800	.428
700	.768	2300	.550	3900	.421
800	.750	2400	.539	4000	.415
900	.735	2500	.530	4100	.410
1000	.719	2600	.520	4300	.398
1100	.701	2700	.510	4400	.392
1200	.685	2800	.500	4500	.387
1300	.672	2900	.491	4600	.381
1400	.660	3000	.482	4900	.369
1500	.640	3100	.475	5000	.365

DU Run-5

T = 25.0° C λ = 305nm

Pd = .445mM H^+ = 1.0M cell = 10cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
100	.830	1100	.744	4000	.500
200	.821	1200	.735	4500	.471
300	.815	1400	.711	5000	.449
400	.810	1600	.692	5500	.428
500	.800	1800	.672	6000	.410
600	.795	2000	.654	6500	.395
700	.782	2400	.616	7000	.382
800	.772	2800	.583	8000	.360
900	.762	3000	.569	9000	.343
1000	.752	3500	.531	10,000	.329
				12,000	.305

DU Run–6

T = 25.0° C λ = 310nm
Pd = .445mM H^+ = 1.0M   cell = 10cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
75	.786	3000	.680	5900	.530
100	.790	3100	.670	6000	.524
200	.799	3200	.665	6500	.509
300	.800	3300	.658	7000	.495
400	.802	3400	.650	7500	.481
500	.804	3500	.642	8000	.471
600	.810	3600	.639	8500	.461
700	.810	3700	.631	9000	.454
800	.810	3800	.628	9500	.446
900	.805	3900	.620	10,000	.438
1000	.803	4000	.615	10,500	.431
1100	.802				
1200	.800	4100	.610	11,000	.426
1300	.795	4200	.605	11,500	.420
1400	.789	4300	.600	12,000	.414
1500	.781	4400	.592	12,500	.409
1600	.779	4500	.590	13,000	.404
1700	.770	4600	.582	13,500	.398
1800	.761	4700	.580	14,000	.392
1900	.755	4800	.571	14,500	.387
2000	.750	4900	.570	15,000	.383
2100	.741	5000	.565	15,500	.379
2200	.736	5100	.560	16,000	.375
2300	.730	5200	.556	16,500	.370
2400	.721	5300	.551	17,000	.366
2500	.712	5400	.549	17,500	.361
2600	.709	5500	.545	18,000	.358
2700	.700	5600	.540	18,500	.355
2800	.691	5700	.538	19,000	.351
2900	.685	5800	.531	19,500	.348

DU Run-7

$T = 25.0° C$ $\lambda = 310nm$

$Pd = .445mM$ $H^+ = 1.0M$ cell = 10cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.730	2600	.661	5200	.529
100	.734	2700	.659	5300	.520
200	.740	2800	.651	5400	.519
300	.747	2900	.646	5500	.512
400	.750	3000	.641	5600	.510
500	.751	3100	.632	5700	.506
600	.750	3200	.628	5800	.501
700	.750	3300	.620	5900	.500
800	.750	3400	.615	6000	.496
900	.750	3500	.610	6100	.491
1000	.748	3600	.605	6200	.489
1100	.745	3700	.600	6400	.481
1200	.741	3800	.595	6500	.480
1300	.739	3900	.590	7000	.465
1400	.734	4000	.585	7500	.452
1500	.729	4100	.579	8000	.440
1600	.724	4200	.571	8500	.430
1700	.717	4300	.568	9000	.421
1800	.711	4400	.561	9500	.412
1900	.709	4500	.559	10,000	.406
2000	.700	4600	.551	10,500	.399
2100	.695	4700	.549	11,000	.391
2200	.690	4800	.542	11,500	.386
2300	.682	4900	.540	12,000	.384
2400	.679	5000	.535	12,500	.377
2500	.670	5100	.530	13,000	.370

DU Run-8

T = 25.0° C λ = 340nm

Pd = 5.33mM H^+ = 1.0M cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
28	.246	2000	.739	4000	.888
100	.282	2100	.750	4100	.891
200	.320	2200	.761	4300	.900
300	.354	2300	.771	4500	.905
400	.386	2400	.781	4900	.918
500	.420	2500	.794	5000	.919
600	.450	2600	.800	5300	.920
700	.480	2700		5500	.921
800	.510	2800		6000	.923
900	.534	2900	.824	6500	.925
1000	.560	3000	.832	7000	.923
1100	.584	3100	.840	7500	.921
1200	.605	3200	.848	8000	.920
1300	.622	3300	.85	8500	.917
1400	.643	3400	.860	9000	.910
1500	.660	3500	.863	9500	.904
1600	.679	3600	.870	10,000	.900
1700	.695	3700	.878	10,500	.895
1800	.710	3800	.880	11,500	.882
1900	.721	3900	.885		

DU Run-9

T = 25.0°C λ = 360nm

Pd = 5.33mM H^+ = 1.0M   cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
40	.129	2800	.595	10,000	.800
100	.142	2900	.605	10,500	.800
200	.164	3000	.614	11,000	.800
300	.186	3100	.624	11,500	.800
400	.207	3200	.631	12,000	.799
500	.230	3300	.640	12,500	.798
600	.250	3400	.647	13,000	.795
700	.272	3500	.656	13,500	.794
800	.293	3600	.663	14,000	.791
900	.312	3700	.670	14,500	.790
1000	.330	3800	.680	15,000	.790
1100	.350	3900	.686	15,500	.787
1200	.369	4000	.692	16,000	.785
1300	.385	4100	.699	16,500	.781
1400	.403	4300	.710	17,000	.781
1500	.420	4500	.720	17,500	.780
1600	.436	4900	.739	18,000	.777
1700	.454	5000	.741	18,500	.776
1800	.467	5300	.759	19,000	.771
1900	.481	5500	.760	19,500	.770
2000	.498	6000	.772	20,000	.768
2100	.510	6500	.782	20,500	.765
2200	.522	7000	.791	21,000	.765
2300	.538	7500	.796	21,500	.762
2400	.550	8000	.800	22,000	.760
2500	.560	8500	.800	22,500	.760
2600	.571	9000	.801		
2700	.586	9500	.801		

DU Run-10

T = 50.0° C λ = 310nm
Pd = 5.33mM H^+ = 1.0M   cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
60	.795	3900	.133	7800	.0865
100	.750	4000	.130	7900	.0860
200	.621	4100	.128	8000	.0855
300	.531	4200	.126	8100	.0845
400	.469	4300	.124	8200	.0840
500	.427	4400	.122	8300	.0835
600	.395	4500	.119	8400	.0830
700	.370	4600	.118	8500	.0825
800	.352	4700	.117	8600	.0820
900	.332	4800	.114	8700	.0820
1000	.319	4900	.113	8800	.0810
1100	.304	5000	.112	8900	.0805
1200	.291	5100	.110	9000	.0800
1300	.275	5200	.109	9100	.0795
1400	.266	5300	.108	9500	.0780
1500	.256	5400	.107	10,000	.0760
1600	.247	5500	.106	10,500	.0740
1700	.238	5600	.104	11,000	.0730
1800	.229	5700	.102	11,500	.0720
1900	.222	5800	.1015	12,000	.0690
2000	.214	5900	.101	12,500	.0685
2100	.207	6000	.100	13,000	.0675
2200	.201	6100	.098	13,500	.0660
2300	.194	6200	.098	14,000	.0655
2400	.189	6300	.097	14,500	.0655
2500	.183	6400	.096	15,000	.0645
2600	.178	6500	.095	15,500	.0645
2700	.173	6600	.0945	16,000	.0640
2800	.169	6700	.094	16,500	.0635
2900	.159	6800	.093	17,000	.0630
3000	.160	6900	.092	17,500	.0630
3100	.156	7000	.0915	18,000	.0625
3200	.154	7100	.091	18,500	.0625
3300	.150	7200	.091	19,000	.0625
3400	.146	7300	.089	19,500	.0625
3500	.144	7400	.0885	20,000	.0625
3600	.141	7500	.088	20,500	.0625
3700	.138	7600	.0875	21,000	.0625
3800	.136	7700	.0870	A_∞	.0568

DU Run-11

T = 50.0° C λ = 320nm

Pd = 5.33mM H^+ = 1.0M cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
35	.700	3400	.215	6800	.1335
100	.789	3500	.2105	6900	.1325
200	.765	3600	.2065	7000	.1315
300	.706	3700	.2025	7100	.130
400	.642	3800	.199	7300	.1275
500	.603	3900	.1955	7500	.1255
600	.568	4000	.192	7700	.1235
700	.536	4100	.189	8000	.1205
800	.510	4200	.1855	8500	.116
900	.484	4300	.183	9000	.112
1000	.460	4400	.179	9500	.1085
1100	.443	4500	.1765	10,000	.1055
1200	.424	4600	.173	10,500	.1025
1300	.406	4700	.172	11,000	.1005
1400	.390	4800	.1695	11,500	.098
1500	.374	4900	.1670	12,000	.0955
1600	.361	5000	.165	12,500	.0945
1700	.348	5100	.1625	13,000	.093
1800	.335	5200	.1595	13,500	.091
1900	.325	5300	.1570	14,000	.090
2000	.314	5400	.155	14,500	.088
2100	.303	5500	.154	15,000	.0875
2200	.295	5600	.151	15,500	.086
2300	.287	5700	.150	16,000	.085
2400	.277	5800	.1485	16,500	.045
2500	.270	5900	.1475	18,500	.082
2600	.2625	6000	.145	19,000	.081
2700	.2545	6100	.144	19,500	.0805
2800	.2475	6200	.1420	20,000	.0805
2900	.242	6300	.1415	20,500	.0800
3000	.235	6400	.140	21,000	.0800
3100	.231	6500	.138	21,500	.079
3200	.225	6600	.137	22,000	.0780
3300	.220	6700	.135	23,500	.076

DU Run-12

T = 55.0° C λ = 420

Pd = 5.33mM H^+ = 1.0M   cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.084	1600	.2625	3600	.303
100	.117	1650	.2645	3700	.305
150	.140	1700	.266	3800	.3055
200	.156	1750	.2675	3900	.307
250	.169	1800	.2685	4000	.308
300	.178	1850	.270	4100	.3095
350	.186	1900	.272	4200	.311
400	.194	1950	.273	4300	.312
450	.198	2000	.274	4400	.3125
500	.203	2200	.278	4500	.314
550	.207	2250	.280	4600	.315
600	.211	2300	.281	4800	.316
650	.215	2350	2825	4900	.317
700	.219	2400	.284	5000	.318
750	.222	2450	.285	5500	.321
800	.226	2500	.286	6000	.324
850	.229	2550	.286	6500	.327
900	.232	2600	.2875	7000	.330
950	.235	2650	.289	7500	.3325
1000	.237	2700	.290	8000	.335
1050	.240	2750	.2905	8500	.336
1100	.242	2800	.292	9000	.338
1150	.244	2850	.292	9500	.339
1200	.247	2900	.293	10,000	.340
1250	.249	2950	.2945	10,500	.342
1300	.251	3000	.295	11,000	.3425
1350	.253	3100	.296	11,500	.345
1400	.255	3200	.298	12,000	.345
1450	.2575	3300	.300	12,500	.345
1500	.2595	3400	.301	13,000	.3455
1550	.261	3500	.302	A_∞	.352

DU Run-13

T = 55.0° C λ = 340
Pd = 5.33mM H^+ = 1.M cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
10	.420	1800	.515	5400	.312
50	.670	1900	.500	5500	.310
100	.822	2000	.489	5600	.307
150	.900	2100	.475	5700	.305
200	.930	2200	.467	5800	.302
250	.932	2300	.459	5900	.300
300	.920	2400	.450	6000	.298
350	.900	2500	.441	6100	.296
400	.880	2600	.433	6200	.295
450	.860	2700	.426	6300	.293
500	.840	2800	.419	6400	.291
550	.819	2900	.411	6500	.289
600	.798	3000	.406	6600	.288
650	.775	3100	.400	6700	.285
700	.760	3200	.390	6800	.285
750	.740	3300	.387	6900	.283
800	.728	3400	.383	7000	.281
850	.711	3500	.377	7100	.279
900	.695	3600	.371	7200	.277
950	.681	3700	.366	7300	.276
1000	.665	3800	.364	7400	.275
1050	.651	3900	.359	7500	.274
1100	.640	4000	.355	7600	.2725
1150	.630	4100	.352	7700	.271
1200	.619	4200	.347	7800	.270
2150	.609	4300	.344	7900	.269
1300	.599	4400	.340	8000	.269
1350	.589	4500	.336	8100	.266
1400	.580	4600	.333	8200	.265
1450	.570	4700	.329	8300	.264
1500	.561	4800	.329	8400	.263
1550	.553	4900	.325	8500	.262
1600	.545	5000	.322	8900	.258
1650	.538	5100	.319	9000	.256
1700	.530	5200	.316		
1750	.522	5300	.314		

DU Run-14

T = 55.0° C   λ = 350

Pd = 5.35mM H^+ = 1.0M   cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.761	2450	.702	4950	.5495
100	.990	2500	.699	5000	.546
150		2550	.693	5100	.542
200	1.15	2600	.690	5200	.539
250	1.19	2650	.684	5300	.535
300	1.19	2700	.680	5400	.531
350	1.17	2750	.675	5500	.529
400	1.15	2800	.670	5600	.525
450	1.14	2850	.667	5700	.521
500	1.11	2900	.661	5800	.5195
550	1.10	2950	.659	5900	.515
600	1.08	3000	.653	6000	.512
650	1.055	3050	.650	6100	.509
700	1.04	3100	.645	6200	.506
750	1.02	3150	.643	6300	.502
800	1.00	3200	.640	6400	.500
850	.990	3250	.637	6500	.499
900	.976	3300	.632	6600	.496
950	.960	3350	.629	6700	.492
1000	.942	3400	.625	6800	.490
1050	.930	3450	.621	6900	.488
1100	.920	3500	.620	7000	.486
1150	.904	3550	.617	7100	.484
1200	.894	3600	.612	7200	.482
1250	.880	3650	.610	7300	.480
1300	.870	3700	.609	7400	.479
1350	.860	3750	.604	7500	.476
1400	.850	3800	.601	7600	.473
1450	.8405	3850	.599	7700	.471
1500	.831	3900	.596	7800	.470
1550	.8205	3950	.595	7900	.469
1600	.814	4000	.591	8000	.468
1650	.806	4050	.590	8100	.465
1700	.795	4100	.586	8200	.462
1750	.790	4150	.583	8300	.462
1800	.782	4200	.580	8400	.461
1850	.774	4250	.578	8500	.460
1900	.770	4300	.575	8600	.458
1950	.760	4350	.574	8700	.457
2000	.751	4400	.571	8800	.455
2050	.748	4450	.570	8900	.454
2100*	.740	4600*	.563	9000*	.452

*Continued on following page.

Time	Abs.	Time	Abs.	Time	Abs.
2150	.735	4650	.561	9100	.451
2200	.730	4700	.560	9200	.450
2250	.721	4750	.557	9300	.449
2300	.7195	4800	.554	9400	.447
2350	.711	4850	.551	A_∞	
2400	.709	4900	.550		

DU Run-15

T = 55.0° C   λ = 323

Pd = 5.33mM H^+ = 1.0M   cell - 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.840	1450	.360	4200	.191
100	.860	1500	.353	4300	.187
150	.823	1550	.345	4400	.185
200	.781	1600	.339	4500	.184
250	.748	1650	.332	4600	.180
300	.710	1700	.325	4700	.179
350	.681	1750	.320	4800	.176
400	.653	1800	.316	4900	.175
450	.630	1900	.305	5000	.172
500	.606	2000	.296	5500	.165
550	.589	2100	.286	6000	.157
600	.569	2200	.279	6500	.151
650	.548	2300	.270	7000	.1455
700	.530	2400	.264	7500	.140
750	.516	2500	.256	8000	.137
800	.500	2600	.251	8500	.135
850	.483	2700	.245	9000	.1305
900	.471	2900	.235	9500	.1275
950	.459	3000	.230	10,000	.125
1000	.448	3100	.226	10,500	.124
1050	.436	3200	.221	11,000	.1225
1100	.425	3500	.211	11,500	.121
1150	.414	3600	.206	12,000	.120
1200	.404	3700	.204	12,500	.119
1250	.395	3800	.200	13,000	.119
1300	.385	3900	.198	13,500	.118
1350	.375	4000	.195	14,000	.117
1400	.368	4100	.193		

DU Run–16

$T = 62.8°\ C$ $\lambda = 325$

$Pd = 5.53mM$ $H^+ = 1.0mM$ cell = 1cm

All time in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.907	1600	.240	3300	.168
100	.819	1650	.2355	3400	.1665
150	.755	1700	.2315	3500	.165
200	.704	1750	.229	3600	.1645
250	.650	1800	.226	3700	.161
300	.610	1850	.2215	3800	.159
350	.569	1900	.2195	3900	.1575
400	.538	1950	.215	4000	.156
450	.504	2000	.2135	4100	.155
500	.475	2050	.210	4200	.154
550	.450	2100	.2075	4300	.153
600	.429	2150	.204	4400	.1515
650	.410	2200	.2025	4500	.1504
700	.390	2250	.2005	4600	.150
750	.374	2300	.199	4700	.1495
800	.359	2350	.196	4800	.1490
850	.344	2400	.195	4900	.1475
900	.334	2450	.193	5000	.1470
950	.323	2500	.191	5500	.1452
1000	.313	2550	.189	6000	.1425
1050	.306	2600	.187	6500	.142
1100	.2975	2650	.186	7000	.142
1150	.289	2700	.1835	7500	.141
1200	.282	2750	.182	8000	.1405
1250	.275	2800	.180	8500	.140
1300	.269	2850	.179	9000	.140
1350	.264	2900	.177	9500	.140
1400	.259	2950	.176	10,000	.140
1450	.2525	3000	.175	14,500	.1420
1500	.2480	3100	.173	16,500	.1430
1550	.244	3200	.1704	3 days	.144

DU Run-17

$T = 62.8°$ C $\lambda = 325$

Pd = 5.33mM $H^+ = 1.0$M   cell = 1cm

All time in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.97	1300	.282	3000	.186
100	.88	1350	.277	3100	.1835
150	.800	1400	.272	3200	.181
200	.730	1450	.268	3300	.178
250	.679	1500	.262	3400	.176
300	.630	1550	.257	3500	.175
350	.590	1600	.253	3600	.173
400	.555	1650	.248	3700	.171
450	.521	1700	.244	3800	.1705
500	.492	1750	.241	3900	.168
550	.465	1800	.238	4000	.1665
600	.445	1850	.234	4400	.1620
650	.427	1900	.231	4500	.1615
700	.408	1950	.227	4600	.160
750	.390	2000	.225	4700	.1595
800	.375	2050	.222	4800	.159
850	.362	2100	.220	4900	.158
900	.350	2200	.214	5000	.1574
950	.338	2300	.2095	5500	.155
1000	.329	2400	.206	6000	.154
1050	.320	2500	.202	6500	.153
1100	.3125	2600	.198	7000	.1520
1150	.303	2700	.194	8500	.1520
1200	.297	2800	.192	9000	.152
1250	.289	2900	.190	10,000	.1525

DU Run-18

T = 63.1° C λ = 350

Pd = 5.33mM H^+ = 1.0M   cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.892	1700	.570	3350	.448
100	1.13	1750	.561	3400	.446
150	1.15	1800	.558	3450	.441
200	1.11	1850	.550	3500	.440
250	1.075	1900	.546	3550	.439
300	1.03	1950	.540	3600	.439
350	.985	2000	.535	3650	.436
400	.950	2050	.530	3700	.435
450	.920	2100	.525	3750	.433
500	.890	2150	.520	3800	.432
550	.860	2200	.515	3850	.430
600	.838	2250	.510	3900	.430
650	.810	2300	.509	3950	.429
700	.791	2350	.502	4000	.428
750	.774	2400	.500	4100	.425
800	.755	2450	.495	4200	.424
850	.740	2500	.491	4300	.420
900	.721	2550	.489	4400	.420
950	.711	2600	.485	4500	.418
1000	.700	2650	.480	4600	.417
1050	.685	2700	.478	4700	.415
1100	.672	2750	.472	4800	.413
1150	.660	2800	.471	4900	.411
1200	.650	2850	.470	5000	.410
1250	.640	2900	.468	5500	.406
1300	.630	2950	.465	6000	.402
1350	.620	3000	.461	6500	.400
1400	.614	3050	.460	7000	.399
1450	.605	3100	.458	7500	.399
1500	.597	3150	.455	8000	.397
1550	.590	3200	.451	8500	.397
1600	.581	3250	.450		
1650	.577	3300	.449		

DU Run-19

T = 63.2° C　　λ = 350

Pd = 5.33mM　　H^+ = 1.0M　　cell = 1cm

All time in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.965	1150	.746	2600	.478
100	1.12	1200	.637	2700	.471
150	1.15	1250	.627	2800	.466
200	1.09	1300	.616	2900	.461
250	1.04	1350	.608	3000	.457
300	1.00	1400	.600	3100	.453
350	.96	1600	.571	3200	.450
400	.925	1700	.560	3250	.449
450	.895	1750	.551	3300	.447
500	.861	1800	.546	3400	.443
550	.840	1850	.539	3500	.440
600	.819	1900	.535	3600	.437
650	.795	1950	.530	3700	.434
700	.775	2000	.525	3800	.431
750	.755	2050	.520	3900	.430
800	.739	2100	.515	4000	.428
850	.720	2150	.511	4500	.419
900	.709	2200	.507	8000	.395
950	.692	2250	.501	9500	.395
1000	.680	2300	.498	10,000	.395
1050	.670	2400	.490	13,000	.395
1100	.656	2500	.484	25,000	.395

DU Run–20

T = 63.5° C λ = 400

Pd = 5.53mM H^+ = 1.0M   cell = 1cm

All times in seconds

Time	Abs.	Time	Abs.	Time	Abs.
50	.280	850	.550	2300	.540
100	.360	900	.551	2400	.539
150	.408	950	.551	2500	.538
200	.438	1000	.551	2600	.535
250	.460	1100	.552	2700	.535
300	.475	1200	.5525	2800	.535
350	.490	1300	.552	2900	.534
400	.503	1400	.551	3000	.533
450	.513	1500	.5505	3100	.532
500	.520	1600	.5495	3200	.532
550	.529	1700	.5495	3500	.529
600	.535	1800	.547	3600	.529
650	.537	1900	.544	4000	.529
700	.541	2000	.543	4500	.527
750	.545	2100	.541	5000	.527
800	.457	2200	.540	6500	.525

DK 1A Run–21

T = 38.8° C   λ = 330

Pd = 5.33mM H^+ = 1.0M   cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1	.476	58	.608	380	.240
2	.558	60	.599	390	.239
3	.630	70	.563	400	.235
4	.685	80	.532	420	.230
5	.730	90	.504	440	.223
6	.765	100	.479	460	.220
7	.788	110	.458	480	.217
8	.810	120	.438	500	.212
9	.823	130	.419	520	.209
10	.831	140	.403	540	.207
12	.839	150	.389	560	.202
14	.838	160	.375	580	.199
16	.830	170	.369	600	.193
18	.820	180	.352	620	.191
20	.808	190	.341	640	.189
22	.795	200	.332	660	.189
24	.780	210	.325	680	.189
26	.769	220	.316	700	.181
28	.754	230	.310	720	.180
30	.742	240	.301	740	.177
32	.732	250	.297	760	.176
34	.720	260	.290	780	.172
36	.710	270	.286	800	.171
38	.698	280	.280	820	.168
40	.688	290	.275	840	.165
42	.676	300	.270	860	.165
44	.665	310	.264	880	.163
46	.655	320	.261	900	.163
48	.649	330	.258	920	.159
50	.639	340	.254	940	.158
52	.630	350	.250	960	.156
54	.622	360	.248	980	.153
56	.613	370	.243	1000	.152

DK 1A Run-22

T = 38.8° C　　$\lambda = 310$

Pd = 5.33mM　　$H^+ = 1.0M$　　cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1	.724	16	.450	70	.191
2	.730	18	.421	75	.180
3	.733	20	.395	80	.171
4	.725	25	.350	85	.162
5	.708	30	.315	90	.158
6	.684	35	.290	95	.149
7	.660	40	.270	100	.141
8	.634	45	.256	110	.130
9	.608	50	.240	120	.120
10	.578	55	.226	130	.110
12	.540	60	.211	140	.102
14	.489	65	.200	150	.094
				160	.089

DK 1A Run-26

T = 40° C　　$\lambda = 396$

Pd = 5.33mM　　$H^+ = 1.0M$　　cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1	.050	13	.268	45	.405
2	.075	14	.280	50	.411
3	.100	15	.288	55	.416
4	.122	16	.294	60	.425
5	.146	17	.305	65	.430
6	.167	18	.311	70	.435
7	.189	19	.317	75	.439
8	.202	20	.321	80	.441
9	.220	25	.349	85	.445
10	.231	30	.369	90	.448
11	.245	35	.384	95	.450
12	.256	40	.394	100	.453

DK 1A Run-23

T = 38.8° C λ = 396

Pd = 5.33mM H^+ = 1.0M cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1	.052	16	.329	35	.417
2	.074	17	.336	40	.430
3	.102	18	.344	45	.441
4	.128	19	.354	50	.451
5	.153	20	.360	55	.458
6	.175	21	.365	60	.462
7	.199	22	.370	65	.468
8	.220	23	.378	70	.473
9	.238	24	.382	75	.478
10	.255	25	.386	80	.481
11	.270	26	.390	85	.482
12	.285	27	.395	90	.486
13	.298	28	.399	95	.488
14	.307	29	.400	100	.489
15	.319	30	.404	105	.492

DK 1A Run-24

$T = 38.8°\ C$ $\lambda = 400$

$Pd = 5.33mM$ $H^+ = 1.0M$ cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
2	.040	24	.246	70	.332
4	.075	26	.254	75	.339
6	.105	28	.260	80	.342
8	.130	30	.269	90	.349
10	.155	35	.282	100	.356
12	.174	40	.291	110	.360
14	.190	45	.302	120	.365
16	.203	50	.310	130	.369
18	.217	55	.317	140	.372
20	.228	60	.322		
22	.237	65	.329		

DK 1A Run-25

T = 40.0° C λ = 310

Pd = 5.33mM H^+ = 1.0M cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1	.724	45	.256	145	.099
2	.730	50	.240	150	.094
3	.732	55	.226	155	.091
4	.725	60	.212	160	.089
5	.708	65	.200	165	.085
6	.683	70	.191	170	.082
7	.660	75	.80	175	.079
8	.632	80	.171	180	.078
9	.606	85	.161	185	.076
10	.577	90	.157	190	.072
11	.550	95	.150	195	.069
12	.530	100	.141	200	.069
13	.509	105	.136	210	.066
14	.489	110	.130	220	.061
15	.469	115	.125	230	.058
20	.394	120	.120	240	.054
25	.344	125	.112	250	.052
30	.315	130	.110	260	.050
35	.290	135	.106	A_∞	.040
40	.270	140	.102		

DK 1A Run-27

T = 50.0° C λ = 328
Pd = 5.33mM H^+ = 1.0M   cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1	.615	13	.690	45	.390
2	.750	14	.672	50	.368
3	.824	15	.658	55	.346
4	.855	16	.640	60	.330
5	.860	17	.625	65	.314
6	.843	18	.610	70	.303
7	.822	19	.598	75	.289
8	.800	20	.595	80	.280
9	.775	25	.530	85	.271
10	.750	30	.482	90	.260
11	.730	35	.449	95	.251
12	.710	40	.418	100	.248
				A_∞	.120

DK 1A Run-28

T = 50.0° C λ = 396
Pd = 5.33mM H^+ = 1.0M   cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1	.074	10	.320	19	.370
2	.129	11	.330	20	.372
3	.169	12	.339	25	.385
4	.207	13	.342	30	.395
5	.240	14	.349	35	.400
6	.261	15	.354	40	.403
7	.286	16	.359	45	.406
8	.300	17	.362	50	.410
9	.312	18	.364	A_∞	.411

DK 1A Run–29

T = 58.5° C λ = 300

Pd = 5.33mM H^+ = 1.0M cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
.2	.823	7	.188	23	.084
.4	.735	7.5	.182	24	.0815
.6	.648	8	.175	25	.080
.8	.571	8.5	.168	26	.078
1.0	.515	9	.162	27	.075
1.2	.470	9.5	.158	28	.072
1.4	.435	10	.152	29	.071
1.6	.401	11	.144	30	.0695
1.8	.372	12	.135	35	.064
2	.350	13	.130	40	.060
2.5	.310	14	.120	45	.055
3	.280	15	.115	50	.052
3.5	.260	16	.110	55	.048
4	.245	17	.106	60	.0465
4.5	.232	18	.100	65	.0445
5	.221	19	.098	70	.0435
5.5	.212	20	.092	75	.043
6	.202	21	.090	80	.040
6.5	.195	22	.089		

DK 1A Run—30

T = 59.7° C λ = 360

Pd = 5.33mM H^+ = 1.0M cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1	.5930	11	.700	25	.555
2	.760	12	.684	30	.520
3	.811	13	.672	35	.492
4	.808	14	.660	40	.469
5	.800	15	.649	45	.449
6	.781	16	.636	50	.430
7	.764	17	.625	55	.412
8	.746	18	.612	60	.400
9	.730	19	.605	65	.389
10	.714	20	.596		

DK 1A Run-31

T = 59.7° C λ = 380
Pd = 5.33mM H^+ = 1.0M   cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
.5	.185	4.5	.490	8.5	.520
1.0	.292	5.0	.498	9.0	.521
1.5	.351	5.5	.502	9.5	.522
2.0	.410	6.0	.509	10.0	.524
2.5	.440	6.5	.510	11	.526
3.0	.460	7.0	.512	12	.528
3.5	.474	7.5	.516	13	.528
4.0	.483	8.0	.519	14	.528

DK 1A Run–32

T = 59.7° C λ = 400
Pd = 5.33mM H^+ = 1.M cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
.5	.084	5.5	.290	11	.339
1	.139	6	.298	12	.342
1.5	.181	6.5	.303	13	.348
2	.205	7	.308	14	.350
2.5	.226	7.5	.312	15	.354
3	.240	8	.317	16	.358
3.5	.256	8.5	.321	17	.359
4	.266	9	.325	18	.361
4.5	.276	9.5	.329	19	.361
5	.282	10	.332	20	.361

DK 1A Run–33

T = 59.8° C λ = 420
Pd = 5.33mM H^+ = 1.0M cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1	.2124	13	.2172	25	.2220
2	.2128	14	.2176	26	.2224
3	.2132	15	.2180	27	.2228
4	.2136	16	.2184	28	.2232
5	.2140	17	.2188	29	.2236
6	.2144	18	.2192	30	.2240
7	.2148	19	.2196	32	.2248
8	.2152	20	.2200	34	.2256
9	.2156	21	.2204	35	.2260
10	.2160	22	.2208	40	.2280
11	.2164	23	.2212	45	.2300

DK 1A Run-34

T = 66.4° C   λ = 325

Pd = 5.33mM H^+ = 1.0M   cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
1.0	.837	5.5	.413	22	.179
1.2	.801	6.0	.390	23	.175
1.4	.770	6.5	.370	24	.170
1.6	.740	7.0	.350	25	.166
1.8	.718	7.5	.338	26	.162
2.0	.684	8.0	.321	27	.160
2.2	.661	8.5	.312	28	.156
2.4	.639	9.0	.301	29	.154
2.6	.618	9.5	.290	30	.152
2.8	.596	10.0	.281	31	.150
3.0	.577	11.0	.265	32	.149
3.2	.560	12.0	.251	33	.146
3.4	.542	13.0	.240	34	.1445
3.6	.531	14.0	.231	35	.143
3.8	.513	15.0	.221	36	.141
4.0	.499	16.0	.213	37	.1405
4.2	.485	17.0	.206	38	.140
4.4	.475	18.0	.200	39	.1395
4.6	.460	19.0	.191	40	.1385
4.8	.446	20.1	.188		
5.0	.439	21.0	.181		

DK 1A Run–35

$T = 67.6°$ C
$\lambda = 310$
Pd = 5.33mM
$H^+ = 1.0M$
Cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
.2	.804	2.6	.301	8.0	.139
.4	.682	2.8	.290	8.5	.134
.6	.596	3.0	.275	9.0	.129
.8	.518	3.5	.250	9.5	.122
1.0	.460	4.0	.230	10.0	.120
1.2	.427	4.5	.212	11.0	.112
1.4	.398	5.0	.200	12.0	.105
1.6	.380	5.5	.184	13.0	.100
1.8	.359	6.0	.172	14.0	.095
2.0	.339	6.5	.162	15.0	.092
2.2	.323	7.0	.151	16.0	.089
2.4	.312	7.5	.145	17.0	.087
				A_∞	.059

DK 1A Run-36

T = 70° C λ = 310

Pd = 5.33mM H^+ = 1.0M cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
.1	.718	1.3	.500	4.5	.175
.2	.717	1.4	.475	5.0	.159
.3	.714	1.5	.450	5.5	.145
.4	.705	1.6	.428	6.0	.132
.5	.696	1.7	.409	6.5	.122
.6	.679	1.8	.390	7.0	.113
.7	.660	1.9	.371	7.5	.105
.8	.639	2.0	.350	8.0	.098
.9	.615	2.5	.290	8.5	.091
1.0	.580	3.0	.249	9.0	.085
1.1	.548	3.5	.220	9.5	.080
1.2	.525	4.0	.196	10.0	.076

DK 1A Run–37

T = 70.0° C　　λ = 320

Pd = 5.33mM　　H^+ = 1.0M　　cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
.5	.740	6.5	.240	15	.138
1.0	.700	7.0	.225	16	.131
1.5	.606	7.5	.215	17	.129
2.0	.526	8.0	.205	18	.123
2.5	.467	8.5	.198	19	.120
3.0	.411	9.0	.190	20	.117
3.5	.369	9.5	.185	21	.114
4.0	.340	10.0	.179	22	.111
4.5	.314	11.0	.166	23	.109
5.0	.290	12.0	.157	24	.108
5.5	.271	13.0	.150	25	.105
6.0	.255	14.0	.142	A_∞	.098

DK 1A Run–38

T = 70.0° C　　λ = 396

Pd = 5.33mM　　H^+ = 1.0M　　cell = 1cm

All times in minutes

Time	Abs.	Time	Abs.	Time	Abs.
.1	.120	1.3	.329	2.5	.417
.2	.140	1.4	.342	2.6	.422
.3	.168	1.5	.350	2.7	.428
.4	.173	1.6	.359	2.8	.431
.5	.207	1.7	.367	2.9	.435
.6	.224	1.8	.376	3.0	.439
.7	.244	1.9	.383	3.5	.452
.8	.261	2.0	.389	4.0	.461
.9	.280	2.1	.400	4.5	.471
1.0	.295	2.2	.405	5.0	.479
1.1	.308	2.3	.407	5.5	.481
1.2	.318	2.4	.415		

LIST OF REFERENCES

1. Basolo, F. and Pearson, R. G., Mechanisms of Inorganic Reactions, 2d ed., John Wiley and Sons, Inc., 1967, p. 351-387.

2. Block, B. D., "Sterochemistry of Coordination Number Four," Chemistry of the Coordination Compounds, American Chemical Society Monograph Series, No. 131, Reinhold Publishing Corporation, 1956, p. 354-364.

3. Langford, C. H. and Gray, H. B., Ligand Substitution Processes, W. A. Benjamin Inc., 1965.

4. Cattalini, L. "Intimate Mechanism of Replacements in d^8 Square Planar Complexes," Progress in Inorganic Chemistry, 13, Interscience Publishers, 1970.

5. Pearson, R. G., and Johnson, D. A., J. Am. Chem. Soc., 86, 3983, 1964.

6. Basolo, F., Gray, H. B., and Pearson, R. G., J. Am. Chem. Soc., 82, 4200, 1960.

7. Mellor, J. W., A Comprehensive Treatise on Inorganic and and Theoretical Chemistry, v. XV, Longmans, Green and Co., p. 667.

8. Reinhardt, R. A., and Sparks, R. K., Inorg. Chem., 6, 2170, 1967.

9. Coe, J. S., Hussain, M.D., and Malik, A. A., Inorg. Chim. Acta, 2, 65, 1968.

10. Rasmussen, L., and Jørgensen, C. K., Acta. Chem. Scand., 22, 2315, 1968.

11. Reinhardt, R. A., Brenner, N. L., and Sparks, R. K., Inorg. Chem., 6, 254, 1967.

12. Skoog, D. A., and West, D. M., Fundamentals of Analytical Chemistry, Hold, Rinehart and Winston, 1966.

13. Treadwell, F. D. and Hall, W. T., Analytical Chemistry, v. II, John Wiley and Sons, Inc., 1942, p. 140.

14. Frost, A. A. and Pearson, R. G., Kinetics and Mechanism 2d ed., John Wiley and Sons, Inc., 1961, p. 166ff and 49-50.

15. Ashley, K. R., and Hamm, R. E., *Inorg. Chem.*, *5*, 1645, 1966.

16. Nonlinear Least Squares Program and Plotting Routine Program were Designed by Dr. R. A. Reinhardt.

17. Reinhardt, R. A., and Coe, J. S., *Inorg. Chim. Acta.*, *3*, 438, 1969.

18. Reinhardt, R. A., and Kinney, G. F., United States Naval Postgraduate School Research Paper, No. 15, *Operational Analogues for Kinetic Studies*, November 1957.

19. Aprile, F., Martin, D. S., Jr., *Inorg. Chem.*, *1*, 551, 1962.

20. Coe, J. S., and Lyons, J. R., *Inorg. Chem.*, *9*, 1775, 1970.

21. Poë, A. J., and Vaughan, D. H., *Inorg. Chim. Acta.*, *1*, 225, 1967.

22. Tucker, M. A., Colvin, C. B. and Martin, D. S., Jr., *Inorg. Chem.*, *3*, 1373, 1964.

23. Reinhardt, R. A. and Monk, W. W., *Inorg. Chem.*, *9*, 2026, 1970.

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Naval Postgraduate School Monterey, California 93940	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP

3. REPORT TITLE

THE KINETICS OF SUCCESSIVE AQUATION REACTIONS
OF
TETRAAMMINEPALLADIUM(II) ION

4. DESCRIPTIVE NOTES *(Type of report and, inclusive dates)*

Master's Thesis; June 1971

5. AUTHOR(S) *(First name, middle initial, last name)*

William Jennings DeBerry, Jr.
Ensign, United States Naval Reserve

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
June 1971	92	23

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	

10. DISTRIBUTION STATEMENT

Approved for public release; distribution unlimited.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY Naval Postgraduate School Monterey, California 93940

13. ABSTRACT

Solutions of tetraamminepalladium(II) perchlorate were made up and analyzed.

The following acid hydrolysis reactions of tetraamminepalladium (II) ion were studied by ultraviolet spectroscopy. First order rate constants were evaluated for each step of the reaction series at various temperatures. Activation parameters were determined.

$$\mathrm{Pd(NH_3)_4^{2+}} \xrightarrow{k_1} \mathrm{Pd(NH_3)_3OH_2^{2+}} \xrightarrow{k_2} \underline{cis}\text{-}\mathrm{Pd(NH_3)_2(OH_2)_2^{2+}} \xrightarrow{k_3}$$

$$\mathrm{Pd(OH_2)_3NH_3^{2+}} \xrightarrow{k_4} \mathrm{Pd(OH_2)_4^{2+}}$$

At $T = 25°\mathrm{C}$, $\mu = 1\mathrm{M}$: $k_1 = 11.0\times10^{-4}\ \mathrm{sec}^{-1}$, $k_2 = 5.6\times10^{-4}\ \mathrm{sec}^{-1}$, $k_3 = 0.58\times10^{-4}\ \mathrm{sec}^{-1}$, $k_4 = 0.10\times 10^{-4}$

Mechanisms for the consecutive reactions are proposed, and cis and trans effects are discussed.

PRECEDING PAGE BLANK

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Tetraamminepalladium(II) ion						
Tetraaquopalladium(II) ion						