MECHANISTIC STUDIES OF REACTIONS OF SOME PLATINUM METAL COMPLEXES

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by

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ABSTRACT

The kinetics of the reactions of some anionic and cationic halogenoplatinate(IV) complexes with halide ions have been studied by spectrophotometric methods; the majority of the reactions were sufficiently fast to be followed using the stopped-flow technique. The reactions of trans- $Pt(CN)_4X_2^{2-}$ and trans- $PtOx_2X_2^{2-}$ (X = Cl, Br) with iodide are first order in both iodide and complex concentration and the mechanism probably involves a rate determining reduction of the Pt(IV) complex to Pt(II) followed by a fast reoxidation. The rates of the reactions appear to be related, in the majority of cases, to the thermodynamic ease of reduction, this indicates that both Pt-X bond breaking and X-I bond making play an important part in determining the rates of reaction. Several equilibrium constants for reduction of these complexes by iodide, bromide and chloride, as well as estimates of values for the replacement of chloride and bromide by iodide in trans- $Pt(CN)_4X_2^{2-}$, have been obtained.

A study of the reaction of trans- Pt $en_2Cl_2^{2+}$ (en = ethylenediamine) with iodide to form trans- Pt $en_2I_2^{2+}$ shows that the rate is first order in [Pt(II)] and presumably the

complex reacts by the bridged redox mechanism. However, the complexes trans- Pt tet enX_2^{2+} (X = Cl, Br; tet = N, N, N^1, N^1, tetramethylethylenediamine) are reduced by iodide to I_3^- and Pt(II) and the mechanism is believed to be similar to that found in the anionic complexes. The reaction of trans- Pt tet en Cl_2^{2+} with bromide to form trans- Pt tet en Br_2^{2+} is found to follow a two term rate law with one of the terms being independent of [Pt(II)]. This [Pt(II)] independent term may represent a redox path similar to that found in the anionic complexes.

The kinetics of the reactions of hydrochloric acid with cis- and trans- Pd $(NH_3)_2Cl_2$, trans- $Pd(Et_2NH)_2Cl_2$, $Pd(Et_4dien)Cl^+$, $Pd(dien)Cl^+$ and Pd en Cl_2 (Et_4dien = 1, 1, 7, 7, tetra-ethyldiethylenetriamine, dien = diethylenetriamine) have been followed spectrophotometrically. The kinetic behaviour of the non-chelated complexes is typical of planar d^8 complexes with a two term rate law, $k_{obs} = k_1 + k_2[Cl^-]$, being observed. The hydrogen ions are necessary only to neutralise the released ammonia or amine. However, even the removal of the last coordinated nitrogen atom in the chelated complexes shows a dependence on $[H^+]$ and sometimes a greater

than first order dependence on [Cl^-] is observed. The mechanism proposed for these chelated complexes involves the formation of a five coordinate reactive intermediate of the type [$PdCl_4NH_2C_2H_4NH_3$]$^-$ which is stabilised by intramolecular hydrogen bonding and reacts to form $PdCl_4^{2-}$ only after further attack by a hydrogen ion. The complex dependence on [Cl^-] probably indicates that this attack by a hydrogen ion can be assisted in some way by the presence of an additional chloride ion. The kinetic parameters are discussed in terms of relative kinetic *cis*- and *trans*- effects.

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CHAPTER I

The Mechanism of Interchange Reactions of Halogenoplatinate(IV) Complexes

PART I

The Reactions of <u>Trans</u>- $Pt(CN)_4X_2^{2-}$ and <u>Trans</u>- $PtOx_2X_2^{2-}$ with Iodide Ion

Introduction

Compounds of Pt(IV) are invariably octahedral and it forms a vast number of stable and kinetically inert complexes. It would be expected that Pt(IV) with its $(t_{2g})^6$ configuration would resemble such isoelectronic ions as Co(III) and Rh(III) in its inertness to nucleophilic attack. In fact the small size and larger positive charge of the Pt(IV) would tend to increase the crystal field splitting and bond strength by attracting the ligands closer to the metal suggesting that Pt(IV) may be more inert to nucleophilic substitution than Rh(III) etc. A large amount of data on the rates of substitution in Pt(IV) complexes seem to refute this suggestion; indeed a surprising degree of lability has been observed which can be ascribed to the ability of the reaction to proceed by a path alternative to the usual SN mechanism.

Studies(1),(2) on the cationic complexes of the type $[PtA_4X_2]^{2+}$, (A = NH_3 or $\frac{1}{2}$ en, and x = Br, Cl, and OH) and their substitution reactions with halide ions have been explained in terms of Pt(II) catalysis. The general mechanism is outlined below, (the four equatorial ligands, NH_3 or $\frac{1}{2}$ en have been omitted for clarity).

$$\mathrm{Pt(II)} + \mathrm{Y}^- \rightleftharpoons \mathrm{Pt(II)\text{-}Y} \qquad \ldots \quad 1$$

$$\mathrm{Y\text{-}Pt(II)} + \mathrm{X\text{-}Pt(IV)} - \mathrm{X} \longrightarrow \mathrm{Y\text{-}Pt(IV)\text{-}X} + \mathrm{Pt(II)\text{-}X} \quad .. \; 2$$

followed by

$$\mathrm{Y\text{-}Pt(II)} + \mathrm{Y\text{-}Pt(IV)} - \mathrm{X} \longrightarrow \mathrm{Y\text{-}Pt(IV)\text{-}Y} + \mathrm{Pt(II)\text{-}X} \quad .. \; 3$$

It was found that in the reaction

$$\underline{\text{trans}}\text{- } \mathrm{Pten_2X_2}^{2+} + \mathrm{Pt(l\text{-}pn)_2}^{2+} \longrightarrow \underline{\text{trans}}\text{- } \mathrm{Pt(l\text{-}pn)_2X_2}^{2+} + \mathrm{Pten_2}^{2+}$$

(l-pn = l-propylenediamine)

the efficiency of the bridging group, X, in order of decreasing rate was Br > Cl > OH. Similarly, in the reaction

$$\mathrm{Pten_2}^{2+} + \underline{\text{trans}}\text{- } \mathrm{Pten_2Cl_2}^{2+} + 2\mathrm{Y}^- \longrightarrow \underline{\text{trans}}\text{- } \mathrm{Pten_2Y_2}^{2+} + \mathrm{Pten_2}^{2+} + 2\mathrm{Cl}^-$$

the efficiency of the non bridging group, Y, was such that the rate was rapid with such ligands as Br and Cl but very slow with ligands such as OH and NO_3.

This bridged redox mechanism was also found in the reactions of(3) $PtCl_6^{2-}$ with Br^- and(4) $PtBr_6^{2-}$ with Cl^- where the rates were found to be inhibited by oxidising agents and accelerated by reducing agents and Pt(II).

The base hydrolysis of $[PtA_5Cl]^{3+}$ to give $[PtA_5OH]^{2+}$ has been studied(5) and it was suggested that the predominant species in the basic solutions was the amido complex which was involved in the hydrolysis reaction and it may have been the only reactive Pt(IV) species. It was not possible to differentiate between the possible mechanisms, SN_{1CB} or SN_{2CB}, but, the reaction did involve the conjugate base.

Although the exchange of $PtCl_6^{2-}$ with radiochloride was very slow in the dark, fast exchange occurs in the light(6). Oxidising agents such as $IrCl_6^{2-}$ and Cl_2 were found to inhibit the reaction in the light but a variety of reducing agents including $SnCl_2$ and $Na_2S_2O_3$ were found to accelerate the reaction. It was postulated that the exchange was a light catalysed chain reaction involving the formation of a labile $Pt(III)Cl_5^{2-}$ intermediate.

The photochemical exchange of(7) $PtBr_6^{2-}$ with Br^- was attributed to a similar chain mechanism involving a Pt(III) intermediate, the exact mechanism being:

$$PtBr_6^{2-} \underset{k_2}{\overset{\phi}{\rightleftharpoons}} PtBr_5^{2-} + Br \quad .... \quad 4$$

$$PtBr_6^{2-} + PtBr_5^{2-} \overset{k_3}{\rightleftharpoons} PtBr_5^{2-} + PtBr_6^{2-} \qquad ..... \quad 5$$

Both $PtBr_5^{2-}$ and Br can exchange rapidly with free Br^-. This leads to the expression for the quantum yield for exchange, ϕ , given below

$$\phi = \phi_1 + \frac{K\ [PtBr_6^{2-}]}{I^{\frac{1}{2}}}$$

where ϕ_1 is the quantum yield for exchange through reverse of 4, $K = k_3(\phi_1/k_2)^{\frac{1}{2}}$ and I is the light intensity. Quantum yields of up to 500 have been reported. As $\phi_1 \leqslant 1$ then, $\phi \propto [PtBr_6^{2-}]$ as was found experimentally.

PtF_6^{2-} reacts with iodide(8) ion to give PtI_6^{2-} only in the presence of H^+. The rate is not dependent on $[I^-]$ but is dependent on $[PtF_6^{2-}]$ and $[H^+]$. It is probable that the breaking of a Pt-F bond may be assisted by the proton hydrogen -bonding to the fluorine ion.

A radiotracer and spectrophotometric study of the reactions of(9) $PtCl_6^{2-}$ and(10) $PtBr_6^{2-}$ with iodide showed that in the presence of certain inhibitors of the Pt(III) mechanism, the rates of substitution were first order in complex and iodide ion concentration and unaffected by Pt(II). The $PtBr_6^{2-}$ reacted in three distinct stages to form PtI_6^{2-}, each stage corresponding to the replacement of a pair of trans bromide ions. The $PtCl_6^{2-}$ has also been shown(11) to react in three distinct stages, but in this case, it is not yet clear whether the three stages correspond to the successive replacement of the three pairs of trans chloride ions. The mechanism involved a rate determining reduction of the complex to Pt(II) by what is effectively the transfer of X^+ (X = Cl or Br) to the iodide, re-oxidation to Pt(IV) then follows with the iodine atom of the IX appearing to end up in the product complex.

In order to obtain a greater insight into the special factors operating in this redox mechanism an obvious extension was to study the halide interchange reactions of complexes of the type <u>trans</u>-$[PtA_4X_2]^{n-}$ which contain only one pair of trans halides. In this work a study has been made of the halide interchange reactions of the anionic complexes <u>trans</u>-$Pt(CN)_4X_2^{2-}$ and <u>trans</u>-$PtOx_2X_2^{2-}$ ($Ox^{2-} = C_2O_4^{2-}$). Also, where possible a study of the redox equilibria has been made to see whether any correlation exists between the rates and the thermodynamic ease of reduction.

Experimental

Materials

Potassium tetrachloroplatinate (II), sodium hexachloroplatinate (IV), sodium tetrabromoplatinate (II) and sodium hexachloroiridate (IV) were obtained from Johnson, Matthey and Co. Ltd. and were used as received. Standard solutions of sodium perchlorate, sodium chloride, sodium bromide and sodium iodide were made up by weighing out the dry finely powdered G.P.R. salts into graduated flasks, and dissolving them in distilled water.

Instruments

U.V. and visible spectra were measured with a Perkin Elmer 137 U.V. recording spectrophotometer, and absorbances at a fixed wavelength were measured with a Unicam S.P.500 spectrophotometer. The spectra were calibrated with holmium and didymium glass. The Raman spectra were measured with a Carey Laser Raman spectrophotometer model 81.

The rates of the slower reactions were followed in a similar manner to that used in the study of the reactions of the chloro aminepalladium (II) complexes with hydrochloric acid. However, the majority of the reactions studied were sufficiently fast for the stopped-flow technique to be necessary. The apparatus was a slightly modified version of a design by Professor Sturtevant(12) and was capable of measuring transmission changes for monochromatic light, from a tungsten or deuterium lamp source and a Hilger Watts monochromater D 246, between 230 and 750 mμ. A R.C.A. IP 28 photomultiplier detected the light transmitted through the reacting solutions and the resulting changes were displayed on the screen of a Solarton CD 1400 oscilloscope and photographed with a Shackman AC/2/25 35mm. oscilloscope camera. So that the signal would be displayed on the whole of the screen, calibration filters, consisting of a 2mm. silica cell in a metal housing, were used. With distilled water in the observation cell and in the silica cell, the bottom line of the screen was set. The top line was set using as a calibration liquid in the silica cell either the product solution, if a decrease in transmission was being observed, or one of the reactants, if an increase in transmission was being observed. Also displayed on the screen of the oscilloscope was a sinusoidal time calibration trace obtained from the standard mains frequency of 50 c.p.s. The developed negatives were projected on to a sheet of graph paper measuring 16 x 22.5 cms. from which measurements of transmission against time could be taken. Water, which could be thermostatted at between 15 and 50°C, was circulated around a copper jacket in which were enclosed the two syringes (2 ml.) containing the reactants, the Teflon mixing chamber and the 2mm. path length silica reaction cell. By the time the reacting mixture reaches the observation cell the efficiency of mixing is better than 98% and the fastest reactions capable of being studied with this apparatus would have a half time of ca 5 m.secs. A more detailed description of the stopped-flow assembly used in these experiments can be found in D.J. Hewkin, Ph.D. Thesis London 1967.

Each value of the quoted rate constants, when measured using the stopped-flow technique, was the average of not less than three measurements. In all the experiments the difference of the individual measurements from the average, or quoted rate constant, was never greater than 9% and was usually a lot smaller than this.

A brief study was made of a previously studied reaction to test the functioning of the apparatus. The reaction studied was the decomposition of carbonic acid in water following the method described by Dalziel(13), table (1). Three runs were carried out at each of three temperatures and the rate constants and activation parameters compared with those of other workers as shown in table (2).

Table 1

Carbonic acid decomposition

T(°C)	Individual measurements of rate constant ($sec.^{-1}$)	Average rate constant ($sec.^{-1}$)
18.4	11.6	
	11.9	12.0
	12.4	
24.7	21.6	
	20.9	21.3
	21.3	
35.0	53.4	
	52.7	52.6
	51.8	

From which $Ea = 16.0$ kcal/mole.

$k_{18^oC} = 11.5\ sec.^{-1}$

Table (2)

Rate parameters for carbonic acid decomposition

Worker	$^{a}k_{18_O}$(sec.$^{-1}$)	E_a(kcal./mole)	T.range	Technique
This work	11.5	16.0	18-35	Stopped-Flow
Scheurer(b)	11.8	16.1	23-27	" "
Moore(c)	11.5	15.9	23-30	" "
Dalziel(d)	12.3	16.9	19-23	Continuous Flow
Brinkman(e)	12.9	-	-	-

(a) Calculated from the activation energy where necessary

(b) J.Phys.Chem., 62, 809 (1958)

(c) Ph.D. Thesis, Northwestern University, 1964.

(d) Reference 13.

(e) Phil.Trans.Roy.Soc., A 232, 65 (1933)

The trans- $Pt(CN)_4X_2^{2-}-I^-$ and trans- $PtOx_2X_2^{2-}-I^-$ Reactions.

Preparation of complexes.

Potassium tetracyanoplatinate(II) was prepared by adding a slight excess of G.P.R. potassium cyanide to an aqueous solution of potassium tetrachloroplatinate(II). The solution was concentrated by boiling, cooled and the resulting precipitate filtered and dried in an oven at 140°C. This procedure gave the yellow anhydrous salt.

Potassium trans-dichlorotetracyanoplatinate(IV) dihydrate(14) was prepared by oxidising a concentrated hydrochloric acid solution of potassium tetracyanoplatinate(II) with hydrogen peroxide or chlorine. On concentrating and cooling a yellow-white complex was obtained which after two recrystallisations from dilute hydrochloric acid gave white crystals. If the oxidation was incomplete the precipitate obtained was copper brown. This compound corresponds to the composition(15) $K_2PtCl_2(CN)_45K_2Pt(CN)_4nH_2O$ which has been shown to be polymeric, consisting of chains of planar $Pt(CN)_4^{2-}$ with coplanar arrangement, the chloride ions being present in cavities.

Potassium trans- dibromotetracyanoplatinate(IV) dihydrate(14) was prepared by oxidising a hydrobromic acid solution of $K_2Pt(CN)_4$ with bromine. On concentrating and cooling bright yellow crystals of the complex were obtained. These were recrystallised from dilute hydrobromic acid.

Potassium trans- diiodotetracyanoplatinate(IV) was not isolated as a pure solid because partial decomposition occurred on concentrating the solution. It was, however, possible to prepare solutions of the complex quite easily by adding to an aqueous solution of $K_2Pt(CN)_4$ a solution containing an equimolar amount of both iodine and potassium iodide.

Solutions of trans- $Pt(CN)_4Cl_2^{2-}$ and trans- $Pt(CN)_4Br_2^{2-}$ of about 10^{-4} molarity were stable over a period of days as judged by their unchanging absorption spectra. Solutions of trans- $Pt(CN)_4I_2^{2-}$, however, were stable only in the presence of sufficient tetracyanoplatinate(II) and iodide ion to prevent reduction and hydrolysis.

Potassium bis-oxalatoplatinate(II) dihydrate(16) was prepared by adding a two fold excess of AnalaR potassium oxalate to an aqueous solution of potassium chloroplatinate(II). The solution was heated on a steam bath for about half an hour, cooled and the resulting yellow precipitate of the complex filtered. The precipitate was recrystallised from water and dried in the air.

Potassium trans- dichlorobisoxalatoplatinate(IV) monohydrate was prepared by the method of Werner and Grebe(17) in which chlorine was passed into a warm aqueous solution of potassium bisoxalatoplatinate(II). The original yellow solution goes dark, then red and finally bright yellow. On concentrating and cooling in an atmosphere of chlorine, bright yellow crystals of the complex were obtained. The crystals were filtered and dried in the air.

Potassium trans- dibromobisoxalatoplatinate(IV) has not been reported previously and was prepared by oxidising a warm aqueous solution of potassium bisoxalatoplatinate(II) with bromine. Bromine vapour was continually passed into the reaction vessel while the solution was concentrated and cooled. The dark red crystals of the complex were filtered and dried in the air.

Aqueous solutions of potassium trans-diiodobisoxalatoplatinate(IV) were prepared by adding to potassium bisoxalatoplatinate(II) a solution containing an equimolar amount of both iodine and potassium iodide. Decomposition of the solution occurred on concentrating with the result that the pure solid diiodo complex was not isolated.

Solutions of trans- $PtOx_2I_2^{2-}$ decomposed over a period of half an hour with formation of a black precipitate. There was no spectroscopic evidence for the formation of PtI_6^{2-} in these solutions. The solids $K_2PtOx_2Cl_2H_2O$ and $K_2PtOx_2Br_2$ were stable in the air for short periods but darkened in colour after a few days; they were, however, stable indefinitely in an atmosphere of the corresponding halogen. Aqueous solutions of the chloro and bromo complexes of 10^{-5} - 10^{-4} molarity were stable over a period of a few hours as judged by their unchanging absorption spectra; their spectra were also unchanged by the addition of free halide ions.

The two chloro and the two bromo complexes were analysed spectrophotometrically by reduction with an excess of sodium iodide, the triiodide formed being estimated spectrophotometrically at 353 mμ. At this wavelength the triiodide spectrum has a maximum(18) with an extinction coefficient of $26{\cdot}4\ 10^3 l.mole^{-1}.cm^{-1}$. Weights of complexes were such that absorbances of ca. 0.4 were obtained in 1 mm. or 1 cm. cells. This method was also used to determine the concentrations of the solutions of trans- $Pt(CN)_4I_2^{2-}$.

The analyses together with details of the absorption spectra in the near ultraviolet, and of the Raman spectra of aqueous solutions of the complexes, are given in tables (3) and (4). No peak was observed in the Raman spectrum of trans-$PtOx_2I_2^{2-}$, this may have been due to the opacity of the solution or decomposition by the laser beam.

The reaction of iodide with trans- $Pt(CN)_4Cl_2^{2-}$

At low iodide concentrations trans-$Pt(CN)_4I_2^{2-}$ was formed which has an absorption maximum at 405 mμ. The rates of formation of this complex were followed by observing the decrease in transmittance of the reactant solutions at this wavelength. The equilibrium constant for replacement of chloride by iodide was large enough for the reaction to go to completion even in the presence of 0.07 M. sodium chloride which was used to maintain a constant ionic strength.

It was found that trans- $Pt(CN)_4I_2^{2-}$ was easily reduced by free iodide with the result that the range of iodide ion concentration, even in the presence of an excess of $Pt(CN)_4^{2-}$, was severely restricted. However, the pseudo first order rate plots were usually linear for one to two half lives and where they were curved the initial slopes were taken as a measure

Table 3

Compound	Calculated % Pt	Found
$K_2Pt(CN)_4Cl_22H_2O$	40.3	41.0
$K_2Pt(CN)_4Br_22H_2O$	34.0	34.9

Complex	Electronic Spectra				
	λ max. (mμ)			E (l.mole.$^{-1}$cm.$^{-1}$)	
	(a)	(b)	(c)	(a)	(c)
trans- $Pt(CN)_4Cl_2^{2-}$	284	286	-	522	-
	330(Sh)	330(Sh)	-	~220	-
trans- $Pt(CN)_4Br_2^{2-}$	342	344	-	1,200	-
trans- $Pt(CN)_4I_2^{2-}$	405	-	-	5,600	-
$Pt(CN)_4^{2-}$	280	-	280	1,600	1,590

.../contd.

Table (3) contd.

Complex	Raman Spectra		
	V_3 (cm.$^{-1}$)		Force constant(m.dynes/A^o)
	(a)	(d)	(d)
<u>trans</u>- $Pt(CN)_4Cl_2^{2-}$	333	330	2.09
<u>trans</u>- $Pt(CN)_4Br_2^{2-}$	203	(200)	1.73
<u>trans</u>- $Pt(CN)_4I_2^{2-}$	142	(141)	1.37

(a) This work

(b) I.I. Chernyaev, A.V. Babkov and N.N. Zheligovskaya, J. Inorg.Chem. (U.S.S.R.), 8, 1279 (1963).

(c) H.B. Gray and C.J. Ballhausen, J.Amer.Chem.Soc., 85, 260, (1963).

(d) L.I. Jones and J.M. Smith, Inorg.Chem., 4, 1677 (1965); the values in parentheses were obtained indirectly from infrared studies.

Table 4

Compound	Calculated % Pt	Found
$K_2PtOx_2Cl_2H_2O$	36.2	37.1
$K_2PtOx_2Br_2$	32.0	32.2

Complex	Electronic Spectra		Raman Spectra
	λ max.(mμ)	E(1.mole.$^{-1}$cm.$^{-1}$)	V_3(cm.$^{-1}$)
<u>trans</u>- $PtOx_2Cl_2{}^{2-}$	350(sh) 450(sh)	~300 ~ 35	336
<u>trans</u>- $PtOx_2Br_2{}^{2-}$	267 320(sh)	27,000 2,900	204
<u>trans</u>- $PtOx_2I_2{}^{2-}$	312	~22,000	
$PtOx_2{}^{2-}$	286	3,900	

of the rate constant. The results are given in table (5). An analysis of the data showed that the standard deviation of the quoted values was about ±6%. The activation enthalpies and entropies were obtained graphically and the limits of uncertainty assigned to them were approximate standard deviations, based on the uncertainty of the rate constants.

In order to follow the reaction in such a way that pseudo first order conditions were more closely obtained, the range of iodide concentrations was extended. Under these conditions extensive reduction of the product trans- $Pt(CN)_4I_2^{2-}$ occurred. The rate of reduction of $1{\cdot}5.10^{-4}$.M. diiodo complex by 5.10^{-2}.M. iodide was found to be too fast to measure with the stopped-flow apparatus. The reactions of the chloro complex were followed by observing the decrease in transmittance at 353 mμ accompanying the formation of I_3^- , one of the reduction products which has an absorption maximum at this wavelength. A complication of this procedure was that reduction to I_3^- was not complete resulting in a variation of the product which is reduced throughout the reaction.

$$\text{If} \qquad K_r = \frac{[Pt(CN)_4^{2-}][I_3^-]}{[Pt(CN)_4I_2^{2-}][I^-]}$$

Table (5)

Rate constants for the reaction

<u>trans</u>- $Pt(CN)_4Cl_2^{2-} \xrightarrow{I^-}$ <u>trans</u>- $Pt(CN)_4I_2^{2-}$

$[Pt^{IV}] = 5.0 \times 10^{-4}$M. $\mu = 0.07$ M.

T(°C)	$10^3[Pt^{II}]$M	$10^3[I^-]$M	$k_{obs}(sec.^{-1})$	$k_2(l.mole.^{-1}sec.^{-1})$
22.0	3.4	3.65	0.58	159
22.0	3.4	2.42	0.40	165
22.0	0.8	2.42	0.45	186
22.0	1.0	3.65	0.60	164
22.0	1.0	3.65	0.62(A)	170
30.2	0.8	2.42	0.61	252
38.9	0.8	2.42	0.85	351
47.6	0.8	2.42	1.10	455
23.4	1.0	4.2	4.01(B)	954
23.4	1.0	4.2	3.85(C)	917

(A) $[IrCl_6^{2-}] = 7.10^{-5}$M.

(B) $[Pt^{IV}] = 6.9\ 10^{-4}$M.; $\mu = 1.0$ M. with $NaClO_4$

(C) $[Pt^{IV}] = 6.9\ 10^{-4}$M.; $\mu = 1.0$ M. with NaCl.

$\Delta H^{\ddagger} = 6.0 \pm 0.3$ kcal./mole

$\Delta S^{\ddagger} = -28$ cal/mole/deg.

then $$[\mathrm{Pt(CN)_4Cl_2}^{2-}] = [\mathrm{Pt}]_t - \left\{[\mathrm{Pt(CN)_4I_2}^{2-}] + [\mathrm{Pt(CN)_4}^{2-}]\right\}$$

where $[\mathrm{Pt}]_t$ = total concentration of platinum present.

thus $$[\mathrm{Pt(CN)_4Cl_2}^{2-}] = [\mathrm{Pt}]_t - [\mathrm{Pt(CN)_4I_2}^{2-}]\left\{1 + \frac{K_r[\mathrm{I}^-]}{[\mathrm{I_3}^-]}\right\}$$

$$= [\mathrm{Pt}]_t - [\mathrm{Pt(CN)_4}^{2-}]\left\{1 + \frac{[\mathrm{I_3}^-]}{K_r[\mathrm{I}^-]}\right\}$$

$$= [\mathrm{Pt}]_t - [\mathrm{I_3}^-]\left\{1 + \frac{[\mathrm{I_3}^-]}{K_r[\mathrm{I}^-]}\right\}$$

It has been assumed that $[\mathrm{I_3}^-] \gg [\mathrm{I_2}]$ i.e. the equilibrium of $\mathrm{I}^- + \mathrm{I_2} \rightleftharpoons \mathrm{I_3}^-$ lies to the right which is justified by the large excess of iodide ion. Also $[\mathrm{I_3}^-] = [\mathrm{Pt(CN)_4}^{2-}]$ which is true only if no $[\mathrm{Pt(CN)_4}^{2-}]$ was present initially. Thus the concentration of product i.e. $[\mathrm{Pt(CN)_4}^{2-}] + [\mathrm{Pt(CN)_4I_2}^{2-}]$ is equal to

$$[\mathrm{I_3}^-]\left\{1 + \frac{[\mathrm{I_3}^-]}{K_r[\mathrm{I}^-]}\right\} \text{ and not } [\mathrm{I_3}^-].$$

The value of K^r used was $2.4.10^{-2}$ which was the value estimated at 25°C (see below). The effect of the correction term,

$\left(1 + \frac{[I_3^-]}{K_r[I^-]}\right)$, was to decrease the apparent rate constant at 0.02 M. iodide concentration by nearly 7%. This was the same iodide ion concentration used in the determination of the temperature dependence and the same value of K_r was used at each temperature. However, the value of $|\Delta H^o|$ would have to be greater than about 5 kcal./mole. for this approximation to cause a systematic error of more than 0.5 kcal./mole in the activation enthalpy.

The ionic strength was maintained at 1.0 M. with sodium perchlorate. The pseudo first order rate plots were linear over one to two half lives and the standard deviations of the quoted rate constants were calculated to be about ±3%. The results are given in table (6).

The reaction of iodide with trans- $Pt(CN)_4Br_2^{2-}$

This reaction was considerably faster than that of the chloro complex and as a result could only be studied at low iodide ion concentrations by observing the decrease in transmittance at 405 mμ , the absorption maximum of trans-

Table 6

Rate constants for the reaction

<u>trans</u>- $Pt(CN)_4Cl_2^{2-} \xrightarrow{I^-} Pt(CN)_4^{2-} + I_3^-$

$[Pt^{IV}] = 6.10^{-5}M.$ $\mu = 1;0$ M.

$T(^\circ C)$	$10^2[I^-]M.$	$k_{obs}(sec.^{-1})$	$k_2(l.mole.^{-1}sec.^{-1})$
20.0	1.0	7.8	780
20.0	2.0	16.6	830
20.0	2.0	16.6	830
20.0	2.0	16.5	825
20.0	5.0	43.3	866
20.0	7.0	61.3	876
27.6	2.0	22.3	1,120
34.3	2.0	30.8	1,540
44.9	2.0	40.1	2,000

$\Delta H^* = 6.0 \pm 0.3$ kcal./mole

$\Delta S^* = -25$ cal.mole^{-1}deg.$^{-1}$

$Pt(CN)_4I_2^{2-}$. The ionic strength was held constant at 0.075 M. with sodium bromide, the equilibrium constant for replacement of bromide by iodide was sufficiently large for the reaction to go to completion. The first order rate plots obtained were linear for at least one half life but were not very accurate because their rates were on the limit of the stopped-flow assembly. The results are given in table (7).

The reduction of <u>trans</u>- $Pt(CN)_4I_2^{2-}$

The rate of reduction of this complex at an iodide ion concentration sufficient to cause an appreciable amount of reduction to I_3^- was, as noted earlier, too fast to be measured even using the stopped-flow technique. An attempt was made to follow the reduction in the presence of hydroxide ion to remove the I_3^- and so drive the reaction to completion. The reaction of I_3^- with OH^- was too fast to measure by the stopped-flow technique. In this way it was hoped to be able to reduce the iodide ion concentration needed and hence reduce the rate

Table (7)

Rate constants for the reaction

<u>trans</u>- $Pt(CN)_4Br_2^{2-} \xrightarrow{I^-}$ <u>trans</u>- $Pt(CN)_4I_2^{2-}$

$[Pt^{IV}] = 4\ 0.\ 10^{-4}M.$

$\mu = 0.075$ M.

T = 20.9°C.

$10^3[I^-](M)$	$10^3[Pt^{II}](M)$	$k_{obs}(sec.^{-1})$	$10^{-4}k(l.mole^{-1}sec.^{-1})$
1.45	0.5	108	7.5
1.45	2.1	107	7.4
2.20	2.1	195	8.9

of reduction. The reaction was followed by observing the ~~increase~~ increase in transmittance at 405 mμ accompanying the loss of the diiodo complex. The ionic strength was maintained at 0.05 M. with sodium perchlorate. The first order rate plots were linear for at least one half life and the results are given in table (8).

The reaction of iodide with *trans*- $PtOx_2Cl_2^{2-}$.

In the absence of added potassium bisoxalatoplatinate(II) the reaction was found to occur in two stages as evidenced by the accompanying spectroscopic changes in the ultraviolet and visible region. The changes during the first stage corresponded to the formation of two broad peaks at 290 mμ and 310 mμ and a shoulder at 350 mμ , the changes were complete in less than ten minutes at 0.05 M. sodium iodide and an ionic strength of 0.5M. Under the same conditions the second stage saw the formation of two peaks at 343 mμ and 500 mμ with a shoulder at 445 mμ , the changes being complete in about two hours. From the visible and near ultraviolet spectrum this last product was identified as the hexaiodoplatinate(IV) ion(19).

Table (8)

Rate constants for the reaction

<u>trans</u>- $Pt(CN)_4I_2^{2-} \xrightarrow{I^-/OH^-} Pt(CN)_4^{2-}$

$[Pt^{IV}] = 1{\cdot}5.10^{-4}M.$

$\mu = 0{\cdot}05$ M.

T = 17·1°C.

$10^3[OH^-](M)$	$10^4[I^-](M)$	$k_{obs}(sec.^{-1})$
1·25	2·00	42
1·25	2·00	44^A
2·50	2·00	85
2·50	4·45	106
3·75	4·45	~150

A $[Pt(CN)_4^{2-}] = 7{\cdot}2.10^{-4}M.$

However, if equimolar amounts of potassium bisoxalatoplatinate (II) were added to potassium <u>trans</u>- dichlorobisoxalatoplatinate (IV) prior to the start of the reaction, it was again found to be a two stage reaction with roughly comparable rates under the same conditions as without the added Pt(II) complex but the spectroscopic changes were different. The first stage was accompanied by the formation of a single peak at 312 mμ with no evidence of a peak around 280 mμ or 350 mμ ; the second stage again saw the formation of PtI_6^{2-}. <u>Trans</u>- $PtOx_2I_2^{2-}$, the product of the first stage, was thus easily reduced by free iodide ions unless sufficient $PtOx_2^{2-}$ was present.

The first stage of the reaction was followed by observing the increase in absorbance at 312 mμ , the ionic strength of the solutions were held constant with mixtures of sodium chloride, iodide, and perchlorate. Fresh solutions of the complex were made up for each kinetic run and the activation enthalpies and entropies were estimated graphically. The results are given in table (9).

The reaction of iodide with <u>trans</u>- $PtOx_2Br_2^{2-}$

This reaction was considerably faster than that of the chloro complex and was studied using the stopped-flow technique. Potassium bisoxalatoplatinate(II) was present in all the

Table (9)

Rate constants for the reaction

$\underline{trans}$- $PtOx_2Cl_2{}^{2-} \longrightarrow \underline{trans}$- $PtOx_2I_2{}^{2-}$

$[Pt^{IV}] = (3\cdot3 - 4\cdot9)\ 10^{-5}M.$

$\mu = 0\cdot05$ M.

$T(^{o}C)$	$[I^{-}](M)$	$10^{4}[Pt^{II}](M)$	$k_{obs}(min.^{-1})$	$k_2(l.mole^{-1}min.^{-1})$
4·6	0·0097	2·9	0·0690	7·11
13·4	0·0097	2·9	0·0781	8·05
18·6	0·0097	2·9	0·0880	9·09
25·0	0·0097	2·7	0·0980	10·1
25·0	0·00625	3·4	0·0642	10·3
25·0	0·00821	2·9	0·0837	10·2
25·0	0·00821	2·9	0·0782	9·53[A]
25·0	0·0100	3·3	0·0991	9·91[B]
25·0	0·0125	3·4	0·127	10·2
25·0	0·0125	7·2	0·124	9·92
25·0	0·0125	7·2	0·126	10·1[C]
25·0	0·0125	7·2	0·124	9·92[D]
25·0	0·0375	3·4	0·331	8·83
25·0	0·050	3·4	0·515	10·3
31·5	0·0097	2·7	0·110	11.3

A $[IrCl_6{}^{2-}] = 3\cdot23.10^{-6}M.$

B $[IrCl_6{}^{2-}] = 5\cdot7.10^{-6}M.$

C $[Cl^{-}] = 0\cdot0188$ M.

D $[Cl^{-}] = 0\cdot0375$ M.

$\Delta H^{\neq} = 2\cdot5$ kcal. $mole^{-1}$

$\Delta S^{\neq} = -54$ cal.$mole.^{-1}deg.^{-1}$

reactant solutions to prevent extensive reduction of the product diiodo complex, the rate of formation of which was studied by observing the decrease in transmittance at 312 mμ. The ionic strength was held constant with sodium perchlorate. The first order rate plots were linear for over two half lives and the standard deviation of the quoted rate constants was calculated to be ±8%. The results are given in table (10).

Equilibrium Studies

The redox equilibrium

$$\underline{\text{trans}}\text{-}\ Pt(CN)_4I_2^{2-} + I^- \rightleftharpoons Pt(CN)_4^{2-} + I_3^- \quad \ldots\ldots \quad (6)$$

was studied by measuring the increase in absorbance at 353 mμ, an absorption maximum of I_3^- (18), in increasing amounts of added iodide. Added $Pt(CN)_4^{2-}$ was present initially so that the iodide concentrations corresponding to convenient amounts of reduction were very much greater than the concentration of complex. However, the iodide concentrations were not sufficiently large to prevent some dissociation of I_3^- into I_2 and I^-. Since the absorbance due to $Pt(CN)_4^{2-}$ and I_2 at this wavelength was negligible, the following equations can be derived.

Table (10)

Rate constants for the reaction

$\underline{\text{trans}}\text{- PtOx}_2\text{Br}_2{}^{2-} \xrightarrow{I^-} \underline{\text{trans}}\text{- PtOx}_2\text{I}_2{}^{2-}$

$[Pt^{IV}] = (0{\cdot}9 - 1{\cdot}2)10^{-4}M.$

$\mu = 0\ 025\ M.$

$T(^{o}c)$	$[I^-](M)$	$10^4[Pt^{II}](M)$	$k_{obs}(sec^{-1})$	$10^{-3}k_2(l.mole^{-1}sec.^{-1})$
15·9	0·005	1·86	19·3	3·86
20·6	0·005	1·86	22·6	4·52
25·0	0·005	1·86	26·2	5·24
25·0	0·00125	2·12	6·86	5·29
25·0	0·0025	2·12	13·0	5·20
25·0	0·005	2·12	25·0	5·00
25·0	0·005	2·12	25·0	5·00[A]
25·0	0·005	3·42	24·9	4·98
25·0	0·005	3·42	25·6	5·12[B]
25·0	0·0075	3·42	38·2	5·09
25·0	0·010	3·42	46·1	4·61
30·3	0·005	1·86	30·6	6·13
36·8	0·005	1·86	36·2	7·24

A $[Br^-] = 0{\cdot}020\ M.$

B $[IrCl_6{}^{2-}] = 9{\cdot}5.10^{-6}M.$

$\Delta H^{\neq} = 4{\cdot}8$ kcal/mole

$\Delta S^{\neq} = -25\ cal.mole.^{-1}deg.^{-1}$

$$
\begin{aligned}
A &= E_a[\mathrm{Pt(CN)_4I_2}^{2-}] + E_b[I_3^-] \\
&= Ea[\mathrm{Pt(CN)_4I_2}^{2-}]_o - Ea\left\{[I_2] + [I_3^-]\right\} + E_b(I_3^-] \\
&= E_a[\mathrm{Pt(CN)_4I_2}^{2-}]_o + [I_3^-]\left\{E_b - E_a - \frac{E_a}{K[I^-]}\right\} \quad ..... \quad (7)
\end{aligned}
$$

$$
\begin{aligned}
[\mathrm{Pt(CN)_4I_2}^{2-}] &= [\mathrm{Pt(CN)_4I_2}^{2-}]_o - \left\{[I_2] + [I_3^-]\right\} \\
&= [\mathrm{Pt(CN)_4I_2}^{2-}]_o - [I_3^-]\left\{1 + \frac{1}{K[I^-]}\right\} \quad ... \quad (8)
\end{aligned}
$$

$$
[\mathrm{Pt(CN)_4}^{2-}] = [\mathrm{Pt(CN)_4}^{2-}]_o + [I_3^-]\left\{1 + \frac{1}{K[I^-]}\right\} \quad ... \quad (9)
$$

where A is the absorbance, and E_a and E_b are the extinction coefficients of <u>trans</u>- $\mathrm{Pt(CN)_4I_2}^{2-}$ and I_3^- respectively. The subscript zero designates the initial concentration i.e. the concentrations in the absence of any reduction; K (= 714 $M.^{-1}$)(18) is the formation constant of I_3^- from I_2 and I^-.

The redox equilibrium constant, K_r, can be calculated from equations (7)-(9), the experimental data together with the equilibrium constants derived from the are given in table (11).

Table 11

The Equilibrium

trans- $Pt(CN)_4I_2^{2-} + I^- \rightleftharpoons Pt(CN)_4^{2-} + I_3^-$

$T = 25^\circ C$

$\mu = 0.5$ M.

$[Pt(CN)_4I_2^{2-}]_0 = 2.97 . 10^{-4}$M.

$[Pt(CN)_4^{2-}]_0 = 3.41 . 10^{-4}$M.

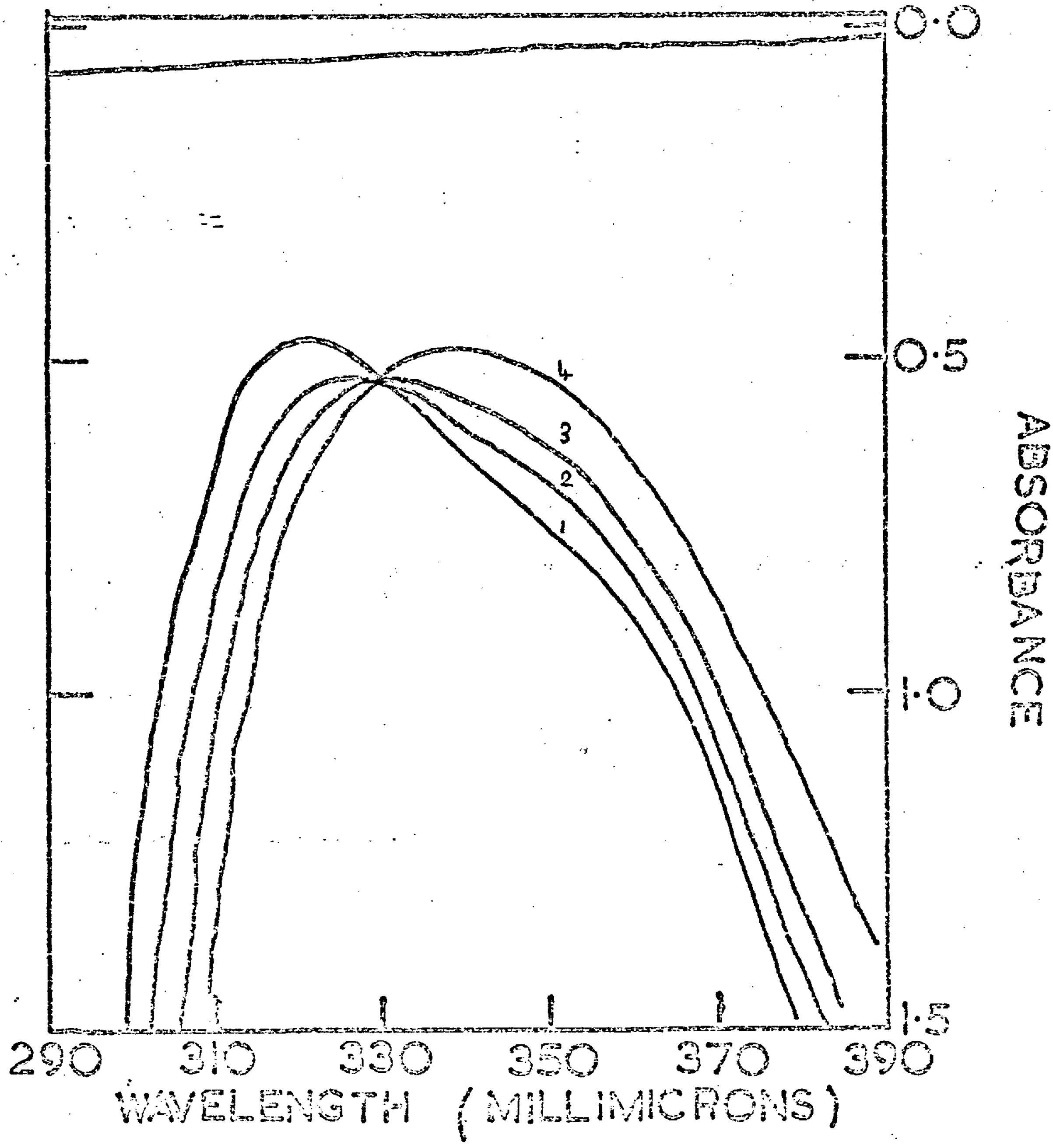
$10^3[I^-]$(M)	$A^{(a)}$	10^2Kr
0	0·045	-
6·49	0·216	2·15
9·24	0·264	2·19
12·0	0·314	2·40
17·5	0·371	2·35
21·6	0·415	2·51
31·9	0·480	2·53

$\bar{K}_r = (2.36 \pm 0.06)10^{-2}$

a. at 353 mμ in 0·1 cm.cells

Addition of free chloride or bromide to trans- $Pt(CN)_4I_2^{2-}$ in an attempt to determine the equilibrium constant for replacement of the iodide by chloride or bromide resulted in reduction of the complex. The absorbance at 405 mμ, an absorption maximum of $Pt(CN)_4I_2^{2-}$, was reduced as the amounts of these ions were increased but addition of small amounts of free iodide failed to reverse the decrease in absorbance and thus simple replacement of iodide by these ions could not be occurring. Addition of a large amount of bromide to the diiodo complex gave a spectrum which had no absorption maxima at 240 and 340 mμ, due to the bromo complex, but instead resembled that of $Pt(CN)_4^{2-}$. If $Pt(CN)_4^{2-}$ were present initially, addition of chloride gave a clean isosbestic point at 330 mμ, figure 1, and a rather poor one at 350 mμ was obtained on addition of bromide. The spectral changes occurred immediately on the addition of halide but the product solutions were unstable at high halide concentrations and so the spectra were measured as quickly as possible after mixing the solutions. The concentrations of the halide were sufficiently large in all the solutions for the iodine formed to be converted completely to I_2Br^-, the formation constant of which is 12.5 M^{-1} [20], or I_2Cl^- which has a formation constant of 1.7 M^{-1} [21]. An expression for the equilibrium constant of the reaction

Figure 1.



Addition of NaCl to trans-$Pt(CN)_4^{2-}$
in the presence of $Pt(CN)_4^{2-}$.

trans- $[Pt(CN)_4I_2]^{2-}$ + $X^- \rightleftharpoons Pt(CN)_4]^{2-}$ + I_2X^- can be derived as shown

$$A = E_a[Pt(CN)_4I_2{}^{2-}] + E_b[I_2X^-]$$

$$= E_a\left\{[Pt(CN)_4I_2{}^{2-}]_o - [I_2X^-]\right\} + E_b[I_2X^-]$$

$$= E_a[Pt(CN)_4X_2{}^{2-}]_o + [I_2X^-]\left\{E_b - E_a\right\}$$

$$= A_o - [I_2X^-]\left\{E_a - E_b\right\}$$

$$\therefore\ [I_2X^-] = \frac{A_o - A}{E_a - E_b}$$

$$[Pt(CN)_4{}^{2-}] = [Pt(CN)_4{}^{2-}]_o + [I_2X^-]$$

$$[Pt(CN)_4I_2{}^{2-}] = [Pt(CN)_4I_2{}^{2-}]_o - [I_2X^-]$$

$$\therefore\ K = \left\{\frac{A_o - A}{E_a - E_b}\right\}\left\{\frac{[Pt(CN)_4{}^{2-}]_o + (A_o - A)/(E_a - E_b)}{[Pt(CN)_4I_2{}^{2-}]_o - (A_o - A)/(E_a - E_b)}\right\}\frac{1}{[X^-]}$$

where A_o and A are the absorbances before and after addition of halide respectively; E_a and E_b are the extinction coefficients of the diiodo complex and I_2X^- respectively. The absorbances of both X^- and $[Pt(CN)_4{}^{2-}]$ are negligible at this wavelength. The absorbance data together with the derived constants are shown in tables (12) and (13).

In an attempt to measure the equilibrium constants for replacement of the bromide or chloride ligands by iodide in the system trans- $Pt(CN)_4X_2{}^{2-}$, it was found that only a very small excess of iodide ion was needed to convert the original complex completely to the diiodo species. As noted above, large excesses of free bromide or chloride reduced the diiodo complex thus making it impossible to study the equilibria in the presence of a high concentration of the free halide, when the amount of iodide needed to replace the chloride or bromide would have been greatly increased. Measurements of the increase in absorbance at 405 mμ in increasing amounts of iodide ion revealed that in 1.0 M. solution of chloride, $\leqslant$ 90% conversion of $1.9.10^{-4}$M. chloro complex into iodo complex was caused by 6.10^{-4}M. iodide in the presence of 5.10^{-5}M.$[Pt(CN)_4{}^{2-}]$. About 10% reduction of the diiodo complex by iodide occurs under these conditions. No attempt to derive accurate equilibrium constants was made in view of the complication due to reduction but, using the

Table (12)

The Equilibrium

$$\underline{\text{trans}}\text{-}\ Pt(CN)_4I_2^{2-} + Br^- \rightleftharpoons Pt(CN)_4^{2-} + I_2Br^-$$

$T = 25.0^\circ C.$

$\mu = 5.0$ M.

$[Pt(CN)_4I_2^{2-}]_o = 6.07.10^{-5}$M.

$[Pt(CN)_4^{2-}]_o = 8.31.10^{-5}$M.

$E_{I_2Br^-} = 1{,}110$ l.mole^{-1}cm.$^{-1}$ at 405 mμ.

$[Br^-]$(M)	$A^{(a)}$	10^4K
0	1.360	-
0.156	1.042	2.65
0.313	0.903	2.51
0.625	0.723	2.56
1.25	0.535	3.31
1.88	0.481	2.93
2.50	0.440	2.91

$$\bar{K} = (2.81 \pm 0.12)10^{-4}$$

(a) in 4 cm. cells.

Table (13)

The Equilibrium

<u>trans</u>- $Pt(CN)_4I_2^{2-} + Cl^- \rightleftharpoons Pt(CN)_4^{2-} + I_2Cl^-$

$T = 25 \cdot 0^{\circ}C.$
$\mu = 5{\cdot}0$ M.

$[Pt(CN)_4I_2^{2-}]_o = 1{\cdot}60.10^{-4}M.$

$[Pt(CN)_4^{2-}]_o = 3{\cdot}08.10^{-4}M.$

$E_{I_2Cl^-} = 671$ 1.mole^{-1}cm.$^{-1}$ at 405 mμ .

$[Cl^-]$(M)	$A^{(b)}$	10^5K
0	0•894	–
0•74	0•796	6•32
1•02	0•763	6•58
1•30	0•750	5•82
1•85	0•700	6•14
2•50	0•661	5•97
3•70	0•605	5•76
5•00	0•551	5•83

$$\bar{K} = (6{\cdot}06 \pm 0{\cdot}11)10^{-5}$$

(b) in 1 cm. cells.

above figures an upper limit of <u>ca.</u> 10^5 was obtained for the average constant.

Solutions which were $4.8.10^{-5}$M. in bromo complex, 0.01 M. in bromide, and 4.10^{-4}M. in $Pt(CN)_4{}^{2-}$ showed isosbestic points at 317 and 365 mμ for total iodide concentrations exceeding <u>ca.</u> 6.10^{-5} M. These presumably correspond to the overlap of the spectra of the iodobromo and diiodo complexes. Because of this simplification, together with the absence of reduction under these conditions, an attempt was made to obtain values of the equilibrium constants using measurements of absorbance at 405 mμ of the above solution in increasing amounts of iodide. The exact equation for substitution of both bromides is

$$0 = (A-A_0) + (A-A_1).K_1.\frac{[I^-]_f}{[Br^-]} + (A-A_2).K_1K_2\frac{[I^-]^2_f}{[Br^-]^2} \quad \ldots (10)$$

A_0, A_1 and A_2 are the absorbances of pure <u>trans</u>- $Pt(CN)_4Br_2{}^{2-}$, <u>trans</u>- $Pt(CN)_4BrI^{2-}$ and <u>trans</u>- $Pt(CN)_4I_2{}^{2-}$ respectively and A is the absorbance of a solution containing more than one of the species at a free iodide concentration of $[I^-]_f$. K_1 and K_2 are the stepwise formation constants of <u>trans</u>-

$Pt(CN)_4IBr^{2-}$ and trans- $Pt(CN)_4I_2^{2-}$ respectively. Over the "isosbestic" region where trans- $Pt(CN)_4I_2^{2-}$ and trans- $Pt(CN)_4IBr^{2-}$ are the only species absorbing, equation (10) simplifies to equation (11).

$$(A-A_1) + (A-A_2)K_2\frac{[I^-]_f}{[Br^-]} = 0 \qquad \ldots \qquad (11)$$

$$\therefore \frac{[Br^-]}{K_2} = \frac{(A_2-A)}{(A-A_1)}[I^-]_f$$

$$\text{Also } [I^-]_t = [I^-]_f + [Pt]_t + \frac{K_2[I^-]_f}{[Br^-]}\left\{2[Pt]_t - [I^-]_t + [I^-]_f\right\}$$

The subscript 't' refers to total concentration

$$\therefore [I^-]_t = [I^-]_f + [Pt]_t\frac{(1 + 2K_2[I^-]_f/[Br^-])}{1 + K_2[I^-]_f/[Br^-]}$$

$$= [I^-]_f + [Pt]_t\frac{(A_2 + A - 2A_1)}{(A_2 - A_1)}$$

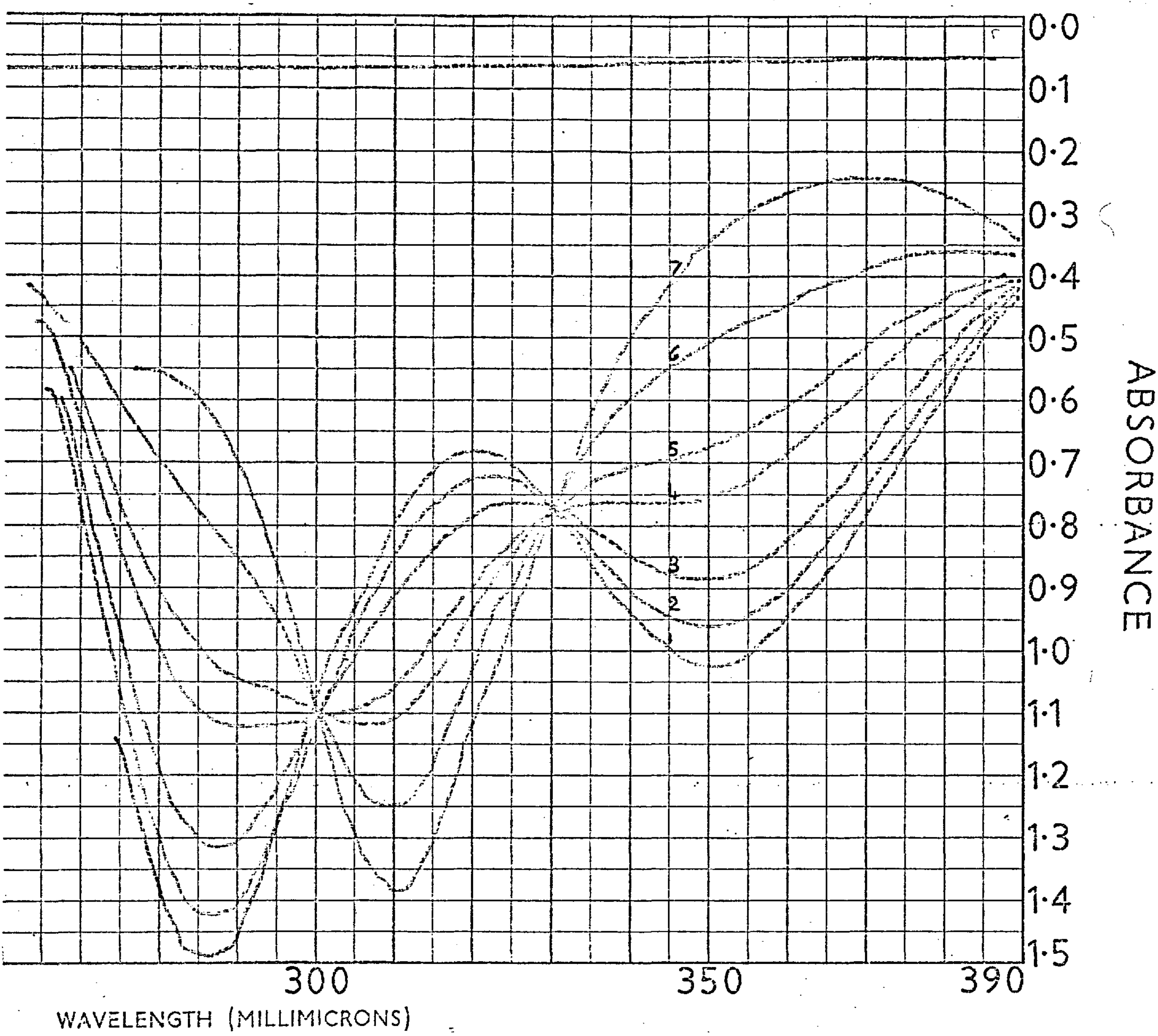
$$\therefore \frac{[Br^-]}{K_2} = \frac{(A_2-A)}{(A-A_1)}[I^-]_t - (A_2-A)[Pt]_t\left\{\frac{1}{A-A_1} + \frac{1}{A_2-A_1}\right\} \ldots (12)$$

Calculations were made using equation (12) from observations on solutions whose $[I^-]_t$ varied from between 8.10^{-5}M. and 13.10^{-5}M. Using various values for A_2 and A_1, the corresponding values of $[Br^-]/K_2$ were calculated. Thus, using values of $A_2 = 1.25$ (4 cm. cells) and $A_1 = 0$, the values of $[Br^-]/K_2$ varied from $1{\cdot}1.10^{-5}$ at the lower $[I^-]_t$, went through a maximum value of $1{\cdot}3.10^{-5}$ and then decreased to $1{\cdot}0.10^{-5}$ at the highest $[I^-]_t$. It would appear from this variation in $[Br^-]/K_2$ that both A_2 and A_1 were too small. however, using slightly different values of A_2 together with different values of A_1, it proved impossible to obtain self consistent sets of equilibrium constants. The limiting value of $[Br^-]/K_2$ seems to be $\gtrsim 10^{-5}$ which gives a value for K_2 of $\lesssim 10^3$.

A study was made of the redox equilibrium

trans- $PtOx_2I_2^{2-} + I^- \rightleftharpoons PtOx_2^{2-} + I_3^-$

by measuring the decrease in absorbance at 353 mμ of a solution of I_3^- in sodium iodide with increasing amounts of added potassium bisoxalatoplatinate (II). As the amount of added Pt(II) was increased the peaks at 287 and 353 m due to I_3^- decreased in intensity while the peak at 312 m due to the diiodo complex increased in height. There were also



Addition of $PtOx_2^{2-}$ to I_3^- in 0.0I M. NaI.

two clean isosbestic points at 300 and 330 mμ. At 353 mμ the only absorbing species are I_3^- and trans- $PtOx_2I_2^{2-}$ and so the following equations can be derived

$$A = E_I[I_3^-] + E_{iv}[Pt^{iv}]$$

$$= E_I[I_3^-]^o - [Pt^{iv}](E_i - E_{iv}] \quad \ldots\ldots \quad (13)$$

$$[Pt^{ii}] = [Pt^{ii}]_o - [Pt^{iv}] \quad \ldots\ldots \quad (14)$$

$$[I_3^-] = [I_3^-]_o - [Pt^{iv}] \quad \ldots\ldots \quad (15)$$

where A is the absorbance and, E_i and E_{iv} are the extinction coefficients of I_3^- and trans- $PtOx_2I_2^{2-}$ respectively; the subscript zero denotes initial concentration. Thus the redox equilibrium constant can be derived from equations (13) to (15). The ionic strength of the solution was held constant with sodium iodide. The experimental data, and the constants derived from them are given in table (14).

Spectroscopic Interactions

The spectra of the ions trans- $Pt(CN)_4Cl_2^{2-}$ and trans- $Pt(CN)_4Br_2^{2-}$ were found to change on addition of free halide ions.

Table (14)

The equilibrium

$$\underline{\text{trans}}\text{- } PtOx_2I_2^{2-} + I^- \rightleftharpoons PtOx_2^{2-} + I_3^-$$

$T = 25.0^\circ$ C

$\mu = [I^-] = 0.01$ M.

$E_{iv} = 2,000$

$[I_3^-]_o = 3.88.10^{-5}$M.

$A^{(a)}$	$10^5[Pt^{II}]_o^{(b)}$(M)	10^3K
1.023	—	—
0.967	0.35	1.84
0.903	0.69	1.37
0.826	1.21	1.54
0.766	1.73	1.81
0.698	2.25	1.75
0.618	2.77	1.48
0.540	3.46	1.42
0.450	4.15	1.17
0.376	5.19	1.17
0.314	6.92	1.34
0.287	8.65	1.61

$$\bar{K} = (1.50 \pm 0.07).10^{-3}$$

(a) at 353 mμ in 1 cm. cells

(b) Total amount of $[Pt^{II}]$ added

The increase in absorbance was linear with concentration of halide up to 4·0M. (μ = 4.0 M.) for the chloro complex at 260 mμ and 280 mμ, and up to 2·0 M. (μ = 5·0 M.) for the bromo complex at 300 and 320 mμ. The spectroscopic changes were rapid and unaffected by the addition of substantial amounts of $Pt(CN)_4^{2-}$. On subtracting the absorbance of the solutions in the absence of free halide from those in its presence no clear maximum was observed. Solutions of the bromo complex in bromide concentrations greater than 2·0 M. decomposed rapidly thus making these measurements unreliable. In the higher chloride concentrations the chloro complex also decomposed, but slowly enough to enable the initial changes to be accurately measured. The gradients, expressed as changes in apparent extinction coefficients per unit halide concentration, are given in table (15).

Table (15)

Spectroscopic interactions between trans- $Pt(CN)_4X_2^{2-}$ and X^-

X	λ(mμ)	μ(M)	$10^3[Pt(CN)_4^{2-}]$ (M)	$\Delta E/[X^-]$($M^{-2}cm.^{-1}$)
Cl	260	4.0	0	62
	270	4.0	0	51
	270	4.0	0.7	50
Br	300	1.0	0	596
	300	1.0	1.0	609
	320	1.0	0.	273
	320	1.0	1.0	290
	300	4.0	0	1016
	320	4.0	0	476

Discussion

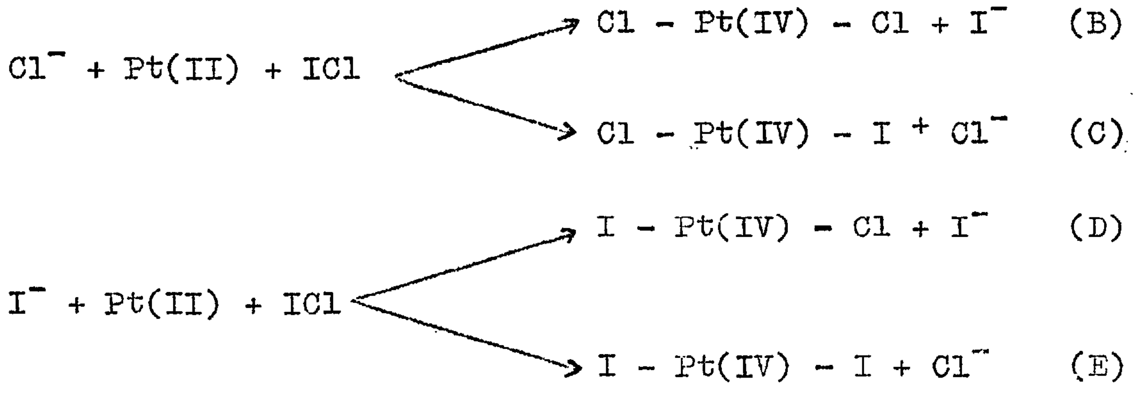
Oxidation of planar Pt(II) species results in trans addition$^{(22)}$. This has been proved in the case of chlorine oxidation of tetramine platinum(II) chloride and also$^{(23)}$ oxidation of l-Pt(i-bn)(m-stien)$^{2+}$ by one or two electron oxidising agents followed by reduction with similar reducing agents which resulted in very little racemisation (i - bn = 2 methyl, 1, 2, propanediamine and m-stien = meso 1, 2, diphenyl, 1, 2, ethane diamine). Trans addition gives a molecule with symmetry D_{4h} which should have only one vibration active in the Raman corresponding to the A_{1g} metal-halogen symmetric stretch whereas cis addition gives a molecule belonging to the point group C_{2v} which would have two vibrations active in both the Raman and infrared corresponding to the A_1 and B_1 metal-halogen stretches. The trans configuration was thus assigned to these compounds.

The data in table (5) show that the rate of replacement of chloride ion in trans- $Pt(CN)_4Cl_2^{2-}$ by iodide is first order in iodide concentration. The rates of the reaction were unaffected by the presence of 14 mole % of $IrCl_6^{2-}$ and of varying amounts of $Pt(CN)_4^{2-}$ so that any mechanism involving labile Pt(III)$^{(6)}$, or bridged species such as

Pt(IV) - Cl - Pt(II)$^{(3)}$, as intermediates can be ignored. Table (6) shows that the rate of reduction of the chloro complex by iodide was also approximately first order in iodide concentration, however, an additional path involving a square dependence on the iodide concentration can not be completely ruled out. From the Arrhenius plot, the second order rate constant for reduction at 23.4°C can be obtained and is the same (950 l.mole^{-1}cm.$^{-1}$) as the values for substitution at the same temperature and ionic strength (table 5). Also, the activation enthalpies for both substitution and reduction are equal within the experimental uncertainty. It thus appears that the rate determining step in both reactions is the redox reaction (A).

$$\mathrm{Cl - Pt(IV) - Cl + I^- \longrightarrow Cl^- + Pt(II) + ClI} \quad (A)$$

For the sake of clarity the four cyanide ligands in the equatorial plane have been omitted. Basically, this reduction involves a transfer of Cl^+ from the Pt(IV) complex to the I^-. At sufficiently low iodide concentrations and in the presence of sufficiently large concentrations of $Pt(CN)_4^{2-}$, rapid reoxidation of the $Pt(CN)_4^{2-}$ occurs. However, several oxidation reactions are possible as shown in the equations (B - E).



Reaction (B) must be relatively slow as quite large amounts of chloride ion do not appreciably retard the reaction (table 5). Further studies on the $PtCl_6^{2-}$ - I^- reaction at μ = 1.0 M. and T = 35·1°C show that the rate is also unaffected by the presence of quite large amounts of chloride ion : the second order rate constants at 0 and 1.0 M, chloride concentration are 0.0826 and 0.0839 $l.mole.^{-1}$ $sec.^{-1}$ respectively. An alternative reason for this lack of retardation is that the iodine atom of the ICl re-enters the complex on oxidation in preference to the chlorine atom (equations B and C). It was also suggested(10) that the reason why the $PtBr_6^{2-}$ - I^- reaction goes through a different set of intermediates from the PtI_6^{2-} - Br^- reaction was that the iodine atom of the IBr ends up in the Pt(IV) complex on reoxidation. It was not possible to determine whether the iodo chlorocomplex was formed as an intermediate but if it is, then its reduction by iodide must be assumed to be much faster than that of the dichloro complex. This is to be expected from the high trans effect of iodide.

The data for the reaction of the di-bromo complex with iodide are not very detailed but they indicate that the same type of mechanism is operative with the Br-Pt(IV)-Br group being reduced about 500 times faster than the Cl-Pt(IV)-Cl.

The data (table 8) for the reduction of trans $Pt(CN)_4I_2^{2-}$ indicate that the reaction is not simply a rate determining reduction of the complex by iodide followed by a very rapid reaction of the iodine formed with hydroxide. It would appear that the hydroxide ion is involved in the rate determining step and direct reduction by the hydroxide ion could be feasible.

The reactions of trans $PtOx_2Cl_2^{2-}$ and trans $PtOx_2Br_2^{2-}$ with iodide are both first order in iodide and complex concentration (tables 9 and 10) and are unaffected by the presence of $PtOx_2^{2-}$ and $IrCl_6^{2-}$. Here again the same redox mechanism may be invoked with the Br-Pt-Br group being reduced, under roughly comparable conditions about 3.10^4 times faster than the Cl-Pt-Cl. Another similarity lies in the observation that the rates are unaffected by quite large amounts of chloride or bromide so that a similar reaction to that given in equation (B) can be ruled out. The low values of the activation enthalpies coupled with the large negative values of the activation entropies are rather surprising but low activation enthalpies are by no means unknown. Thus the rate(24) of the reaction of acidified permanganate with iodide is known to follow the rate law

$$\frac{-d[MnO_4^-]}{dt} = [MnO_4^-][I^-]\left\{k_1 + k_2[H^+]\right\}$$

with values for the activation enthalpies and entropies of $\Delta H_1^{+} = 1.3$ kcals.mole^{-1}, $\Delta S_1^{*} = -46$ cals.mole.$^{-1}$deg.$^{-1}$, $\Delta H_2^{*} = 3.8$ kcals.mole.$^{-1}$, $\Delta S_2^{*} = -14$ cals.mole.$^{-1}$deg.$^{-1}$. The reaction(2a) of <u>trans</u> $Pt(NH_3)_4ClBr$ with Br^- to give <u>trans</u> $Pt(NH_3)_4Br_2^{2-}$ has an activation enthalpy of 3 kcals.mole.$^{-1}$ and an activation entropy of -30 cals.mole.$^{-1}$deg.$^{-1}$.

Although the exact values of the equilibrium constants for replacement of chloride or bromide by iodide could not be obtained for the cyanide complexes, the rough values, as expected for Pt(IV) complexes, are quite large. The average equilibrium constant for replacement of bromide by iodide was $\leqslant 2.10^3$ which can be compared with the value of 500 ($\log_{10} \beta_6 = 16$) for replacement of bromide by iodide in $PtBr_6^{2-}$ (25). This would seem to indicate that the four cyanide ligands have little effect upon the class(26) (b) character or softness(27) of the Pt(IV) ion.

It is possible to calculate a value of the equilibrium constant for replacement of chloride by iodide in the cyanide complexes by comparison of the reduction potentials for reactions (F) and (G)

$$\underline{\text{trans}}\text{-}\ Pt(CN)_4I_2^{2-} + 2e \longrightarrow Pt(CN)_4^{2-} + 2I^- \qquad (F)$$

$$\underline{\text{trans}}\text{-}\ Pt(CN)_4Cl_2^{2-} + 2e \longrightarrow Pt(CN)_4^{2-} + 2Cl^- \qquad (G)$$

By combining the equilibrium constant for reduction of the diiodo complex by iodide with the value of 0.536 V.(28) for the reaction $I_3^- + 2e \longrightarrow 3I^-$, a value of 0.49 V. is obtained for the reduction potential of reaction (F). The value for the reduction potential of reaction (G) is 0.89 V.(29) which gives on subtracting 0.49 V. a value of the average equilibrium constant for replacement of a chloride by iodide. The value obtained is 5.10^6. This can be compared with the value of 10^3 for the average equilibrium constant for replacement of chloride by iodide in $PtCl_6^{2-}$ (25). This calculated value of 5.10^6 is substantially larger than the value expected in view of the concentration of iodide needed to produce significant amounts of <u>trans</u>- $Pt(CN)_4I_2^{2-}$, and also in view of the value of $\lesssim 2.10^3$ obtained for replacement of bromide.

The force constants in table (3) for the cyano complexes decrease by 30% from the Pt-Cl to the Pt-I bonds. The degree of class(b) character is reflected in the narrowing of the bond strength differences between the chloro and iodo complexes, this difference being about 10 kcal./mole. for quite highly class(b) complexes (30). Thus,,if the force constants are directly proportional to the bond strengths, the absolute values of the Pt-Cl and Pt-I bond strengths would be 30 and 20 kcal./mole. respectively, whereas they are certainly greater than this. Generally however, the bond strengths increase as the force constants increase but in these compounds the force constants are probably not closely related to the absolute bond strengths and may possibly indicate that the relative ease of stretching a Pt-I bond over a small distance is much greater compared to stretching it to breaking point.

The equilibrium constants for reduction of the trans-$Pt(CN)_4I_2^{2-}$ by chloride bromide and iodide can be combined to give values of the equilibrium constants for interchange of halide ion in I_2X^-. The values obtained, together with those obtained from the literature(18)(20)(21) are given below.

Equilibrium	K from lit.	K. Expt.
$I_2Br^- + I^- \rightleftharpoons I_3^- + Br^-$	57	84
$I_2Cl^- + I^- \rightleftharpoons I_3^- + Cl^-$	411	389
$I_2Cl^- + Br^- \rightleftharpoons I_2Br^- + Cl^-$	7·2	4·6

Comparison of the experimentally derived values with those from the literature shows that the agreement is quite good for the constant derived from the values of the reduction equilibrium with iodide and chloride but less good for those involving the reduction by bromide. However, not such a good isosbestic point was observed in the study of the reduction equilibrium by bromide ion which may imply that some trans-$Pt(CN)_4Br_2^{2-}$ was formed. Another possibility is the existence of other equilibria involving I_2Br^- (21) which would complicate the system.

The values of the equilibrium constants for reduction of trans- $Pt(CN)_4I_2^{2-}$, and of trans- $PtOx_2I_2^{2-}$ by iodide ion can be combined together with the value of 5.10^{-6} for reduction of PtI_6^{2-} by iodide ion(31), to give values of the equilibrium constants for reactions (H) and (J).

$$\text{trans-}\ Pt(CN)_4I_2^{2-} + PtI_4^{2-} \rightleftharpoons Pt(CN)_4^{2-} + PtI_6^{2-} \qquad (H)$$

$$K = 5.10^3$$

$$\text{trans-}\ PtOx_2I_2^{2-} + PtI_4^{2-} \rightleftharpoons PtOx_2^{2-} + PtI_6^{2-} \qquad (J)$$

$$K = 3.10^2$$

These large values of the equilibrium constants can be interpreted as indicating that $I-Pt(IV)-I^{2+}$ is softer than Pt^{2+}. This is in agreement with the high covalency of the Pt(IV)-I bond which results in a lower effective ionic charge in $I-Pt(IV)-I^{2+}$ than in Pt^{2+} . Nuclear quadrupole resonance data(32) on the platinum halides support this: the results were interpreted as showing that in both $PtBr_4^{2-}$ and $PtBr_6^{2-}$ the effective ionic charge on the Pt ion is 0.28, while in PtI_6^{2-} it is -0.20. Jørgensen(33) has also pointed out, on the basis of spectroscopic evidence, that it may be possible for a metal to possess class(b) character in a high as well as in a low oxidation state, with the metal exhibiting class (a) character in the intermediate oxidation states.

The occurrence of a spectroscopic interaction between trans-$Pt(CN)_4Cl_2^{2-}$ and Cl^-, and between trans-$Pt(CN)_4Br_2^{2-}$ and Br^-, is surprising in view of the negative charges on both pairs of ions. No such spectroscopic interaction was observed for the oxalate complexes. Reduction to $Pt(CN)_4^{2-}$ and X_3^- cannot be responsible as addition of relatively large amounts of $Pt(CN)_4^{2-}$ had no effect. In addition, there was no spectroscopic evidence for the formation of Cl_3^- (λmax ~230 mμ) or Br_3^- (λmax ~265 mμ), when the spectra of the solutions in the absence of free halide were substracted from those in its presence. If the interaction be governed by an equilibrium constant, K, of the same form as an ion pair association constant, then the apparent extinction coefficient E is given by the equation

$$E = \frac{E_a + E_b K[X^-]}{1 + K[X^-]}$$

E_a and E_b are the extinction coefficients of trans- $Pt(CN)_4X_2^{2-}$ and its interaction product with X^- respectively. Some idea of the magnitude of K can be obtained from the observation that E increases linearly with $[X^-]$ up to $\gtrsim$ 1.0 M. so that K must be less than ca 0.1 l.mole.$^{-1}$. The gradients quoted in table (15) are thus values of E_bK. and it can be seen that the values of E_b are therefore of the correct order of magnitude for charge transfer absorption. Prue$^{(34)}$ has shown, on the basis of simple collision theory, that for uncharged species there is a contribution to the charge-transfer spectra from encounters between the two species without there being any specific orientation or interaction. This can lead to an apparent association constant of about 0.2 l.mole.$^{-1}$. If the two species are similarly charged the apparent association constant will, naturally, be less, but it is evident that the spectroscopic changes of these platinum complexes are explicable in terms of charge-transfer occurring during collisions.

For the trans- $Pt(CN)_4X_2^{2-}$ complexes there appears to be a relationship between the rates of reduction and the equilibrium constants for reduction. Both trans- $Pt(CN)_4Cl_2^{2-}$ and trans- $Pt(CN)_4Br_2^{2-}$ are reduced about 10^4 times more rapidly by iodide than are $PtCl_6^{2-}$ and $PtBr_6^{2-}$ respectively, under roughly similar conditions whereas trans- $Pt(CN)_4I_2^{2-}$ is thermodynamically about 10^4 times more readily reduced than PtI_6^{2-}. It may be tentatively concluded that, in this system at least, the transition state for reduction more closely resembles the products than the reactants i.e. the amount of Pt-X bond breaking, and of X-I bond making is quite large in the transition state. This conclusion is in contrast to that of Peloso et al(59) who studied the rates of reduction of some trans- PtL_2X_4 (L = P or As donor ligand, X = Br or Cl) compounds. They found that the rates of reduction of the various substrates with the different reducing anions obeyed the linear free energy relationship : $\log K_2 = \log r_o + r_s$ where K_2 is the second order rate constant for reduction of the given substrate by one of the reducing anions, r_o is the second order rate constant for reduction of trans- $Pt(P(C_3H_7)_3)_2Cl_4$ by the same reducing anion, r_s is a constant for the substrate under consideration. Thus the relative effects of the different reducing agents on the kinetics were independent of the substrate and so it was concluded that there was very little bond making between one of the coordinated halides and the reducing anion in the transition state.

The trans- $PtOx_2Br_2^{2-}$ complex is reduced about 450 times more rapidly by iodide than $PtBr_6^{2-}$ under roughly similar conditions whereas trans- $PtOx_2I_2^{2-}$ is thermodynamically 300 times more readily reduced than PtI_6^{2-}. However, trans- $PtOx_2Cl_2^{2-}$ is reduced only about 10 times more rapidly than $PtCl_6^{2-}$. It may be that the trans- $PtOx_2Cl_2^{2-}$ reduction by iodide involves a transition state similar to (A) below and not (B) which is suggested for the trans- $Pt(CN)_4X_2^{2-}$ system.

$$\mathrm{Pt} \text{ ——— } \mathrm{Cl} \text{ ----- } \mathrm{I}^{\ominus} \qquad \text{(A)}$$

$$\mathrm{Pt} \text{ ----- } \mathrm{Cl}^{\oplus} \text{ ——— } \mathrm{I}^{\ominus} \qquad \text{(B)}$$

The transition state (A) would involve transfer of an electron from the $I^{\ominus}$ to the platinum(IV) and not Cl^+ transfer as in (B). There would probably be strict steric requirements in (A) which would account for the very large negative entropy observed, this would, however, be compensated for by the low value of $\Delta H^{\ddagger}$. Although the value of $\Delta H^{\ddagger}$ is larger and the value of $\Delta S^{\ddagger}$ is normal, the reduction of trans- $PtOx_2Br_2^{2-}$ by iodide may involve a similar transition state to (A), the close similarity between the rate of reduction and the thermodynamic ease of reduction being coincidental.

Why there should be any difference between the systems is not quite clear : the Raman data would seem to indicate very little difference in the strengths of the metal-halogen bonds in both pairs of complexes.

Finally the rate constants and activation parameters for the reactions studied here are compared in table (16) with those for other reactions of anionic complexes which are known to involve this redox mechanism. The data for the trans- $PtOx_2X_2^{2-}$ system is also included though as noted above they probably do not react by exactly the same mechanism.

The limits attached to the parameters obtained from reference (10) are approximate estimates of the maximum uncertainties based on the Arrhenius plots. The activation parameters do not show any systemmatic trends. However, the kinetic cis. effect of the cyanide ligands shows up quite clearly in the low value of the activation enthalpy. The values of $\Delta S^{\ddagger}$ are in agreement with the reaction being between doubly and singly charged ions of the same sign, and, the uncertainties which are quite large tend to show that the values of $\Delta S^{\ddagger}$ are much the same within the uncertainties. The qualitative effect of the dependence of the rate constants on ionic strength is also in agreement with this, thus , the second order rate constant at 25°C for the reaction of trans-$Pt(CN)_4Cl_2^{2-}$ with iodide ion increases from $2{\cdot}2.10^2 M.^{-1} sec.^{-1}$ at μ = 0.07 M. to $10{\cdot}0.10^2 M.^{-1} sec.^{-1}$ at μ = 1.0 M.

Table (16)

Rate parameters for halide interchange reactions of some anionic platinum(IV) complexe

	$\Delta H^{\ddagger}$(kcal/ mole)	$\Delta S^{\ddagger}$(cal mole^{-1}deg.$^{-1}$)	$10^{2}k_{2}(25^{\circ}C)$ (M^{-1}sec.$^{-1}$)	μ (M)
(a)$PtCl_6^{2-}$ + I^-	12·1±0·5	-26±2	1:4	0·04
(a)$PtBr_6^{2-}$ + I^-	14±1	- 9±3	400	0·001
(a)*trans*-$PtBr_4I_2^{2-}$ + I^-	12±2	-20±7	35	0·005 or 0·01
(a)*trans*- $PtBr_2I_4^{2-}$ + I^-	15·5±1	-13±3	6	0·01
(a)(b)$PtBr_nI_{6-n}^{2-}$ + Br^-	17·5±1	-14±3	$8\cdot10^{-2}$	1·0 or 2·0
trans- $Pt(CN)_4Cl_2^{2-}$ + I^-	6·0±0·3	-28	$2\cdot2.10^{4}$	0·07
(c)*trans*- $Pt(CN)_4Br_2^{2-}$ + I^-	-	-	$8\cdot10^{6}$	0·075
trans- $PtOx_2Cl_2^{2-}$ + I^-	2·5	-54	16·9	0·05
trans- $PtOx_2Br_2^{2-}$ + I^-	4·8	-25	$5\cdot0.10^{5}$	0·025

(a) Data from reference (10)

(b) $n \geqslant 3$; If n= 3 or 4 then configuration is very probably *cis*.

(c) T = 20·9°C.

An obvious extension of this work would be to study the reduction of these complexes with different reducing agents such as SCN^- and $S_2O_3^{2-}$ to see what effect these have on the mechanism, rates and activation parameters.

PART II

The Halide Interchange Reactions of *Trans*- Pt.tet.en.X_2^{2+}

Introduction

The redox mechanism described in the previous section to account for the substitution reactions of trans- $Pt(CN)_4X_2^{2-}$ and trans- $PtOx_2X_2^{2-}$ is known to occur in substitution reactions of other anionic Pt(IV) complexes(10)(11). However, this mechanism has not been shown to be an important pathway for the substitution reactions of cationic Pt(IV) complexes. It is known, though, that the cations(60) $Pt(diars)_2Cl_2^{2+}$ and $Pt(diars)_2I_2^{2+}$ are reduced by SCN^- and I^- respectively to a Pt(II) species, the rate of reduction being first order in complex and reducing ion concentration. Similarly the reaction(61) of $Pten_3^{4+}$ with $Cr(bipy)_3^{2+}$ resulted in reduction of the Pt(IV) complex with the rate again being first order in complex and $Cr(bipy)_3^{2+}$ concentration.

A study(1a)(62) of the chloride exchange in complexes of the type trans- $PtA_4Cl_2^{2+}$ (A = NH_3 or $\frac{1}{2}$en) showed that the reaction proceeded via the bridged redox mechanism. It was also shown(1a) that the sterically hindered complex trans- $Pt(tetrameen)_2Cl_2^{2+}$ (tetrameen = $NH_2C(CH_3)_2C(CH_3)_2NH_2$) did not undergo chloride exchange because the methyl groups on the chelate ligand prevented the close approach of the Pt(II) complex necessary for the bridged redox mechanism to occur.

It was decided to study the substitution reactions of the less sterically hindered complexes _trans_- Pt.tet.enCl_2^{2+} and _trans_- Pt.tet.enBr_2^{2+} (tet = $(CH_3)_2NCH_2CH_2N(CH_3)_2$) to see whether, by preventing the bridged redox mechanism, the redox mechanism would become a favourable path.

The trans- $[Pt.tet.enX_2]^{2+}$ - halide interchange reactions

Preparation of complexes

Bisethylenediamine platinum(II) chloride was prepared by a method similar to that of Basolo(22) et al in which a slight excess of ethylenediamine was added to a warm solution of chloroplatinate (II) to produce a solution containing $Pten_2^{2+}$ ions. An equivalent of chloroplatinate (II) was added to precipitate the pink $-Pten_2][PtCl_4]$. This was then dissolved in a slight excess of warm aqueous ethylenediamine to give a solution of $Pten_2^{2+}$. The complex was precipitated and washed with alcohol.

Trans- dichlorobisethylenediamine platinum(IV) chloride was prepared by oxidising a solution of $[Pten_2]Cl_2$ with chlorine according to a published method(22). The initial product which was precipitated with an alcohol and hydrochloric acid mixture had a distinctly yellow appearance.

However, after two recrystallisations from water by addition of alcohol and conc. hydrochloric acid the ultra-violet spectrum agreed with that in the literature.

Dichloro ($N\ N\ N^1N^1$ - tetramethylethylenediamine) - platinum(II) was prepared by the published method of Mann$^{(63)}$ and Watson in which the amine was added to a solution containing hexachloroplatinate(IV) ions. The initial orange precipitate of $[PtCl_6][(CH_3)_2\overset{+}{N}H\,CH_2\,CH_2H\overset{+}{N}(CH_3)_2]$ redissolved rapidly with the eventual precipitation of the required yellow complex which was recrystallised from water.

($N\ N\ N^1N^1$ - tetramethylethylenediamine)(ethylenediamine) platinum(II) chloride was prepared by adding slightly more than one equivalent of ethylenediamine to a hot solution of dichloro($N\ N\ N^1N^1$ - tetramethylethylenediamine)platinum(II). After filtering off any insoluble material, the solution was concentrated and the complex precipitated with alcohol. The complex was recrystallised from water by the addition of alcohol and conc. hydrochloric acid.

<u>Trans</u>- dichloro($N\ N\ N^1N^1$ - tetramethylethylenediamine) (ethylenediamine) platinum(IV) chloride was prepared by oxidising a hydrochloric acid solution of $[Pt.tet.en]Cl_2$ with chlorine. An orange precipitate which formed was

filtered off, this was probably the zero charged $[PtLCl_4]$ where L is en or tet. Yellow crystals of the complex were precipitated on concentrating and cooling the solution, these were filtered off and recrystallised twice from dilute hydrochloric acid.

Trans- dibromo(N N N^1N^1 - tetramethylethylenediamine) (ethylenediamine) platinum(IV) bromide was prepared by oxidising a hydrobromic acid solution of $[Pt en tet] Cl_2$ with bromine. The complex which precipitated on concentrating and cooling the solution was obtained as red crystals which were recrystallised twice from dilute hydrobromic acid solution.

Solutions of all these complexes of about 10^{-4} M. were stable over a period of days as judged by their unchanging ultraviolet and visible spectra. The complexes trans- $[Pt tet.en Cl_2]Cl_2$ and trans- $[Pt tet en Br_2]Br_2$ were analysed spectrophotometrically by reduction with an excess of sodium iodide, the I_3^- formed was estimated spectrophotometrically at 353 mμ. Details of the analyses together with the absorption spectra are given in table (17).

TABLE (17)

Complex	$\lambda_{max.}$ (mμ)	ε(l.mole^{-1} cm.$^{-1}$)
Trans-[Pt.en$_2$Cl$_2$]Cl$_2$	332	100[(a)]
	263	960[(a)]
[Pten$_2$]Cl$_2$	279	-
Trans-[Pten.tet.Cl$_2$]Cl$_2$	348	200
Trans-[Pten.tet.Br$_2$]Br$_2$	338	830
[Pten.tet.]Cl$_2$	290	60
	223	450

(a) Literature values:	$\lambda_{max.}$ (mμ)	ε(l.mole^{-1} cm.$^{-1}$)
	332	105
	263	950

Compound	Calculated % Pt.	Found % Pt.
Trans-[Pt.tet.en.Cl$_2$]Cl$_2$	38.0	37.5
Trans-[Pt.tet.en.Br$_2$]Br$_2$	28.2	28.7

The reaction of iodide with trans- $[Pt\,en_2Cl_2]^{2+}$

The product of the reaction, trans- $[Pt\,en_2I_2]^{2+}$, has an absorption maximum at 395 mμ, the value of the extinction coefficient was found to increase with increasing iodide concentration but to be unaffected by varying amounts of added $[Pt\,en_2]Cl_2$ provided sufficient Pt(II) was present to prevent reduction. This was in agreement with previous work(64). By observing the decrease in transmittance at 395 mμ, the formation of the diiodo complex was studied using the stopped-flow technique. The ionic strength was maintained at 1.0 M. with sodium perchlorate and the results are shown in table (18). Linear pseudo first order rate plots were obtained for over two half lives and each quoted rate constant was the average of three separate determinations. The standard deviation of the rate constants was calculated to be ±4%.

The reaction of iodide with trans- $[Pt\,en\,tet\,Cl_2]^{2+}$

The trans- $[Pt\,en\,tet\,Cl_2]^{2+}$ was quantitatively reduced to I_3^- at iodide concentrations greater than 0.01 M. At lower iodide concentrations, and in the presence of a large excess of $[Pt\,tet\,en]Cl_2$, there was no spectroscopic evidence for the formation of the diiodo complex. The visible spectrum

TABLE (18)

Rate constants for the reaction:

<u>Trans</u>-$[Pten_2Cl_2]^{2+}$ $\xrightarrow{I^-}$ <u>Trans</u>-$[Pten_2I_2]^{2+}$

T = 25° C.

μ = 1.0 M.

[Pt(IV)] = (1.96-2.08) 10^{-4} M.

$[I^-]$ (M)	$10^4[Pt(II)]$ (M)	$k_{obs.}$ $(sec.^{-1})$	10^4 k_3 $(M^{-2}$ $sec.^{-1})$
0.1	5.6	2.20	3.93
0.3	5.6	6.29	3.73
0.3	5.6	6.71	3.99 (a)
0.5	5.6	11.4	4.07
0.5	2.82	5.69	4.04
0.5	8.42	17.1	4.05

(a) $[Cl^-]$ = 0.2 M.

of a solution of $[\text{Pt en tet}]^{2+}$ in a five to ten fold excess of I_3^- was identical to that of I_3^- of the same concentration but in the absence of any $[\text{Pt en tet}]^{2+}$.

The rate of reduction of the chloro complex was followed, using the stopped-flow technique, by measuring the decrease in transmittance at 353 mμ which accompanies the formation of I_3^-. The ionic strength was maintained with sodium perchlorate. The results are given in table (19). Linear pseudo first order rate plots were obtained for between one and two half lives and the standard deviation of the individual rate constants was calculated at about ±2%. The activation enthalpies and entropies were obtained graphically.

The reaction of iodide with trans- $[\text{Pt en tet Br}_2]^{2+}$

The complex was reduced quantitatively to I_3^- at iodide concentrations $\gtrsim 0.5$ M. The reaction was followed by measuring the decrease in transmittance at 353 mμ, However, the reaction was only just measurable using the stopped-flow technique at iodide concentrations less than that required for complete reduction. Consequently the pseudo first order rate plots were curved and the initial slopes were taken as a measure of the rate. The results are given in table (20).

TABLE (19)

Rate constants for the reaction:

$\underline{\text{Trans}}\text{-}[\text{Pten.tet.Cl}_2]^{2+} \xrightarrow{I^-} I_3^- + [\text{Pt.tet.en}]^{2+}$

μ = 1.0 M.

[Pt(IV)] = (7.2-7.6) 10^{-5} M.

T(°C)	[I^-] (M)	10^4[Pt(II)] (M)	$k_{obs.}$(sec.$^{-1}$)	k_2(M^{-1}sec.$^{-1}$)
17.3	0.1	1.02	1.00	10.0
17.3	0.1	1.02	0.99	9.9$^{(a)}$
23.2	0.05	0.94	0.79	15.8
23.2	0.1	-	1.65	16.5
23.2	0.1	0.94	1.67	16.7
23.2	0.1	1.78	1.66	16.6
23.2	0.1	2.95	1.64	16.4
23.2	0.3	-	5.15	17.2
23.2	0.5	-	8.21	16.4
25.4	0.1	-	2.00	20.0
34.9	0.1	-	4.23	42.3
43.5	0.1	-	7.75	77.5

(a) [$IrCl_6^{2-}$] = 8.9 10^{-6} M.

$\Delta H^{\neq}$ = 13.7 kcal./mole.

$\Delta S^{\neq}$ = -6.7 cal.mole^{-1} deg.$^{-1}$.

TABLE (20)

Rate constants for the reaction:

$\underline{\text{Trans}}\text{-}[Pt.tet.enBr_2]^{2+} \xrightarrow{I^-} I_3^- + [Pten.tet]^{2+}$

μ = 1.0 M (with $NaClO_4$).

T = 24.9° C.

[Pt(IV)] = $1.51\ 10^{-4}$ M.

$[I^-]$ (M)	10^4 [Pt(II)] (M)	$k_{obs.}$ ($sec.^{-1}$)	k_2 ($M^{-1}\ sec.^{-1}$)
0.025	-	70	2,800
0.050	-	165	3,300
0.050	1.31	154	3,080

The reaction of bromide with trans- $[Pt\,en\,tet\,Cl_2]^{2+}$

The rate of formation of trans- $[Pt\,tet\,en\,Br_2]^{2+}$ was studied by measuring the increase in absorbance at 338 mμ, an absorption maximum of the dibromo complex. The ionic strength was maintained at 1.0 M. with sodium bromide and perchlorate. In the presence of added $[Pt\,tet\,en]Cl_2$ good linear pseudo first order rate plots were obtained for one to two half lives and the rates were a function of the [Pt(II)].. Extrapolation of the plot of k_{obs} against [Pt(II)] to zero [Pt(II)] gave a positive intercept. However, the first order rate plots in the absence of any added Pt(II) were curved and the initial slopes of these plots were more than twice the value of the intercept at zero [Pt(II)]. The results are given in table (21).

Spectroscopic Interaction

The spectrum of the dibromo complex was found to change on addition of free bromide ion, the increase was linear with concentration of Br^-. The spectroscopic changes were rapid and the resulting solutions were stable indefinitely. The results are shown in table (22).

TABLE (21)

Rate constants for the reaction:

$\underline{\text{Trans}}\text{-}[\text{Pt.tet.enCl}_2]^{2+} \longrightarrow \underline{\text{Trans}}\text{-}[\text{Pt.tet.en.Br}_2]^{2+}$

T = 65° C.

μ = 1.0 M.

[complex] = 4.10^{-4} M.

10^4[Pt(II)] (M)	[Br^-] (M)	$k_{obs.}$ (min.$^{-1}$)	$^{(a)}k_a$ (M^{-1} min.$^{-1}$)	$k_b^{(a)}$ (M^{-2} (min.$^{-1}$)
2.19	1.0	0.0646	4.05 10^{-2}	1.1 10^2
5.43	1.0	0.0991		
7.61	1.0	0.125		
7.61	0.5	0.0630		

(a) Values calculated according to the rate law:

$$k_{obs.} = k_a[Br^-] + k_b[Pt(II)][Br^-]$$

TABLE (22)

Spectroscopic interaction between Trans-[Pttet.en.Br_2]Br_2 and Br^-.

λ = 338 mμ. ($\lambda_{max.}$ of Trans-[Pt.tet.en.Br_2]Br_2).
μ = 1.0 M (with NaBr and $NaClO_4$).
T = 25.0° C.
[Pt(IV)] = 2.34 10^{-4} M.

$[Br^-]$ (M)	$A^{(a)}$	$\Delta A/[Br^-]$ (M^{-1})
0	0.194	-
0.33	0.232	0.114
0.66	0.271	0.116
1.0	0.310	0.116
1.0	$0.312^{(b)}$	0.118

(a) 1 cm. cells.
(b) $[Pt.tet.en]^{2+}$ = 1.0 10^{-4} M.

Discussion

Substitution of chloride or bromide by iodide ion does not occur in the compounds <u>trans</u>- $[\mathrm{Pt\ tet\ en\ X_2}]^{2+}$ (X = Cl or Br). Instead the complexes are reduced to I_3^- and presumably $[\mathrm{Pt\ tet\ en}]^{2+}$. The data in tables (3) and (4) show that the reduction is first order in both complex and iodide concentration. The rate of reduction of the chloro complex is unaffected by the presence of 10 mole % of $\mathrm{IrCl_6}^{2-}$. This would seem to indicate that a labile Pt(III) intermediate is not involved and that the reduction process is not two one electron transfers which would necessarily involve a Pt(III) intermediate.

Although it is not possible to make a definite choice as to the exact mechanism, the fact that substitution reactions of some cationic Pt(IV) complexes proceed via a bridged redox mechanism(1) would seem to indicate that the mechanism for the reduction of $[\mathrm{Pt\ tet\ en\ X_2}]^{2+}$ is as shown

$$\mathrm{X - Pt - X}^{2+} + \mathrm{I}^- \xrightarrow{\text{slow}} \mathrm{X \cdots Pt \cdots X \cdots I}^{+}$$

$$\xrightarrow{\text{fast}} \mathrm{X}^- + \mathrm{Pt(II)} + \mathrm{XI}$$

(The four nitrogens in the equatorial plane have been omitted for clarity). This is essentially a transfer of X^+ from the Pt(IV) to the I^- and is similar to the mechanism proposed for the substitution reactions of trans- $Pt(CN)_4X_2^{2-}$.

The absence of any Pt(II) catalysed substitution of the the halide by iodide is probably due to steric effects, the larger iodide ion being prevented from coordinating effectively to the platinum by the two methyl groups on each of two of the nitrogens.

The rate of reduction of the bromo complex is 150 times faster than that of the chloro complex, this ratio is not very different from the values of 400 for the reaction of trans- $Pt(CN)_4X_2^{2-}$ with iodide, and of 300 for the reaction of PtX_6^{2-} with iodide(10). The value of 13.7 k cal./mole for the activation enthalpy can be compared with the value of 16.7 kcal/mole for the reduction of $Pt(diars)_2Cl_2^{2+}$ by SCN^- (60), and with the values given in table (16) for the substitution of Cl^- or Br^- by I^- in PtX_6^{2-}. It can be seen that there is very little difference amongst the values and also the values of $\Delta S^{\neq}$ show no significant trends. However, the more positive value of -7 e.u. for the entropy of activation for the reduction of trans- Pt tet en Cl_2^{2+} by I^- may be due to the more favourable signs of the charges on the two ions coming together; this is rather speculative however in view of the difference in ionic strengths of the solutions. The $\Delta S^{\neq}$ value for the reduction of $Pt(diars)_2Cl_2^{2+}$ by I^- is also more positive (-2 e.u.) but this reaction was studied in methanol. It would thus appear from the similarity in the rate parameters of these systems that they all react by the same redox mechanism.

It might have been predicted that as I^- is a good reducing agent, the redox mechanism could have become a favourable path for the reaction of trans- $Pten_2Cl_2^{2+}$ with I^-. However, the rate is first order in complex, iodide and Pt(II) concentration, the pathway for substitution is therefore by means of the bridged redox mechanism. The rate constants for reactions of the type given below, which are known to proceed via the bridged redox mechanism(1)(62) are

$$X\text{-}Pt(IV)\text{-}X + \overset{*}{Pt}(II) + Y^- \longrightarrow Pt(II) + Y\text{-}\overset{*}{Pt}(IV)\text{-}Y + X^-$$

compared in the table:

X-Pt(IV)-X	Pt*(II)	Y	k_{25^oC}($M^{-2}sec.^{-1}$)
<u>trans</u>- $Pt(NH_3)_4Cl_2^{2+}$	$Pt(NH_3)_4^{2+}$	Cl	6.5
<u>trans</u>- $Pten_2Cl_2^{2+}$	$Pten_2^{2+}$	Cl	15.0
<u>trans</u>- $Pt(NH_3)_4Cl_2^{2+}$	$Pt(NH_3)_4^{2+}$	Br	108
<u>trans</u>- $Pten_2Cl_2^{2+}$	$Pten_2^{2+}$	I	4.10^4

It can be seen that the replacement of 2en by 4(NH_3) has only a relatively small effect upon the rate and so it is possible to compare the rates of substitution for reactions in which the leaving and bridging groups remain the same. The ratio of the rates is approximately $1:10:3.10^3$ for the order of entering groups Cl, Br and I. This order of reaction rates may be partly due to the increase in the value of the formation constant of the species Pt(II) - Y which reacts in a rate determining step with the Pt(IV) complex to form the bridged species. Also, the transition state may be different in each of these reactions. This order of reactivity is in contrast to that found for$^{(2b)}$ the substitution of ammonia in $Pt(NH_3)_5I^{3+}$ by halide ion, where the order of rates was $I^- \lesssim Cl < Br$; there was however a regular trend from Cl to I when the activation enthalpies were considered, the reaction with I^- having the lowest value.

The rate of substitution of chloride by bromide ion in trans- Pt tet en Cl_2^{2+} conforms to the two term rate law $k_{obs} = (k_a + k_b[Pt(II)])[Br]$ with $k_a = 4.05.10^{-2}$ M.$^{-1}$ min.$^{-1}$ and $k_b = 1.1.10^2$M.$^{-2}$min.$^{-1}$ at 65°C. The third order rate constant very probably represents the bridged redox mechanism and the value of the rate constant can be compared to that of 66.10^2M.$^{-2}$min.$^{-1}$ at 25°C. for the reaction of trans-$Pt(NH_3)_4Cl_2^{2+}$ with bromide. Probably the large decrease in rate for the complex trans- Pt tet en Cl_2^{2+} can be ascribed to the increase in steric crowding which hinders the close approach of the Pt(II) species. The k_a term is rather puzzling but it can not represent a residual rate due to some Pt(II) impurity in the Pt(IV) complex for two reasons: the analysis indicated that the complex was pure and if there were some Pt(II) impurity then the first order rate plots should be linear and not curved as was observed. If this k_a

term represents a redox reaction similar to that found in the reduction of trans- Pt tet en Cl_2^{2+} by I^- , then the value of $k_a = 4.05.10^{-2} M.^{-1} min.^{-1}$ can be compared with a value obtained from the activation energy plot, of $2.10^4 M.^{-1} min.^{-1}$ for the reduction of trans- Pt tet en Cl_2^{2+} by iodide. This would seem to indicate that I^- is a far better reducing agent than Br^- .

The observed changes in the spectra of trans- Pt tet en Br_2^{2+} in the presence of bromide ion are similar to that observed(65) for trans- Pt $en_2X_2^{2+}$ and X^- (X = Cl or Br). These changes were accounted for by the formation of an ion pair, the treatment being similar to that given for the trans-$Pt(CN)_4X_2^{2-}$ interaction with halide ion. A similar spectroscopic interaction has been observed(66) between trans-Rh $en_2I_2^+$ and I^- .

CHAPTER II

The Kinetics of Reactions of some Chloro-aminepalladium(II) Complexes with Hydrochloric Acid.

Introduction

A metal ion complex, ML_4, whose geometry is a square plane has two co-ordination positions, one above and one below the plane of the ion, which are open for nucleophilic attack, and in the case of a d^8 metal ion such as Pt(II) there is a vacant p_z orbital(35) which is not involved in the σ- bonding. Thus substitution reactions of square planar metal ions would appear to be best suited to proceed via a pathway in which the entering group is added in the first step to give an intermediate of increased co-ordination number; the vacant p_z valence orbital is available for forming the extra σ-bond required in this process. There is an increasing amount of evidence(36) to support the existence of a trigonal bipyramidal intermediate.

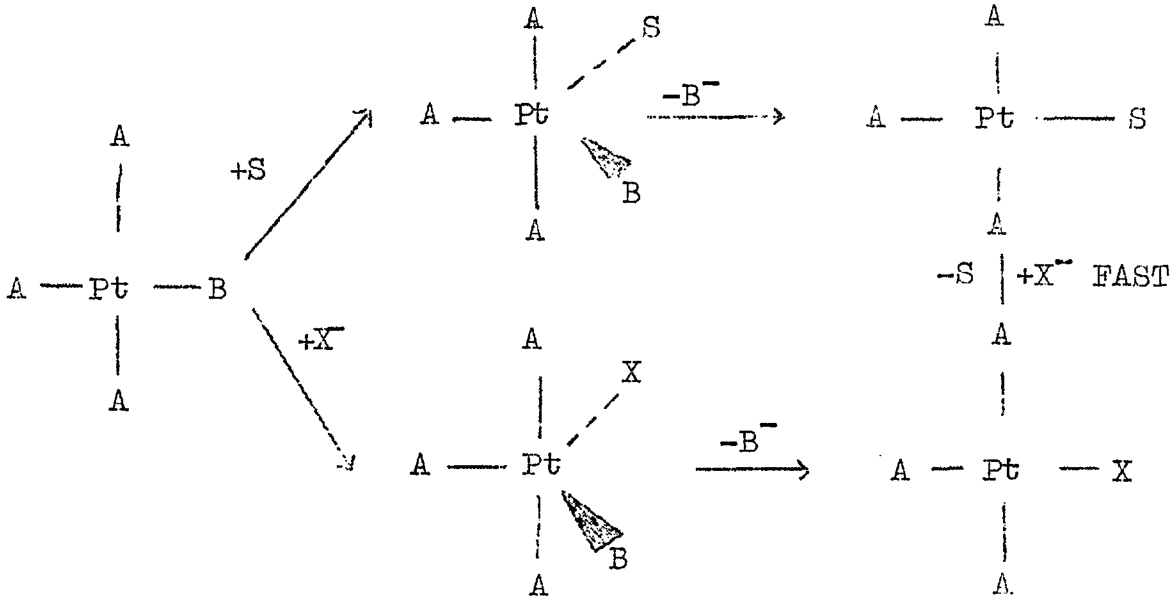
Complexes of Pt(II) are the most stable thermodynamically of those metal ions possessing square planar geometry and because of this the vast majority of studies involving substitution reactions of square planar complexes have been concerned with Pt(II). It has been found(35) that for most substitution reactions of the type

$$PtA_3B^{n+} + X^- \longrightarrow PtA_3X^{n+} + B^-$$

the observed rate constant under pseudo first order conditions i.e. when X^- is in excess, is given by the expression

$$k_{obs} = k_1 + k_2[X^-] \quad \ldots\ldots \quad (1)$$

where k_1 and k_2 are the first-order and second-order rate constants respectively. This two term rate law has been explained in terms of the two path mechanism shown below



The first order rate constant k_1 , which is equivalent to $k_1^{\prime}[S]$ where S is the solvent and k_1^{1} is a second order rate constant, is associated with the pathway involving nucleophilic attack by the solvent followed by a faster displacement of the solvent by the entering nucleophile. The second order rate constant, k_2, represents the direct attack by the nucleophile.

Although there has not been anything like as complete a study of other metals with square planar ions as there has been of Pt(II), from the available data it appears that the mechanism of substitution suggested for Pt(II) can be extended to other similar ions. Thus Au(III) is isoelectronic with Pt(II) and forms stable low-spin, square planar complexes, and the two term rate law now generally accepted as being common for square planar substitution was first postulated(37)(38) in a study of the exchange of $^{(36)}Cl^-$ with $AuCl_4^-$.

Data on the kinetics of substitution of other square planar ions are very sparse due, mainly, to their greater lability. A study(39) of the reaction

$$\text{Pd dien}X^+ + \text{py} \longrightarrow \text{Pd dien py}^{2+} + X^-$$

where X = Cl, Br or I and dien = $H_2NC_2H_4NHC_2H_4NH_2$, showed that it obeyed the two term rate law with the Pd(II) complex reacting about 10^5 times more rapidly than the corresponding Pt(II) complex. This greater lability is probably because the Pd(II) is able to add a fifth group more easily than Pt(II). Recent work(40)(41) on the sterically hindered complexes of the type $[Pd(amine)X]^+$, where amine = various substituted diethylenetriamines and X = Br or Cl, revealed that these complexes reacted much more slowly than the unhindered complex, [Pd dien X]$^+$, and, except for the nucleophile $S_2O_3^{2-}$ and the reaction of [Pd(Et$_4$ dien)Cl]$^+$ with OH$^-$, the rates of the reactions were independent of the reagent concentration. It was suggested that these complexes reacted by a solvent assisted dissociative process, as shown in equations 2 and 3

$$[\mathrm{Pd(amine)X}]^+ + H_2O \xrightarrow{\mathrm{SLOW}} [\mathrm{Pd(amine)H_2O}]^{2+} + X^- \quad \ldots (2)$$

$$[\mathrm{Pd(amine)H_2O}]^{2+} + Y^- \longrightarrow [\mathrm{Pd(amine)Y}]^+ + H_2O \quad \ldots (3)$$

The reaction of [Pd(Et$_4$dien)Cl]$^+$ with OH$^-$ obeys a two term rate law similar to equation 1 : the k_1 path was presumed to be the same as that in equations 2 and 3 above, the k_2 path, however, was assumed to involve a rapid acid-base equilibrium followed by a reaction of the conjugate base as shown in equations 4-6.

$$[\mathrm{Pd(Et_4dien)Cl}]^+ + OH^- \overset{K}{\rightleftharpoons} [\mathrm{Pd(Et_4dien\text{-}H)X}] + H_2O \quad \ldots \quad (4)$$

$$[\mathrm{Pd(Et_4dien\text{-}H)X}] \xrightarrow[\mathrm{SLOW}]{k^1} [\mathrm{Pd(Et_4dien\text{-}H)}]^+ + X^- \quad , \ldots\ldots (5)$$

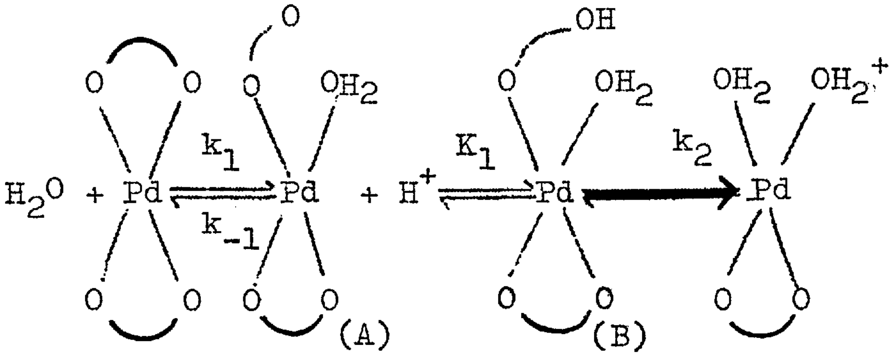
$$[\mathrm{Pd(Et_4dien\text{-}H)}]^+ + H_2O \xrightarrow{\mathrm{fast}} [\mathrm{Pd(Et_4dien)OH}]^+ \quad \ldots\ldots (6)$$

The behaviour of $S_2O_3^{2-}$ was attributed to the large nucleophilic reactivity constant of the ion and also to its double charge which would facilitate ion pair formation.

Pearson and Johnson(42) studied some substitution reactions of acetylacetonatopalladium(II) complexes in acid media. They found that for the reaction

$$Pd(acac)_2 + H^+ + 2H_2O \longrightarrow Pd(acac)(OH_2)_2^+ + Hacac$$

the observed rate constant was a function of the acid concentration. The mechanism proposed was



There is an initial displacement of one end of the chelating acetylacetonate by the water molecule, the half bonded chelate can then either react with a proton to form a species which would lead to product formation or else reclose the chelate ring to form the original complex. Assuming a steady state for (A) and (B), the observed rate constant is given by the expression

$$k_{obs} = \frac{k_1 k_2 K[H^+]}{k_{-1} + k_2 K[H^+]} \quad \ldots\ldots \quad (7)$$

This accounts for the observed dependence of the rate on $[H^+]$ with a limiting rate being attained at high $[H^+]$. In the presence of added nucleophiles such as Cl^- or Br^- there is an additional path to the one given above in which the nucleophile displaces one end of the chelate. The product under these conditions is $[Pd(acac)Cl_2]^-$; the rate of the reaction of Cl^- with both $[Pd(acac)(OH_2)_2]^+$ and $[Pd(acac)OH_2Cl]$ is assumed to be fast. This additional path leads to a second term in the expression for the observed rate constant which is similar to that in equation (7) but contains the extra concentration term $[Cl^-]$ in the numerator. This expression predicts that at a constant $[H^+]$ the variation of k_{obs} with $[Cl^-]$ should obey a two term rate law similar to equations (1). This was found to be so experimentally.

It was decided to extend this work to other palladium complexes containing chelating amines and study the kinetics of replacement of these amines in the presence of hydrogen and chloride ions to see whether similar behaviour occurs. Also, for the sake of comparison, some complexes containing non chelating amines have been studied.

Experimental

Standard solutions of sodium chloride and perchlorate were made up by weighing the dried, finely powdered G.P.R. salts into graduated flasks, and dissolving them in the required volume of distilled water. Standard solutions of lithium chloride were made up by dissolving the G.P.R. salt in distilled water and analysing for chloride by Mohr's method. Ethylene diamine and diethylenetriamine, both technical grade, were obtained from B.D.H., 1, 1, 7, 7, tetraethyldiethylenetriamine was obtained from Ames Laboratories, Milford, Conn., U.S.A. G.P.R. diethylamine was obtained from Hopkins and Williams. The remainder of the reagents were of AnalaR grade.

Kinetic Studies

All the reactions were studied by observing changes in absorbance in the ultraviolet region either by scanning the whole of the spectrum with a Perkin Elmer 137 U.V. spectrophotometer or else by taking measurements at one wavelength with a Unicam S.P.500. The Perkin Elmer recording spectrophotometer was fitted with an Adkins, electrically controlled, thermostatted cell holder which holds cells of up to 1 cm.

path-length, while the Unicam spectrophotometer was fitted with a Unicam cell holder capable of holding cells of path-length up to 4 cm. Thermostatted liquids were circulated through the Unicam cell holder. It was possible to control the temperature of the cells to better than ±0.1°C over a temperature range from about 40 to 80° C in the Perkin Elmer spectrophotometer and from about 5 to 90°C in the Unicam spectrophotometer.

Most of the kinetic runs were followed by mixing rapidly in a silica cell the separate solutions of reagents, which had been thermostatted at the temperature under investigation. The cell was then transferred to the thermostatted compartment of the spectrophotometer. Some of the slower kinetic runs were followed by removing aliquots from a reaction mixture kept in a thermostatted oil bath. The aliquots were rapidly cooled and the absorption spectra recorded.

Large excesses of both hydrogen ions and chloride ions were used to ensure pseudo first order conditions for the reactions. The ionic strengths were kept constant with perchlorate salts. The rate constants were determined graphically by plotting log $(A_{\infty} - A_t)$ against t (A_{∞} and A_t

are the absorbances of the solution at the end of the reaction and after a time t respectively). Activation parameters were also estimated graphically. For the uncharged complexes, the reactions were followed in 5 or 10% aqueous ethanolic solution by dissolving the complex rapidly in 50% ethanol and then diluting immediately with suitable amounts of aqueous solutions of the other reagents. Solutions of these uncharged complexes in 50% ethanol darkened on standing with the eventual formation of a black precipitate. Thus, solutions of the complex trans- $Pd(NH_3)_2Cl_2$ became dark after a period of three to four hours whereas solutions of the complex cis-$Pd(NH_3)_2Cl_2$ were noticeably dark after 10 to 15 minutes. Because of this fresh solutions of these neutral complexes were used for every kinetic run.

Preparation of Complexes

Chloro - 1,1,7,7, tetraethyldiethylenetriaminepalladium(II) chloride

This was prepared by adding the triamine (2 ml.) to a solution of palladium dichloride (0.5 g.) in concentrated hydrochloric acid (1.3 ml.). An orange solid may precipitate, but this dissolves on heating. 6 M. aqueous lithium chloride solution (5 ml.) was added and the mixture cooled in a refrigerator. Bright yellow crystals of the complex were filtered off and washed with ice-cold water and dry ethanol, and air dried. Yields of the order of 10% were obtained by this method, however, yields of about 20% could be obtained of the bromo complex by using sodium bromide in place of lithium chloride. The initial product of the bromo complex was recrystallised from a 50% ethanol-water mixture, and obtained as yellow needles. The chloro complex could then be made in situ by dissolving a known weight of the bromo complex in 0.5 M. aqueous sodium chloride and leaving the solution to stand, at room temperature, for 24 hours. The ultraviolet and visible absorption spectra were then identical with those obtained from the isolated complex.

Chlorodiethylenetriaminepalladium(II) chloride

The complex was prepared according to the published method(39) by adding the triamine to palladium dichloride, but, concentrated lithium chloride solution was used instead of ammonium chloride. The solution was cooled in a refrigerator overnight to precipitate the complex which was filtered off, washed with ice cold water, dry ethanol and ether, and air dried. Yield 25-30%.

Dichloro ethylenediaminepalladium(II)

This compound was prepared according to a published method(43) and was obtained as yellow needles in 50% yield.

Trans- dichlorodiamminepalladium(II)

This complex was prepared in a similar manner to that for the ethylenediamine complex except that AnalaR ammonia was used in place of the ethylenediamine,

Cis- dichlorodiamminepalladium(II)

This was prepared according to Grinberg's method(44). An aqueous solution of ammonium acetate (1.16 gms. in 7.5 mls.) was added to aqueous sodium tetrachloropalladate(II) (0.5 gms. in 5 mls.). The solution was cooled for 40 minutes in a refrigerator and the yellow precipitate was filtered off and washed with ice-cold water, and air dried. (Yield 60%). This compound was shown to be different from the corresponding *trans*- complex by its reaction with potassium iodide dissolved in acetone. The *cis*- complex gave a dark red colour whereas the *trans* gave a pale yellow colour(44).

Trans- dichlorobis(diethylamine)palladium(II)

The amine (0.9 mls.) was added to a solution of sodium tetrachloropalladate(II) (0.5 gms.) in 0.5 M. hydrochloric acid (10 mls.). After filtering, the solution was slightly acidified with 2 M. hydrochloric acid and cooled in the refrigerator. The resulting yellow precipitate was filtered off, washed with water, dry ethanol, and ether, and dried in air (yield 45%). The trans- configuration was assigned on the basis of the preparative method, and on the reaction with iodide in acetone solution.

All the complexes were analysed spectrophotometrically by conversion to tetrachloropalladate(II). A known weight of the complex was heated with 5 mls. of 5 M. hydrochloric acid for several hours at 70°C. The solution was cooled and diluted to 100 mls. so that the final solution had a chloride concentration of 2.0 M. and an ionic strength of 4.5 M. maintained with sodium perchlorate. The tetrachloropalladate (II) ion has an extinction coefficient of $(11.2 \pm 0.05) \times 10^3$ $1.mole.^{-1}$ $cm.^{-1}$ at 279 mμ under these conditions(45). Suitable weights of the complexes were taken to give an optical density in 1 cm. or 1 mm. silica cells of about 0.4. This is the region of maximum sensitivity of the Unicam

S.P.500 spectrophotometer. The analytical data and details of the main absorption maxima and their extinction coefficients are given in table (I).

The agreement in the anlyses between the experimental and the theoretical values is quite good in all cases except that of the complex [Pd(Et_4dien)Cl]Cl which has a low value. This may be due to the presence of some lithium chloride that was used to precipitate the complex. For the remaining complexes the difference between the experimental and calculated values is less than 0.6%, almost half of which could have been caused by the uncertainty in the value of the extinction coefficient of the tetrachloropalladate(II) ion. Any impurities such as trans- $Pd(NH_3)_2Cl_2$ or $[Pd(NH_3)_4][PdCl_4]$, in the cis- $Pd(NH_3)_2Cl_2$ would not be revealed by this analytical procedure however, the differences between the spectra of the cis- and trans- complexes is quite marked. Thus the cis- complex has one maximum at ~ 375 mμ , and the absorbance rises steeply to shoulders at 290 and 260 mμ , whereas the trans- complex has two poorly resolved maxima at 350 and 380 mμ and the absorbance rises steeply to a shoulder at ~250 mμ . It would therefore, be possible to detect any substantial trans impurity in the cis complex.

Table (I)

Analytical data and some details of absorption spectra for some chloro-aminepalladium(II) complexes

Complex	% Pd	
	Found	Calculated
$[Pd(Et_4dien)Cl]Cl$	25.5	27.1
$[Pd(Et_4dien)Br]Br$	22.1	22.1
$[Pd(dien)Cl]Cl$	38.4	37.9
Pd en Cl_2	44.8	44.8
<u>Trans</u>- $Pd(NH_3)_2Cl_2$	50.9	50.3
<u>Cis</u>- $Pd(NH_3)_2Cl_2$	49.8	50.3
<u>Trans</u>- $Pd(Et_2NH)_2Cl_2$	33.3	32.9

Table (I) contd.

Complex	λ(mμ)	E(1.mole.$^{-1}$cm.$^{-1}$)
[Pd(Et$_4$dien)Cl]Cl	350	900$^{(a)}$
[Pd(Et$_4$dien)Br]Br	362	740$^{(a)}$
[Pd(dien)Cl]Cl	330	480$^{(b)}$
$^{(c)}$Pd en Cl$_2$	373, 255(Sh)	-, -
$^{(c)}$*Trans*- Pd(NH$_3$)$_2$Cl$_2$	380, 350, 250(Sh)	-, -, 3.10^3
(c)*Cis*- Pd(NH$_3$)$_2$Cl$_2$	375, 290(Sh), 260(Sh)	-,1.5.10^3, 4.10^3
Trans- Pd(Et$_2$NH)$_2$Cl$_2$	(d)	

(a) These values were obtained in a sufficient excess of free halide ion to suppress hydrolysis.

(b) Cf. E = 500, given by Baddley *et al.*, Inorg, Chem., **2**, 921 (1963).

(c) The weaker absorption bands were detected in saturated solutions for which the concentrations were not known, and no extinction coefficients can be quoted.

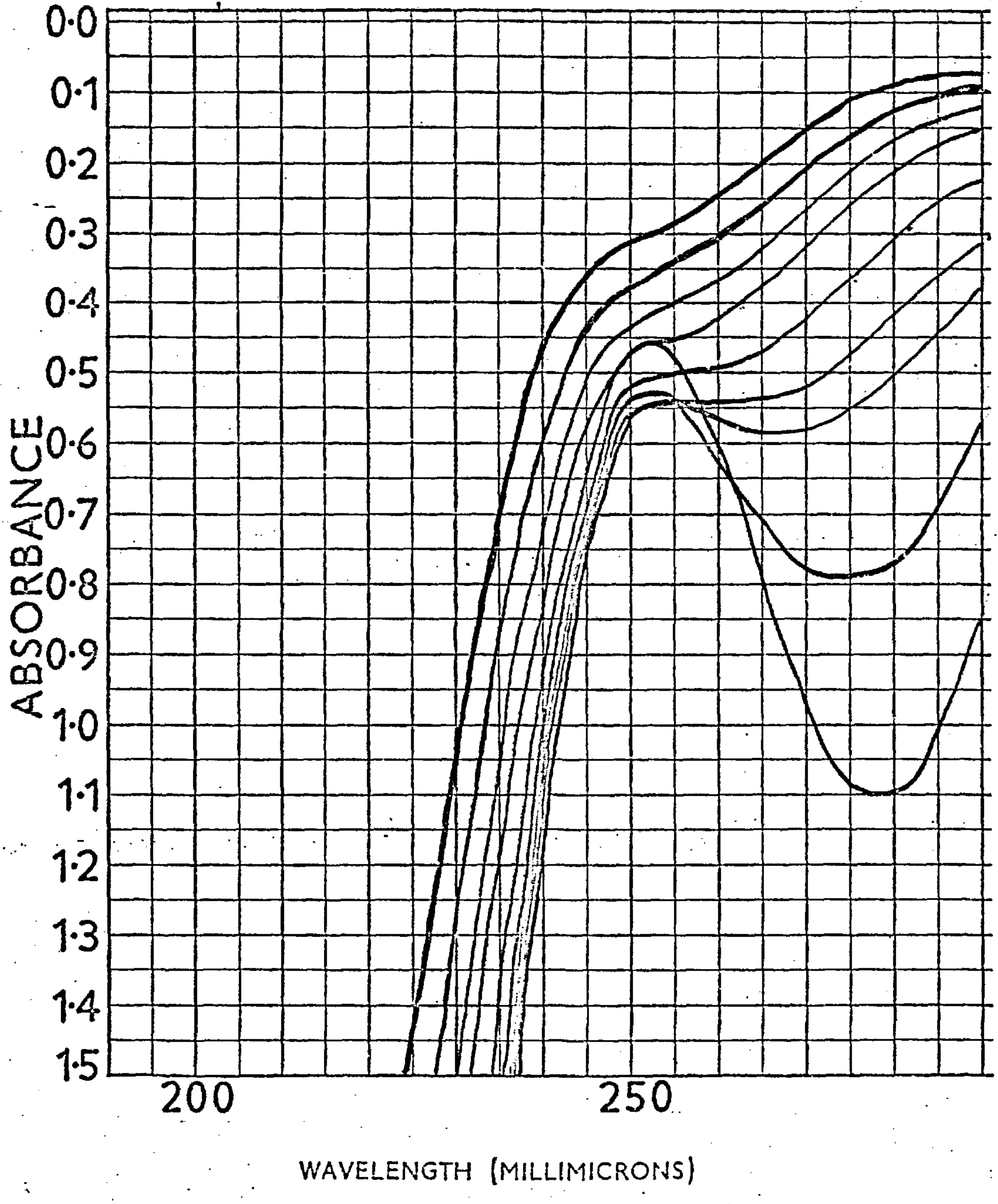
(d) No significant absorption above 300 mμ, absorbance rises steeply to a maximum below 230 mμ.

Results

The $PdenCl_2 \longrightarrow PdCl_4^{2-}$ reaction

When $PdenCl_2$ was reacted with hydrochloric acid in 5 to 10% aqueous ethanol, a two stage reaction was observed with an isosbestic point at 315 mμ during the first stage and at 240 and 263 mμ during the second. There was no reaction in the absence of both hydrogen and chloride ions.

When the first stage was followed to completion in 0.9 M. hydrochloric acid and a few drops of concentrated lithium chloride solution added the reaction recommenced and a new value of the infinite absorbance was reached which was some 20% higher. It was thus apparent that the first stage was an approach to an equilibrium mixture. The first stage was studied at an ionic strength of 4.4 M. where it was found that the rate of approach to the equilibrium was independent of $[H^+]$ above a concentration of 1.8 M. but was first order in $[Cl^-]$. At the acidities of the experiments it is very likely that the intermediate is the ion $Pd(enH)Cl_3$. If this were so then the pK_a of the ion should be very similar to the value of 7 for the first acid dissociation constant of enH_2. Measurements of the pK_a of the acid $Pt(enH)NH_3Cl_2^+$ support this. This compound was made as the chloride salt



Spectral changes during the reaction

$PdenCl_2 \longrightarrow Pd(enH)Cl_3$

according to Drew's method(46). It was not possible to determine the pK_a by a normal pH titration as the acidity of the solution increased steadily owing to the fairly rapid reaction $Pt(enH)NH_3Cl_2^+ \longrightarrow PtenNH_3Cl^+ + H^+ + Cl^-$. An approximate value was obtained by extrapolating the pH of the solutions back to the time of dissolution of the complex, and calculating the pK_a from the formula for the pH of a weak acid i.e. $pH = \frac{1}{2} pK_a - \frac{1}{2}\log.C$. For a 4.10^{-3}M. solution of the complex, the pH at dissolution was 4.9, and this gives a value of 6.4 for the pK_a which compares favourably with the value for the first acid dissociation constant of enH_2^{2+}.

If the reaction of $Pd(enH)Cl_3$ to re-form $PdenCl_2$ is a first order reaction then the situation can be represented as

$$A \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} B$$

the pseudo first order rate constant for the forward reaction k+1, can be evaluated from the equation

$$\frac{x_e}{a} \ln \frac{x_e}{(x_e - x)} = k_{+1}t \qquad \ldots\ldots \qquad (8)$$

where 'a' is the original concentration of A, 'x' is the concentration of B after a time t, and 'x_e' is the concentration of B at equilibrium. Equation (8) can be rewritten in terms of the absorbances of the solution as in equation (9)

$$\frac{(A_\infty)_{obs} - Ao}{(A_\infty)_{theo} - Ao} \ln \frac{(A_\infty)_{obs} - Ao}{(A_\infty)_{obs} - A_t} = k_{+1}t \quad \ldots \quad (9)$$

$(A_\infty)_{theo}$ is the absorbance for complete reaction, $(A_\infty)_{obs}$ is the absorbance at equilibrium A_o is the absorbance at the commencement of the reaction and corresponds to the absorbance of $PdenCl_2$, A_t is the absorbance of the solution at a time t during the reaction. The first stage was followed at 263 mμ, one of the isosbestic points for the two species $Pd(enH)Cl_3$ and $PdCl_4^{2-}$ so that $(A_\infty)_{theo}$ was obtained by converting the complex completely to $PdCl_4^{2-}$. The results are given in table (2). At an ionic strength of 4.4 M. the change in absorbance, in 1 cm. cells was from about 0.1 to 0.4 whereas at an ionic strength of 1.0 M., the change in absorbance was smaller, about 0.15, and hence the rate constants were less accurate. At the lower ionic strength the reaction probably does not go so far to completion, this

TABLE (2)

Rate constants for the reaction $PdenCl_2 \longrightarrow Pd(enH)Cl_3$
Solvent was 10% aqueous ethanol.
[complex] = 7.10^{-5} M.

(i) μ = 4.4 M.

T(°C)	$[H^+]$ (M)	$[Cl^-]$ (M)	10^3 $k_{obs.}$ ($sec.^{-1}$)
25.0	4.44	0.89	0.369
35.0	4.44	0.89	0.90
35.0	4.44	2.67	2.70
35.0	1.78	2.67	2.75
35.0	4.44	4.44	5.00
45.4	4.44	0.89	2.36

(ii) μ = 1.0 M

$[H^+]$ (M)	$[Cl^-]$ (M)	10^3 $k_{obs.}$ ($sec.^{-1}$)
1.00	1.00	36.0
1.00	0.50	20.5
0.50	1.00	36.0

is especially true at the lower chloride concentrations. Thus the range of concentrations available at this ionic strength was limited. It was found however that at both ionic strengths the reaction was first order in $[Cl^-]$ but independent of $[H^+]$.

Using the results of the kinetics of the first stage it was possible to calculate an approximate value for the equilibrium constant, K, for this reaction. Values of K at 35°C and an ionic strength of 4.4 M. were calculated using equation (10).

$$K = \frac{\left\{(A_\infty)_{obs} - A_o\right\}}{\left\{(A_\infty)_{theo} - (A_\infty)_{obs}\right\}} \qquad \frac{1}{[Cl^-]} \qquad \ldots \qquad (10)$$

When $[Cl^-]$ = 0.9, 2.67, and 2.67 M., and $[H^+]$ = 4.4, 4.4, and 1.76 M. the values of K were 15.9, 9.1, and 13.5 $l.mole^{-1}$, respectively.

The kinetics of the second stage were followed at 279 mμ, a maximum in the absorption spectrum of $PdCl_4^{2-}$. The results are given in table (3). At an ionic strength of 1.0 M. the dependence of the rate was slightly less than first order in $[H^+]$ and was slightly greater than first order in $[Cl^-]$, figure (1). However, at an ionic strength of 5.0 M. the

TABLE (3)

Rate constants for the reaction $Pd(enH)Cl_3 \longrightarrow PdCl_4^{2-}$

(i) $\mu = 1.0$ M

Solvent was 10% aqueous ethanol.
[complex] = 7.10^{-5} M T = 40.0°C.

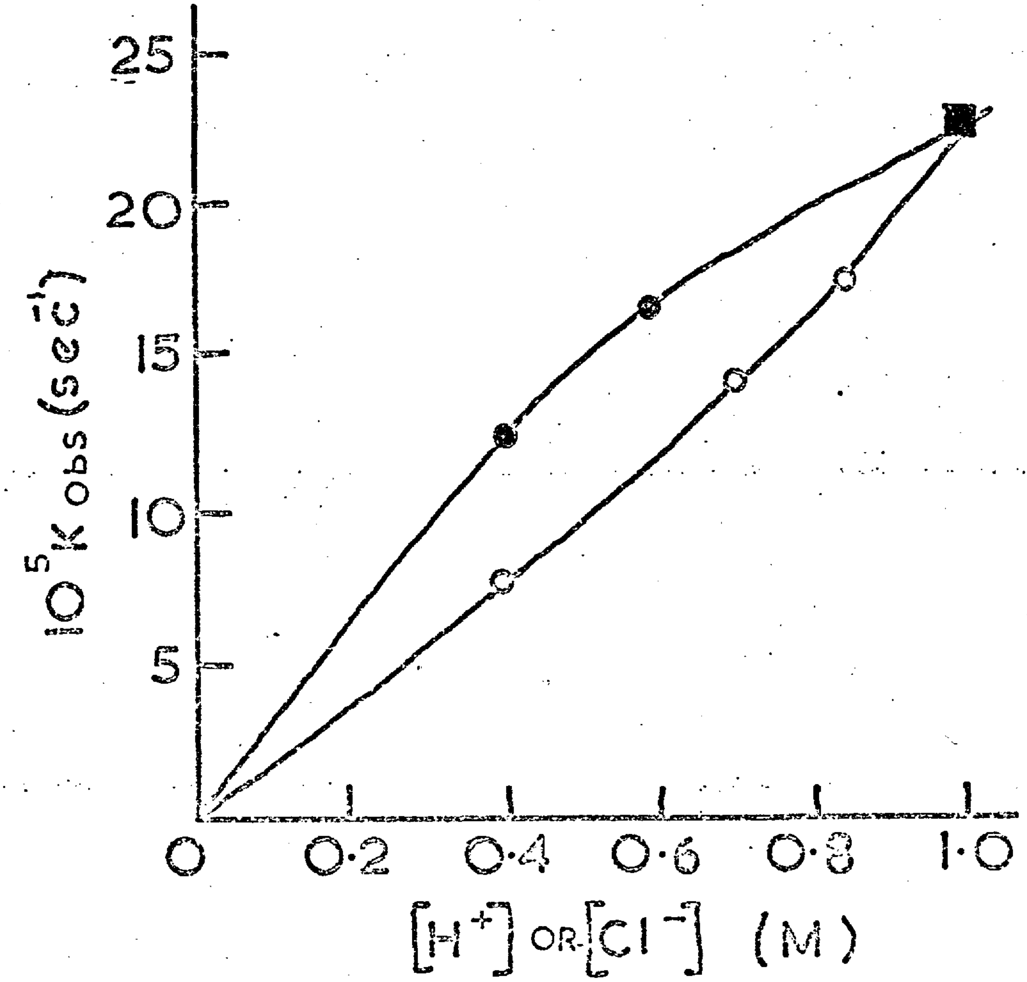
$[H^+]$ (M)	$[Cl^-]$ (M)	10^5 $k_{obs.}$ ($sec.^{-1}$)
1.0	0.4	7.8
1.0	0.7	14.3
1.0	0.85	17.5
1.0	1.0	22.6
1.0	1.0	22.6
0.6	1.0	16.5
0.4	1.0	12.5

(ii) $\mu = 5.0$ M

Solvent was 5% aqueous ethanol.
[complex] = $10.^{-4}$ M.

T(°C.)	$[H^+]$ (M)	$[Cl^-]$ (M)	10^5 $k_{obs.}$ ($sec.^{-1}$)
30.6	5.0	1.0	17.8
40.0	0.2	1.0	27.1
40.0	0.5	1.0	38.0
40.0	1.0	1.0	41.5
40.0	2.5	1.0	42.3
40.0	5.0	1.0	45.1
40.0	1.0	2.5	86.5
40.0	1.0	5.0	178.
44.1	5.0	1.0	77.8
49.0	5.0	1.0	126.

Figure 1.

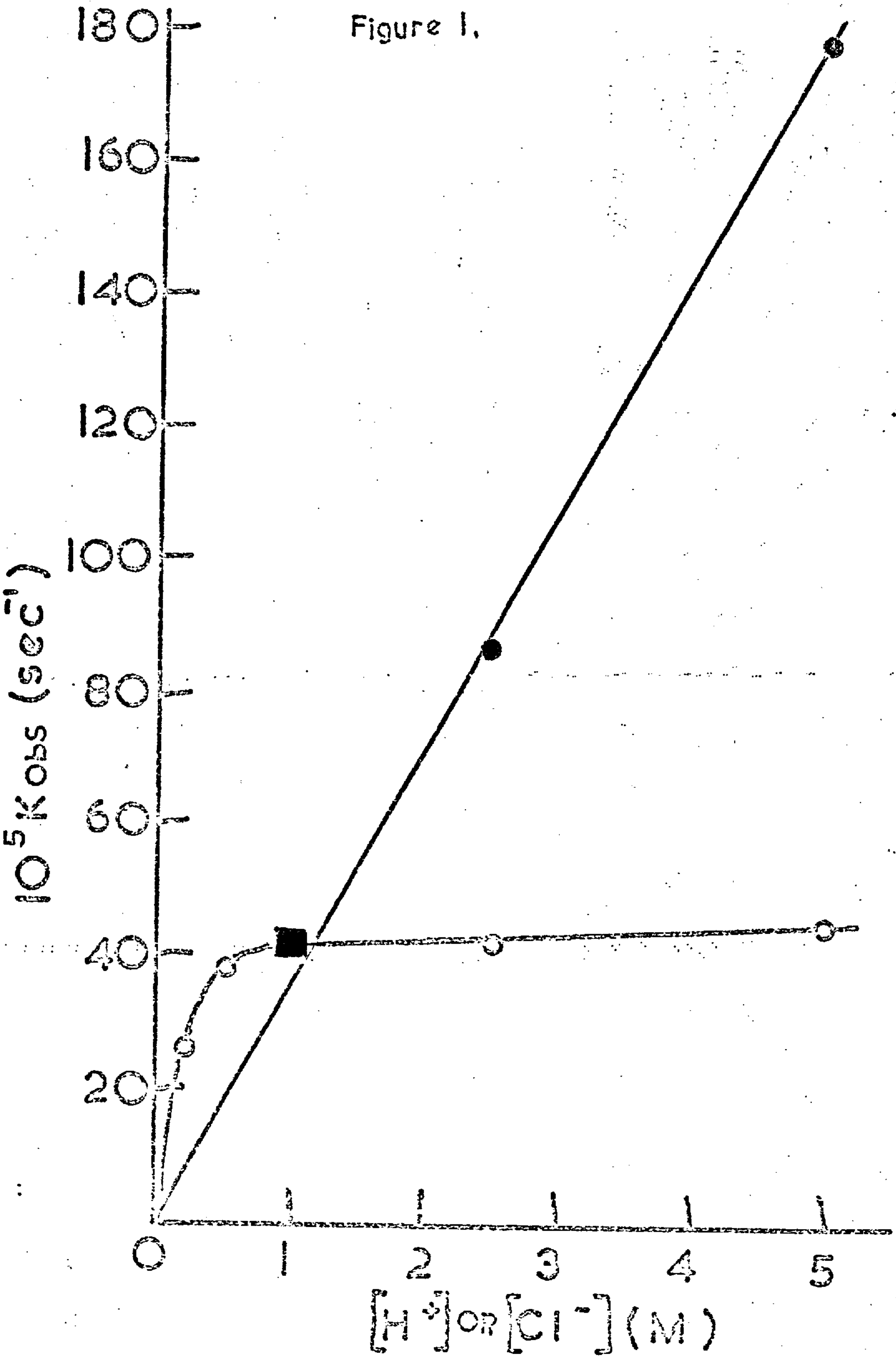


Rate constants for the reaction $Pd(enH)Cl_3 \longrightarrow PdCl_4^{2-}$

(a) μ=I.0M; ●: k_{obs} vs. [H$^+$] with [Cl$^-$] =I.0M;

○: k_{obs} vs. [Cl$^-$] with [H$^+$]=I.0M; ■: [H$^+$]= [Cl$^-$] =I.0M.

Figure 1.



(b) μ =5.0M; ○ : k_{obs} vs. $[H^+]$ with $[Cl^-]$=1.0M;

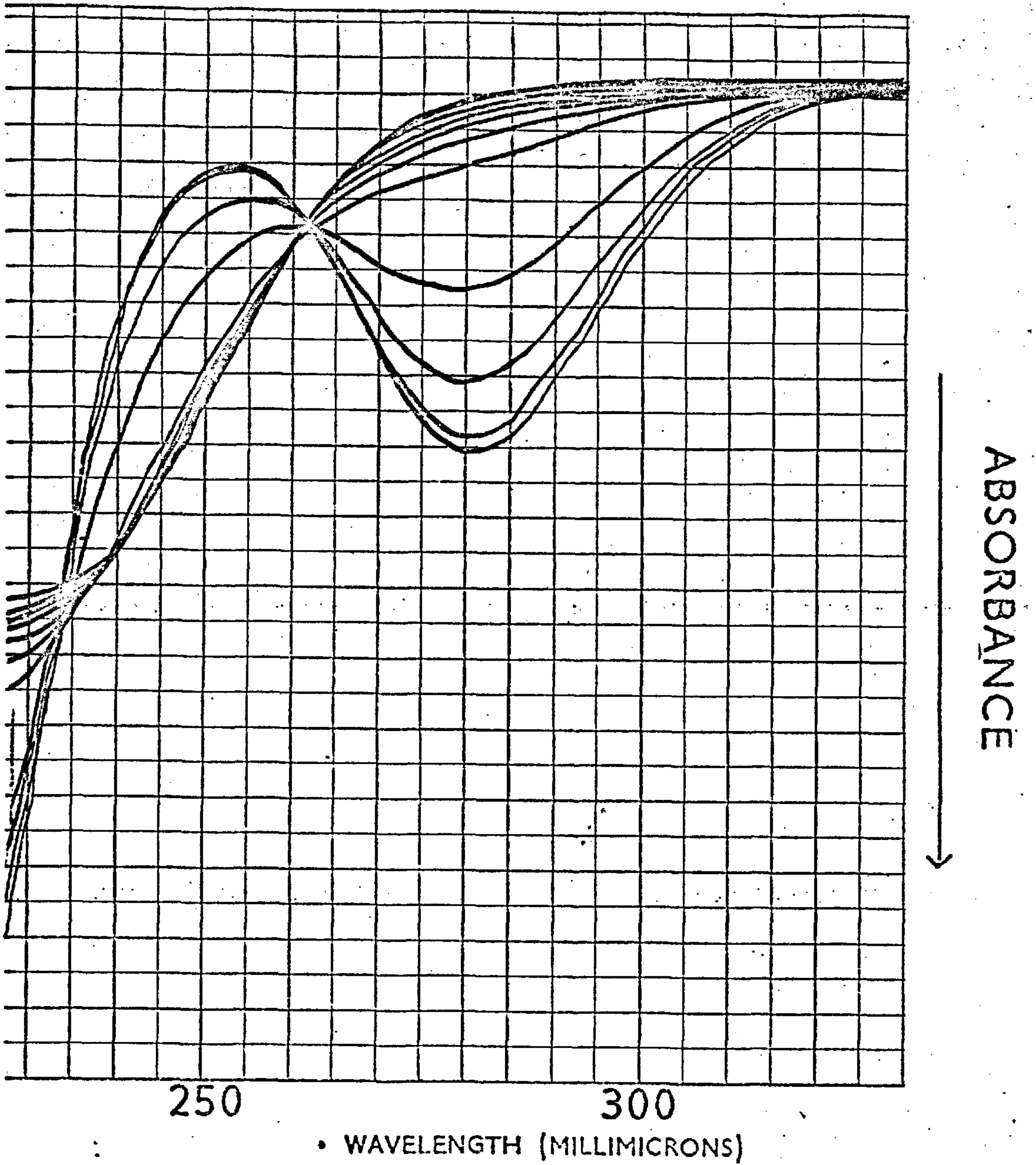
● : k_{obs} vs. $[Cl^-]$ with $[H^+]$=1.0M; ■ : $[H^+]$= $[Cl^-]$ =1.0M.

reaction was first order in $[Cl^-]$ and showed a dependence on $[H^+]$ which decreased sharply above $[H^+] = 1.0$ M.

Activation parameters for both stages are given in table (9).

The $[Pd(Et_4dien)Cl]^+ \longrightarrow PdCl_4^{2-}$ reaction

The reaction of the $Pd(Et_4dien)Cl^+$ ion with hydrochloric acid proceeded in two quite well defined steps, characterised by two successive sets of isosbestic points at 240 and 261 mμ, and at 233 and 262 mμ. Accurate kinetic measurements on the first stage were not possible because of the small absorbance change. However, the second stage showed clearly the formation of the spectrum of $PdCl_4^{2-}$ and the kinetics in solutions of ionic strength 1.0 M. and 5.0 M. were followed at 279 mμ. The results are given in table (4) and figure (2). It can be seen that at $\mu = 1.0$ M. and $[Cl^-] = 1.0$ M. the rate increased with $[H^+]$, appearing to approach a limiting rate, whereas at $[H^+] = 1.0$ M. the reaction was first order in $[Cl^-]$. At $\mu = 5.0$ M. the reaction was slightly faster at $[H^+] = 5.0$ M. than at $[H^+] = 2.0$ M., the $[Cl^-]$ being 5.0 M. The dependence on $[Cl^-]$ was first order up to $[Cl^-] = 2.5$ M. but above this concentration the order of the reaction seemed to increase slightly. Activation parameters are given in table (9)



Spectral changes during the reaction

$\mathrm{Pd(Et_4dien)Cl^{+}} \longrightarrow \mathrm{PdCl_4^{2-}}$

TABLE (4)

Rate constants for the reaction $[Pd(Et_4dien\ H_2)Cl_3]^+ \rightarrow PdCl_4^{2-}$

[complex] = 6 to 8.5 x 10^{-5} M.

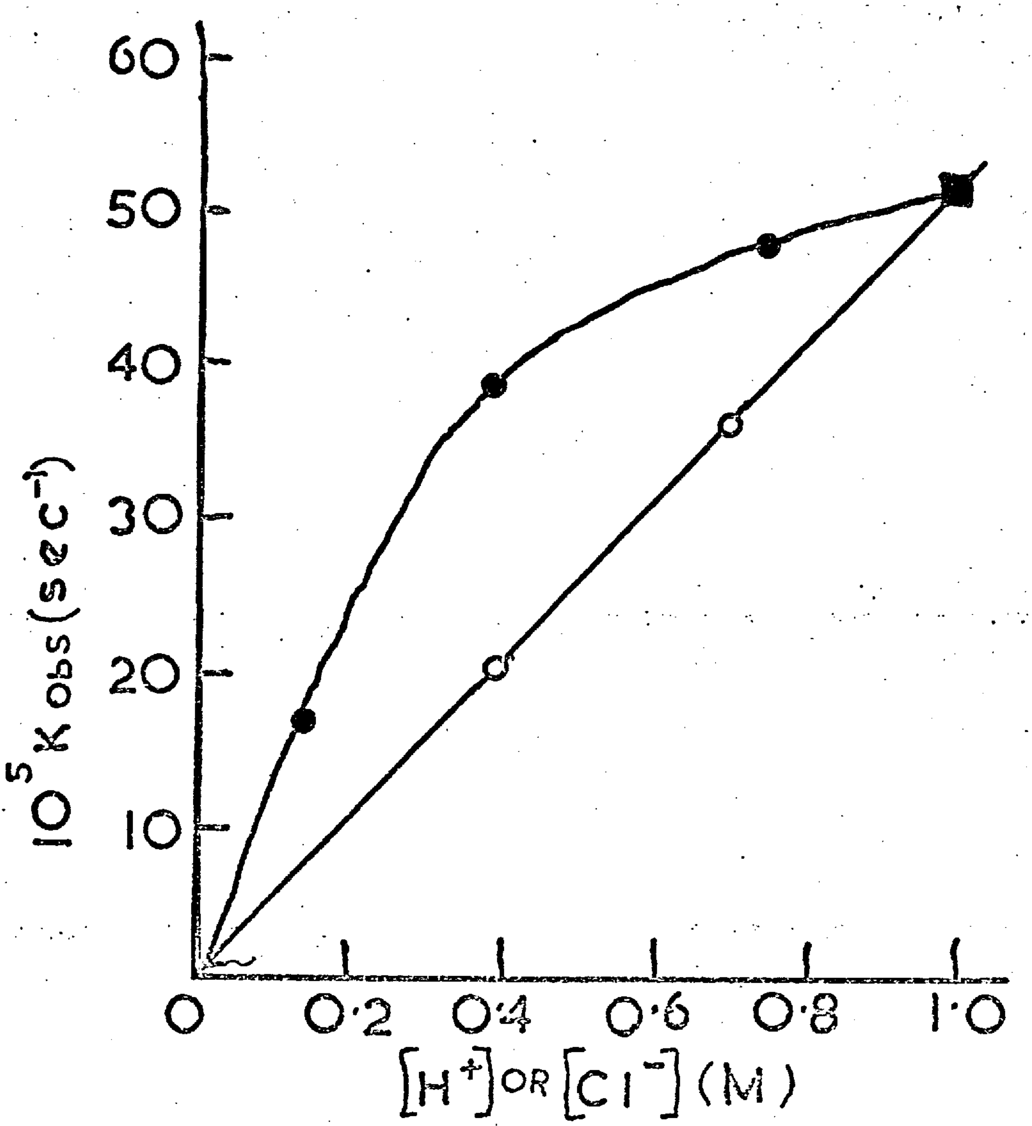
(i) μ = 1.0 M; T = 30.0° C.

$[H^+]$ (M)	$[Cl^-]$ (M)	$10^4\ k_{obs.}$ (sec.$^{-1}$)
1.0	1.0	5.11
1.0	0.7	3.61
1.0	0.4	2.05
0.75	1.0	4.76
0.4	1.0	3.91
0.15	1.0	1.71

(ii) μ = 5.0 M.

T (°C.)	$[H^+]$ (M)	$[Cl^-]$ (M)	$10^4\ k_{obs.}$ (sec.$^{-1}$)
20	5.0	1.0	0.78
20	5.0	2.0	1.64
20	5.0	2.5	2.03
20	5.0	4.0	3.87
20	5.0	5.0	5.36
20	2.0	5.0	4.78
30	5.0	1.0	2.35
39.4	5.0	1.0	6.36

Figure 2.

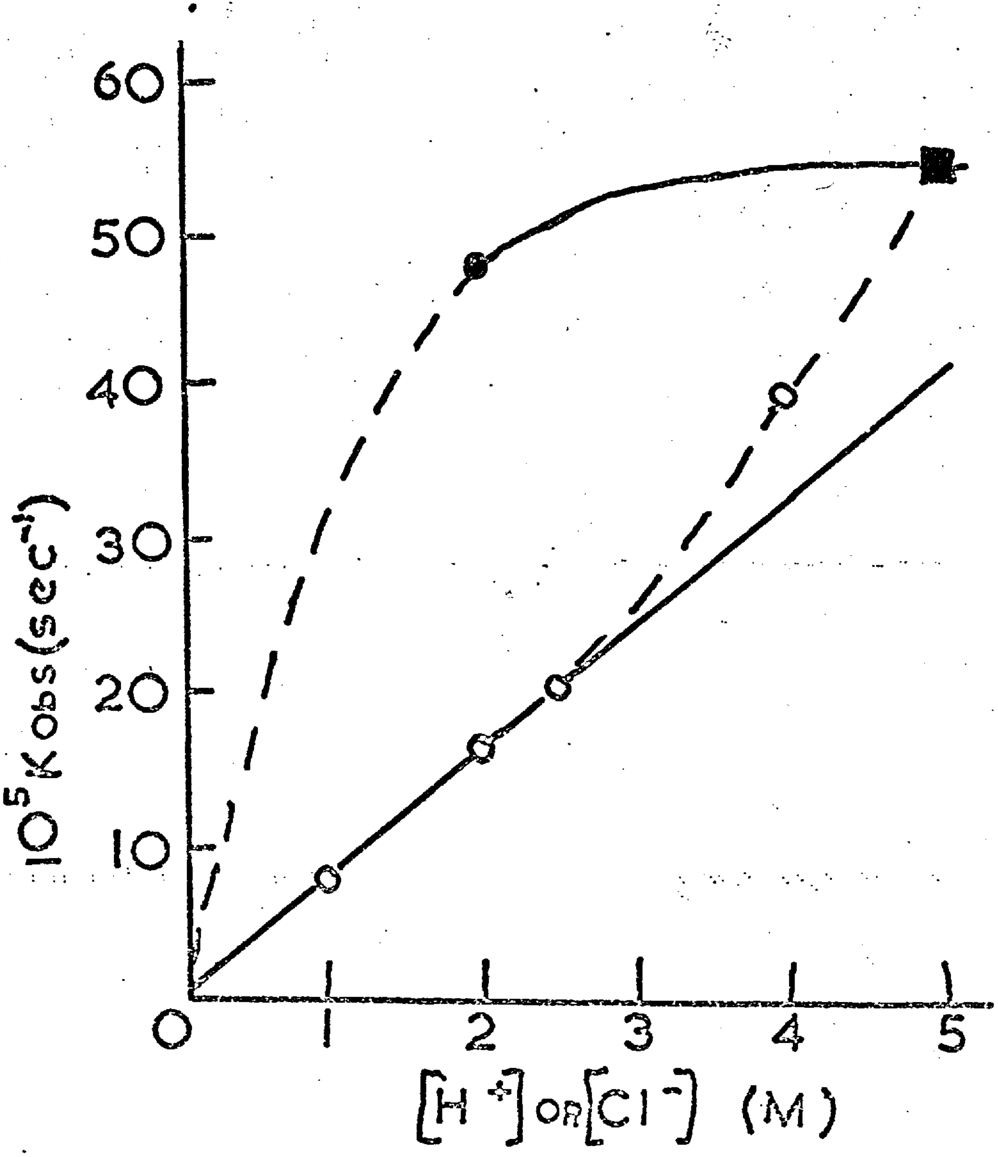


Rate constants for the reaction $Pd(Et_4dienH_2)Cl_3^+ \longrightarrow PdCl_4^{2-}$

(a) μ = 1.0M; ○ : k_{obs} vs. $[Cl^-]$ with $[H^+]$ = 1.0M;

● : k_{obs} vs. $[H^+]$ with $[Cl^-]$ = 1.0M; ■: $[H^+] = [Cl^-]$ = 1.0 M.

Figure 2.



(b) μ=5.0 M; ○: k_{obs} vs. $[Cl^-]$ with $[H^+]$= 5.0 M;

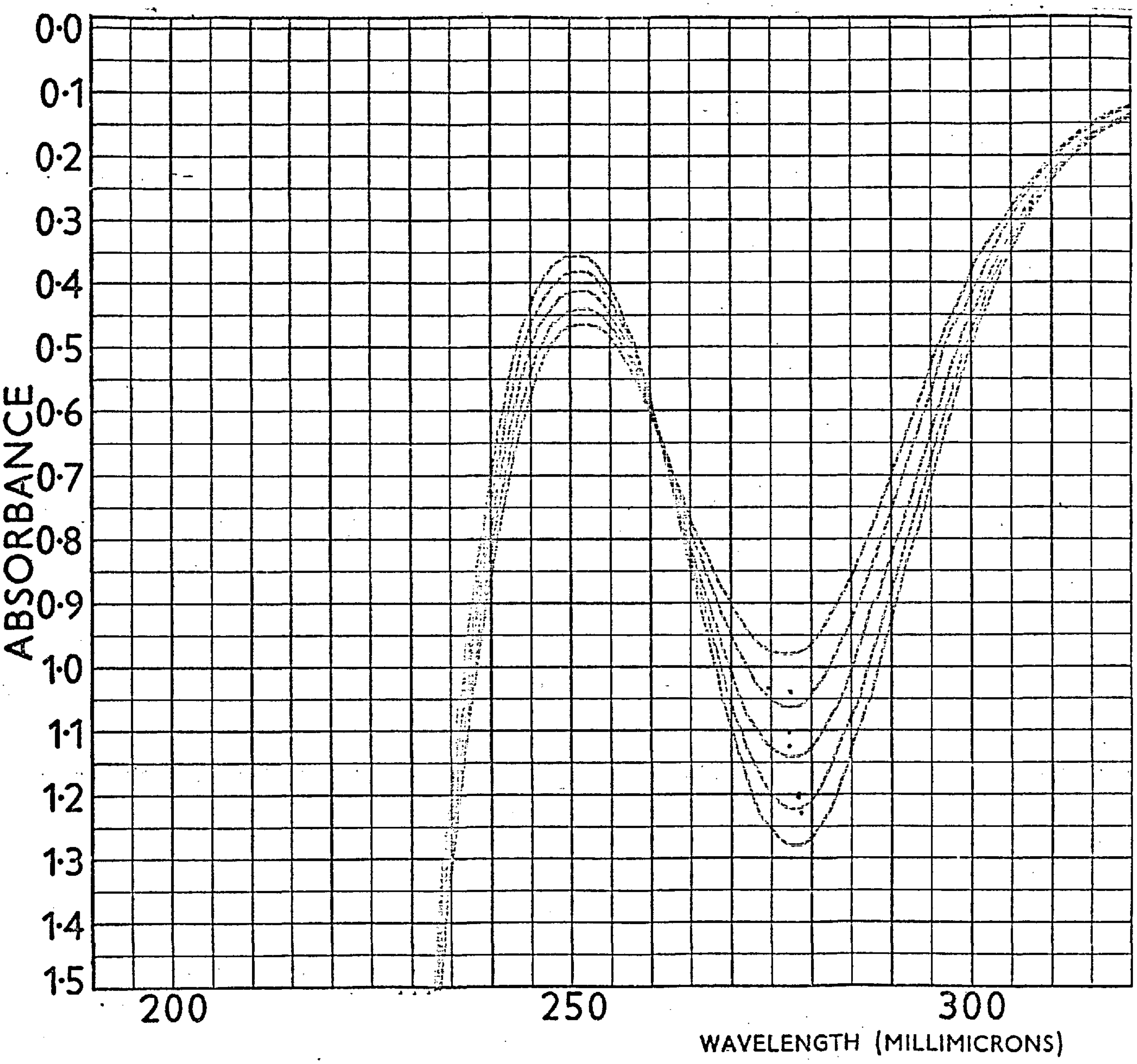
●: $[H^+]$= 2.0 M, $[Cl^-]$= 5.0 M;

■: $[H^+]$= $[Cl^-]$ = 5.0 M.

The $[Pd(dien)Cl]^+ \longrightarrow PdCl_4^{2-}$ reaction

This reaction also went in two stages as evidenced by the two sets of isosbestic points at 302 and 362 mμ, and at ~ 238, 261 and 356 mμ. Unambiguous kinetic data were not obtained for the first stage as increasing either $[H^+]$ or $[Cl^-]$ caused the absorbance change to increase, and the reaction rates increased also. It was not possible to use the same procedure as was used for the $PdenCl_2$ reaction as the second stage was too fast, compared with the first. The second stage, only, was followed by observing the growth of the spectrum of the $PdCl_4^{2-}$ ion at 279 mμ. Unless both hydrogen and chloride ions were present, there was no reaction.

The results are given in table (5) and figure (3). At $\mu = 1.0$ M., the reaction was first order in $[H^+]$ and greater than the first order in $[Cl^-]$ whereas at $\mu = 5.0$ M. the reaction was first order in $[Cl^-]$ but, at a $[Cl^-] = 1.0$ M. the observed rate constants rose to a limiting value as the $[H^+]$ was increased. It was found that in the studies involving variation of $[H^+]$ at a constant $[Cl^-]$ it was necessary to use lithium chloride and perchlorate instead of the sodium salts. This was because poor rate plots were obtained using the sodium salts and the approximate rate constants were some 40% higher than the more accurate ones obtained using



Spectral changes during the reaction

$Pd(dienH_2)Cl_3^+ \longrightarrow PdCl_4^{2-}$

TABLE (5)

Rate constants for the reaction $[Pd(dien\ H_2)Cl_3]^+ \longrightarrow PdCl_4^{2-}$

[complex] = 6.10^{-5} M.

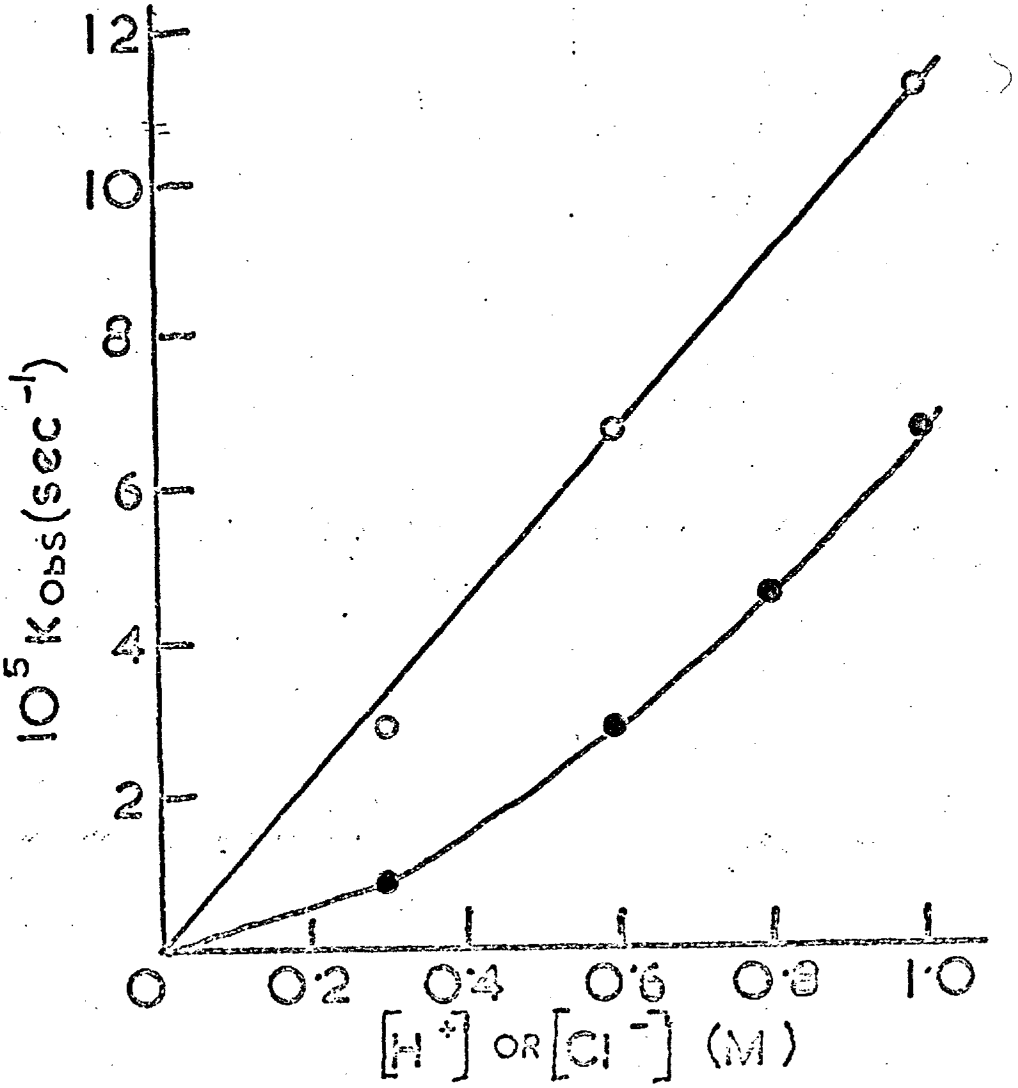
(i) μ=1.0 M; T = 28.7°C.

$[H^+]$ (M)	$[Cl^-]$ (M)	$10^5\ k_{obs.}$ (sec.$^{-1}$)
0.3	1.0	2.93
0.6	1.0	6.71
1.0	1.0	11.1
0.6	0.8	4.6
0.6	0.6	2.9
0.6	0.3	0.89

(ii) μ = 5.0 M.

T(°C.)	$[H^+]$ (M)	$[Cl^-]$ (M)	$10^5\ k_{obs.}$ (sec.$^{-1}$)
4.8	5.0	5.0	15.9
14,5	5.0	5.0	48.8
20.0	5.0	5.0	96.5
25.0	5.0	1.0	34.5
25.0	5.0	3.0	105.
25.0	5.0	5.0	175.
25.0	3.5	3.0	106.
25.0	2.5	2.5	88.6
25.0	1.0	3.0	99.5
25.0	0.5	5.0	175.
25.0	0.2	5.0	142.

Figure 3.

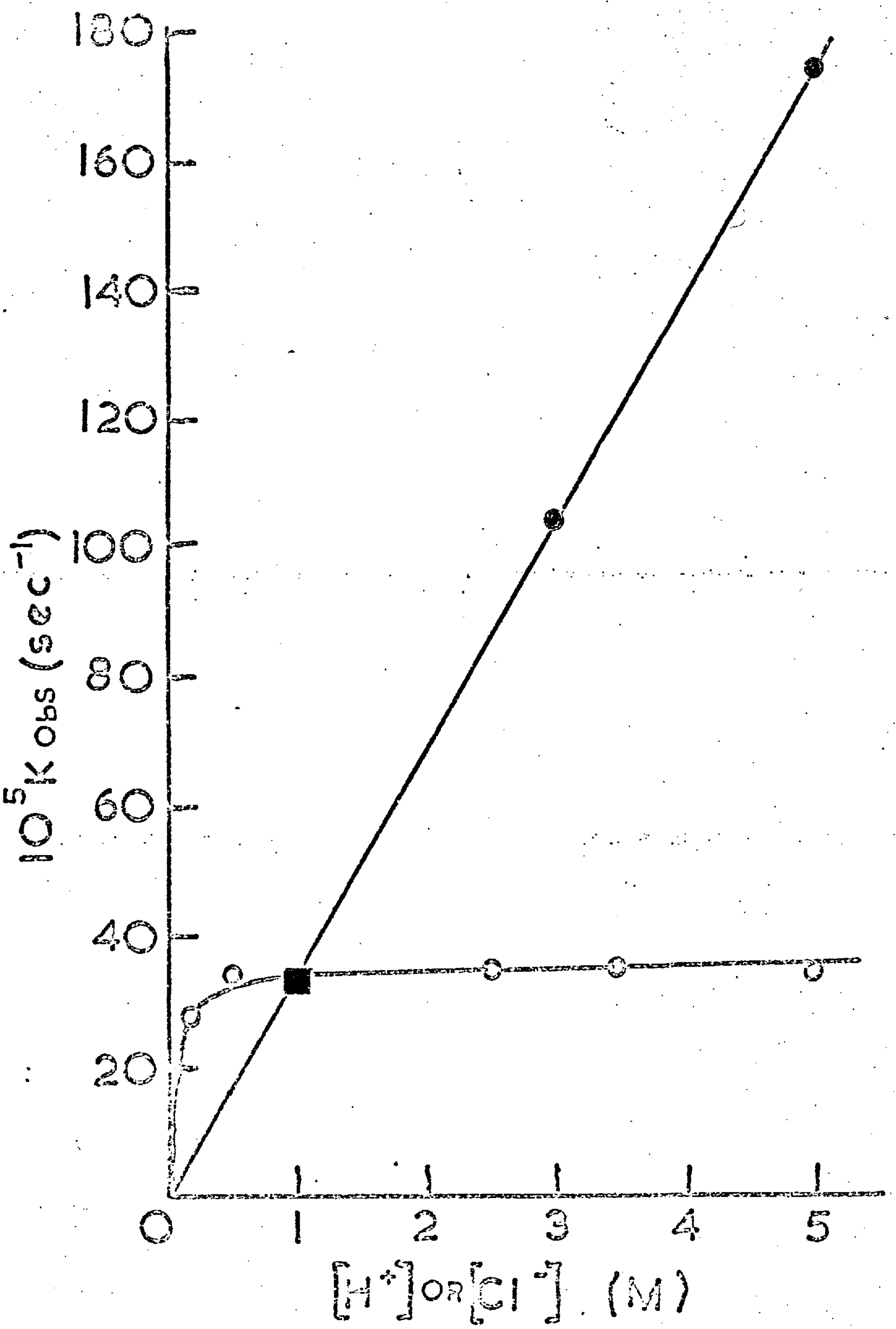


Rate constants for the reaction $Pd(dienH_2)Cl_3^+ \longrightarrow PdCl_4^{2-}$

(a) μ =I.0M; ○: k_{obs} vs. $[H^+]$ with $[Cl^-]$ =I.0M;

●: k_{obs} vs. $[Cl^-]$ with $[H^+]$=0.6M.

Figure 3.

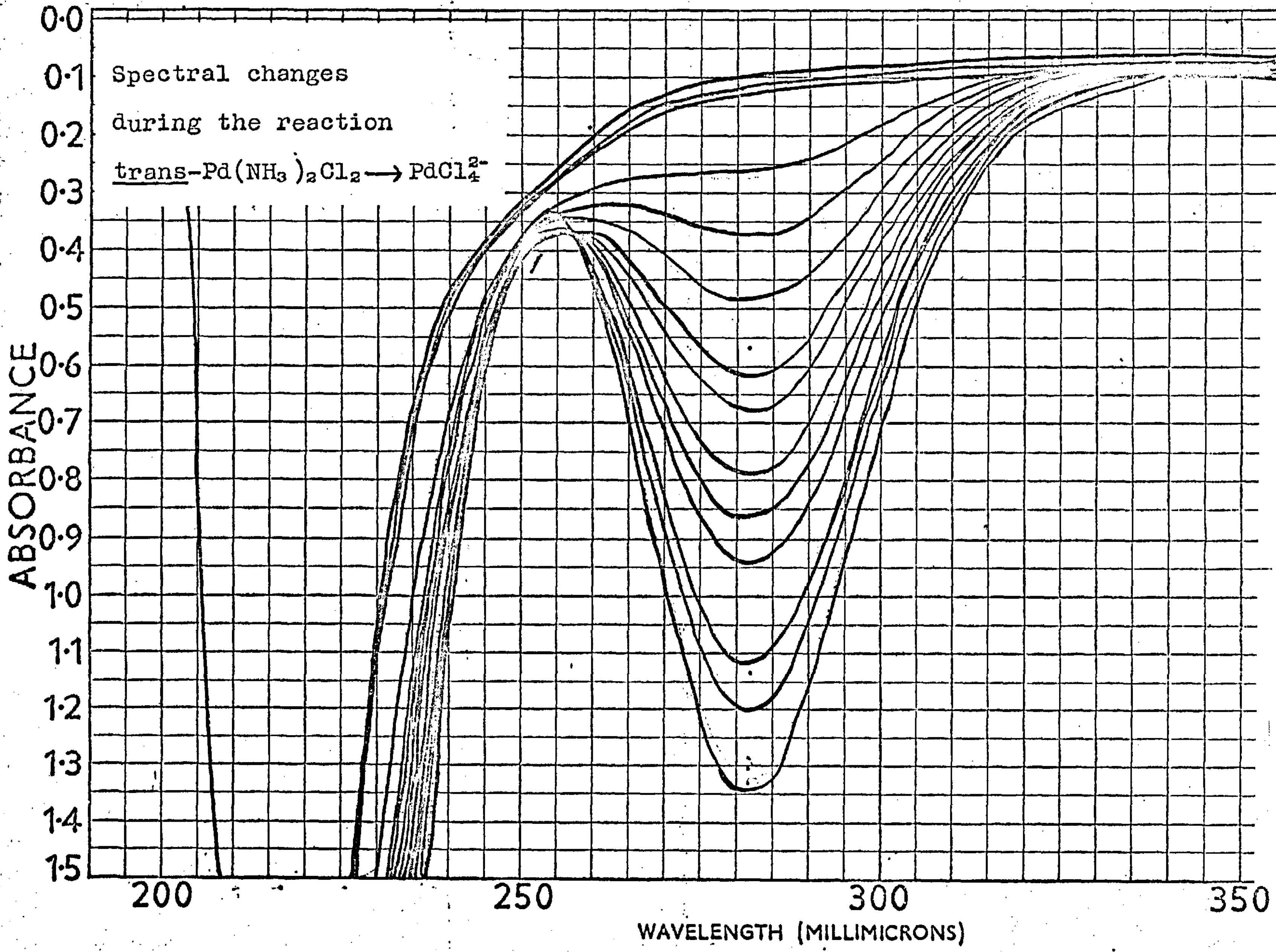


(b) μ = 5.0M; ○: k_{obs} vs. [H^+] with [Cl^-] = 1.0M;
●: k_{obs} vs. [Cl^-] with [H^+] = 1.0M; ■: [H^+] = [Cl^-] = 1.0M.

the lithium salts. At these high ionic strengths, such effects are not uncommon, and, arise because of the difference in activity coefficients between the hydrogen and sodium ions whereas the activity coefficient of the lithium ion is quite close to that of the hydrogen ion(47). The activation parameters are given in table (9).

The trans- $Pd(NH_3)_2Cl_2 \longrightarrow PdCl_4^{2-}$ reaction

This reaction was followed in 5% aqueous ethanol and was found to be a two stage reaction; the second stage had isosbestic points at 246 and 257 mμ. Because the second stage was found to be identical with the second stage of the reaction of cis- $Pd(NH_3)_2Cl_2$ under similar conditions, the product of the first stage was considered to be the ion $Pd(NH_3)Cl_3^-$. Thus the first stage, the formation of $Pd(NH_3)Cl_3^-$ from trans- $Pd(NH_3)_2Cl_2$, was studied at one molar ionic strength by observing the increase in absorbance at 257 mμ, one of the isosbestic points for the second stage. Absorbance changes from 0.2 to 0.6, in 4 cm. cells, were obtained and the rate plots were linear for at least three half times. The results are given in table (6) and figure (4). The rates were independent of $[H^+]$ down to 0.2 M. and the variation with



Spectral changes during the reaction $\underline{\text{trans}}\text{-Pd(NH}_3)_2\text{Cl}_2 \longrightarrow \text{PdCl}_4^{2-}$

TABLE (6)

Kinetic data for the reaction *trans*-$Pd(NH_3)_2Cl_2 \rightarrow Pd(NH_3)Cl_3^-$

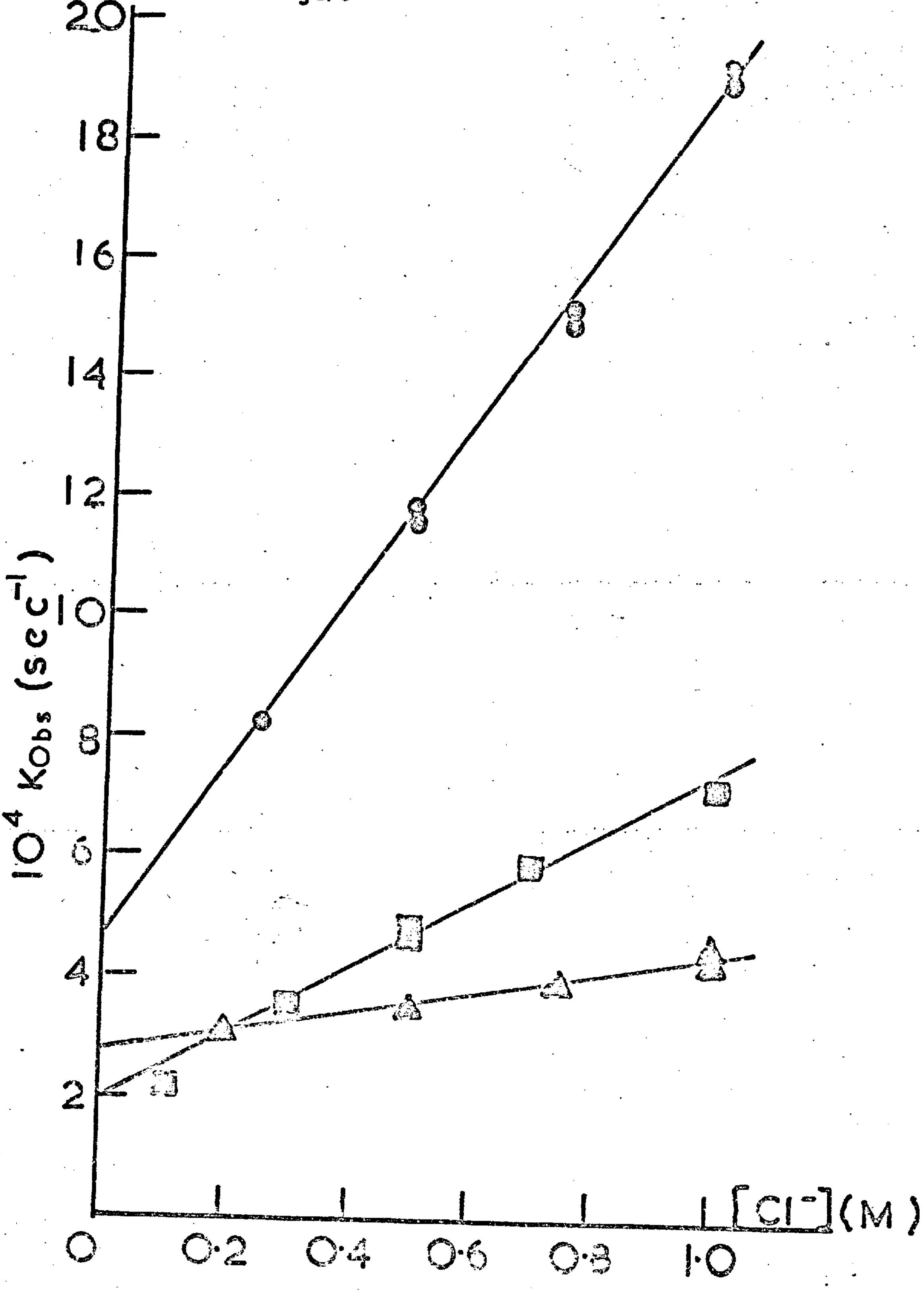
[complex] $\simeq$ 5.10^{-5} M., $[H^+] = 1.0$ M., $\mu = 1.0$ M.

T(°C)	[Cl$^-$] (M.)	10^6 $k_{obs.}$ (sec.$^{-1}$)	10^6 k_1 (sec.$^{-1}$)(a)	10^6 k_2 (M.$^{-1}$ sec.$^{-1}$)
25.0	0.75	8.8	3.7	6.9
25.0	1.00	10.6		
41.4	0.50	57.5	27.6	59.8
41.4	0.80	73.6		
41.4	1.00	87.5		
50.0	0.50	151.	73.0	154
50.0	0.70	183.		
50.0	1.00	211		
55.0	0.50	286.	133	251
55.0	1.00	383.		
60.8	0.10	220.	200	555
60.8	0.30	365.		
60.8	0.50	488		
60.8	0.50	465(b)		
60.8	0.70	595		
60.8	1.00	723		

(a) These values were calculated according to the rate law $k_{obs.} = k_1 + k_2 [Cl^-]$.

(b) $[H^+] = 0.2$ M.

Figure 4.

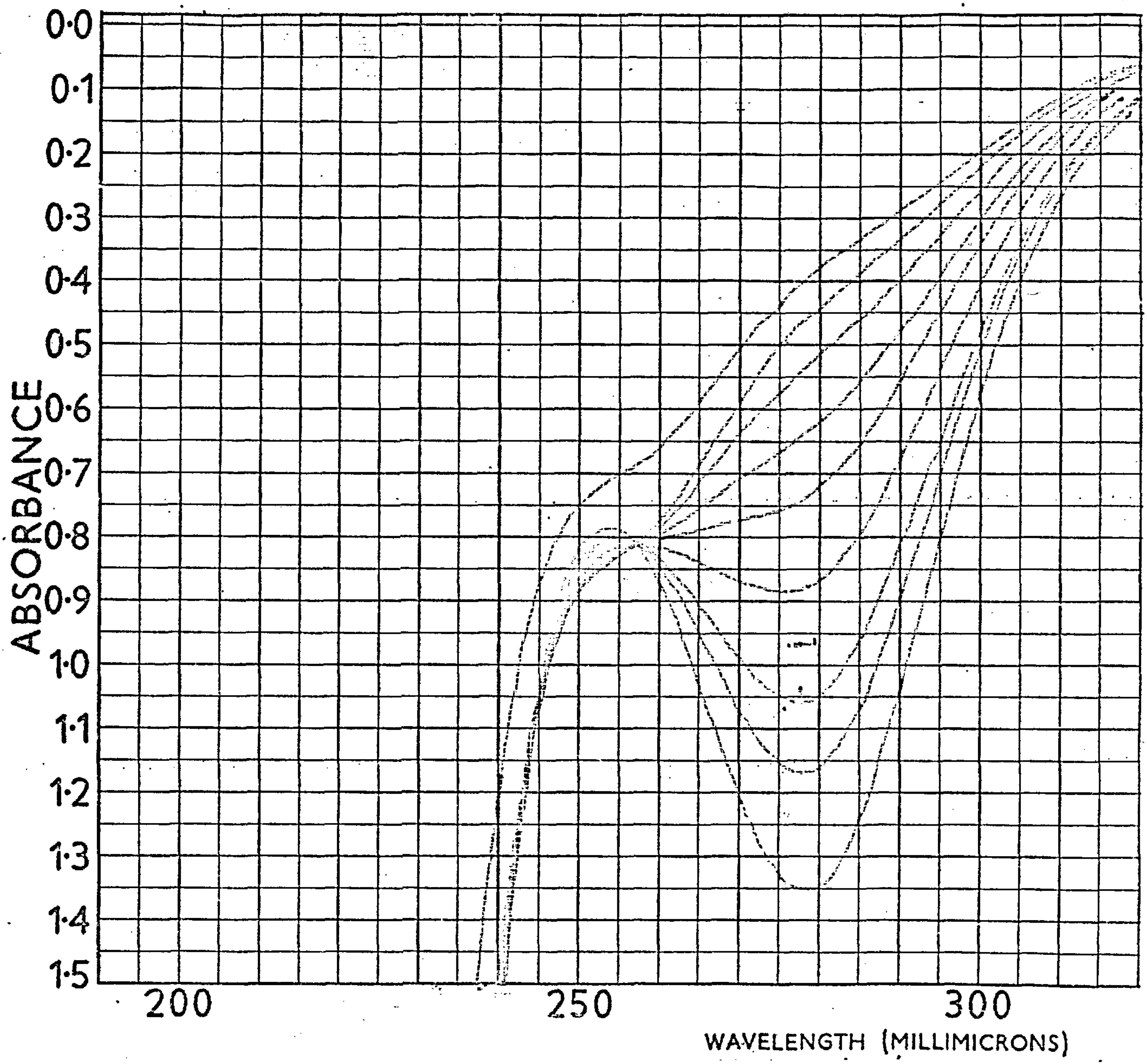


lots of K_{obs} versus [Cl$^-$]. O: cis-$Pd(NH_3)_2Cl_2$ at 25.0° :
: trans-$Pd(NH_3)_2Cl_2$ at 60.8°: Δ: $Pd(NH_3)Cl_3^-$ at 65.3°.

[Cl^-] conformed to the two term rate law common to most reactions of planar d^8 complexes$^{(35)}$. Activation enthalpies and entropies for the reaction are given in table (9).

The cis- $Pd(NH_3)_2Cl_2$• $\longrightarrow PdCl_4^{2-}$ reaction

This reaction also went in two stages in 10% aqueous ethanol, the first stage having an isosbestic point at 330 mμ, and the second having two at 240 and 257 mμ. The difference in rates between the first and second stages was such that the second stage required a temperature of 75° C before it had a similar rate to the first stage at room temperature. The isosbestic points for the second stage were almost identical with those of the second stage of the trans- complex. Also, the cis- complex reacted at room temperature with 0.5 M. perchloric acid to give a solution with an absorption maximum at 385 mμ. Addition of lithium chloride to this solution, rapidly changed the spectrum to one having an absorption maximum at 430 mμ. This spectrum was similar to that obtained as the product of the reaction with hydrochloric acid and was also similar to the spectrum described by Reinhardt et al$^{(48)}$ for the ion $Pd(NH_3)Cl_3^-$. No spectroscopic evidence was obtained for the presence of $PdCl_4^{2-}$ in the sample of the cis complex, and the clean kinetic behaviour



Spectral changes during the reaction

<u>cis</u>-Pd(NH$_3$)$_2$Cl$_2$ ⟶ PdCl$_4^{2-}$

that was observed for the kinetics of this complex must also eliminate the possibility of significant amounts of the Pd $(NH_3)_4{}^{2+}$ ion being present as this reacts readily under these conditions(49)(50). There has been some doubt cast(51) concerning the purity of the cis complex as prepared by Grinberg's method and Layton et al obtained several products by this method. The exact conditions of the preparation seemed to be rather critical but on the basis of the kinetic and spectroscopic evidence it appeared that the samples of the cis complex used in these experiments were quite pure. However, samples were stored in a refrigerator for not more than three days before use to prevent isomerisation. Samples kept for more than three months still gave the characteristic reaction with potassium iodide in acetone so that a substantial proportion of the cis complex was still present after this time. Thus the first stage of the reaction was the conversion of cis- $Pd(NH_3)_2Cl_2$ to $Pd(NH_3)Cl_3^-$.

The kinetics of the first stage were followed at 257 mμ, an isosbestic point of the second stage, at ionic strengths of 1.0 and 5.0 M. Absorbance changes from about 0.2 to 0.5 in 1 cm. cells were obtained and the results are given in table (7) and figure (4). The two term rate law for the

TABLE (7)

Kinetic data for the reaction cis-$Pd(NH_3)_2Cl_2 \rightarrow Pd(NH_3)Cl_3^-$

Solvent was 10% aqueous ethanol.

[complex] = 1.6 10^{-4} M.

(i) μ = 1.0 M., $[H^+]$ = 1.0 M.

T(°C)	Cl^-[M]	10^4 $k_{obs.}$ (sec.$^{-1}$)	10^4 k_1 (sec.$^{-1}$)	10^4 k_2 (M^{-1} sec.$^{-1}$)
5.0	0.50	1.23	0.518	1.40
5.0	0.75	1.58		
5.0	1.00	1.89		
14.8	0.50	3.90	1.61	4.83
14.8	0.75	5.06		
14.8	1.00	6.53		
25.0	0.25	8.36	4.8	14.0
25.0	0.50	11.8		
25.0	0.50	11.9(a)		
25.0	0.75	15.3		
25.0	0.75	15.0(a)		
25.0	1.00	19.4		
25.0	1.00	19.2(a)		
25.0	1.00	19.8(b)		
25.0	1.00	19.6(c)		

(a) in 5% aqueous ethanol.

(b) $[H^+]$ = 0.50 M.

(c) $[H^+]$ = 0.20 M.

TABLE (7) contd.

(ii) μ = 5.0 M. $[H^+]$ = 5.0 M

T(°C)	$[Cl^-]$ (M)	10^4 $k_{obs.}$ ($sec.^{-1}$)	10^4 k_2 (M^{-1} $sec.^{-1}$)
5.0	1.00	1.15	1.18
5.0	2.50	3.00	
5.0	5.00	5.95	
14.8	2.00	7.11	3.41
14.8	3.00	10.8	
14.8	4.00	13.7	
25.0	1.00	11.5	10.7
25.0	1.00	11.8(d)	
25.0	1.50	16.6	
25.0	2.0	22.2	
25.0	2.5	24.2	

(d) $[H^+]$ = 1.0 M.

dependence of the rate upon the $[Cl^-]$ was again observed with the rates being independent of $[H^+]$ above 0.2 M. Some of the reactions at an ionic strength of 1.0 M. were also followed in 5% aqueous ethanolic solutions, and no dependence of the rates on the ethanol concentration was found. Activation parameters are given in table (9), no accurate activation energy was obtained for the term k_1 at $\mu = 5.0$ M. because it was too small, but activation parameters were obtained for both the k_1 and k_2 terms at $\mu = 1.0$ M.

The $Pd(NH_3)Cl_3^- \longrightarrow PdCl_4^{2-}$ reaction

This reaction was followed in 5% aqueous ethanol by observing the growth of the spectrum due to $PdCl_4^{2-}$ at 279 mμ during the second stages of the reactions of either <u>cis</u>- or <u>trans</u>- $Pd(NH_3)_2Cl_2$. Absorbance changes from about 0.1 to 0.7 in 1 cm. cells were obtained. The rate plots obtained by starting with the <u>trans</u>- complex were linear after 3 to 4 reaction half times of the <u>trans</u> complex had elapsed, but those obtained by starting with the <u>cis</u> complex were linear, and agreed with those commencing with the <u>trans</u> complex, only over the last 20% of the reaction even though the isosbestic points remained clean over most of the reaction. Because of the better rate plots obtained when starting with the trans-complex, most of the studies made use of this complex. The results are given in table (8) and figure (4).

At 1.0 M ionic strength the rates were independent of $[H^+]$ down to 4.10^{-3} M. and obeyed a two term rate law in $[Cl^-]$. At 5.0 M. ionic strength the rate constants were again independent of $[H^+]$ above the lowest value of 1.0 M. used, and were first order in $[Cl^-]$, the k_1 term being negligible. Activation parameters are given in table (9).

The trans- $Pd(Et_2NH)_2Cl_2 \longrightarrow PdCl_4^{2-}$ reaction

This reaction also occurred in two stages with an isosbestic point at 252 mμ during the first stage and one at 268 mμ during the second. Only the dependence of the kinetics on $[H^+]$ for the second stage was investigated. The solvent was 10% aqueous ethanol and at an ionic strength of 1.0 M., $[Cl^-]$ = 1.0 M., and T = 80.8°C the rate constants with $[H^+]$ = 1.0, 10^{-2} and 4.10^{-3}M. were 8.48, 8.25, and 8.13 x 10^{-5} sec.$^{-1}$ respectively.

TABLE (8)

Kinetic data for the reaction $Pd(NH_3)Cl_3^- \longrightarrow PdCl_4^{2-}$.

(second stage of the reaction of <u>trans</u>-$Pd(NH_3)_2Cl_2$ with HCl)

Solvent was 5% aqueous ethanol.

[complex] = 6 to 8. 10^{-5} M.

(i) μ = 1.0 M. T = 65.3° C.

$[H^+]$ (M)	$[Cl^-]$ (M)	10^4 $k_{obs.}$ ($sec.^{-1}$)
1.0	0.20	3.16
1.0	0.50	3.53
1.0	0.75	3.59
1.0	1.0	4.49
0.1	1.0	4.53
0.01	1.0	4.57
0.004	1.0	4.29

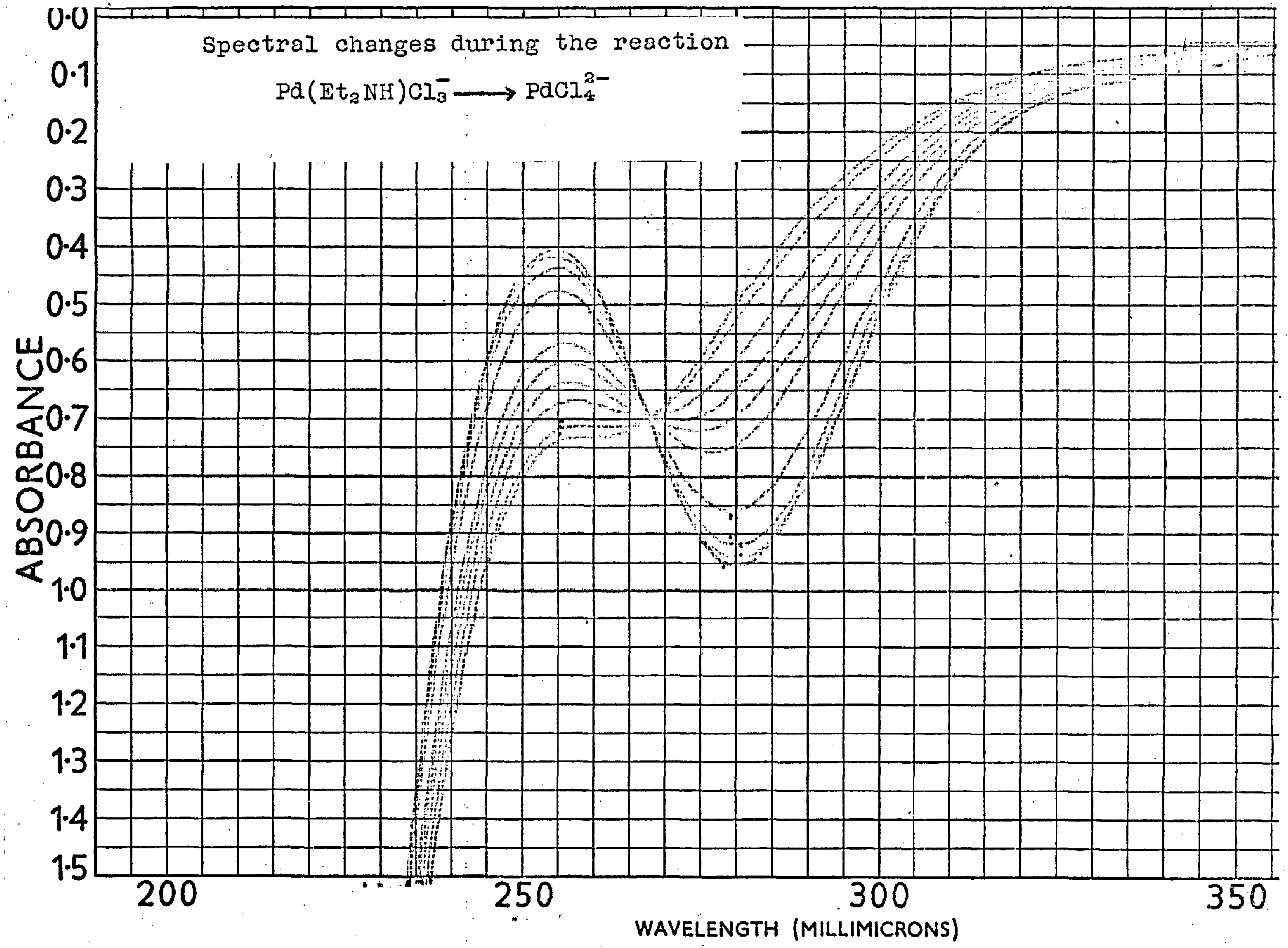
10^4 k_1 = 2.8 $sec.^{-1}$; 10^4 k_2 = 1.7 $l.mole^{-1}$ $sec.^{-1}$.

TABLE (8) contd.

(ii) μ = 5.0 M.

T(°C)	$[H^+]$ (M)	$[Cl^-]$ (M)	10^5 $k_{obs.}$ (sec.$^{-1}$)	10^5 k_2 (M^{-1} sec.$^{-1}$)
40.0	5.0	1.0	1.31	1.31
50.0	1.0	5.0	23.8	4.76
50.0	1.0	5.0	24.6(a)	4.92(a)
50.0	3.0	5.0	23.6	4.72
50.0	3.0	5.0	24.0(a)	4.80(a)
50.0	5.0	5.0	23.2	4.64
50.0	5.0	5.0	23.8(a)	4.76(a)
50.0	5.0	3.0	13.2	4.40
50.0	5.0	1.0	4.23	4.23
54.8	5.0	1.0	7.38	7.38
60.2	5.0	1.0	12.6	12.6
64.8	5.0	1.0	20.9	20.9

(a) Second stage of reaction of cis-$Pd(NH_3)_2Cl_2$ with HCl.



Spectral changes during the reaction

$Pd(Et_2NH)Cl_3^- \longrightarrow PdCl_4^{2-}$

TABLE (9)

Kinetic parameters for reactions of some chloroaminepalladium. (II) Complexes with hydrochloric acid.

	μ (M)	$\Delta H^{\neq}$ (k.cal/mole)	$\Delta S^{\neq}$ (e.u.)	k_{25}, (sec.$^{-1}$)
$PdenCl_2$	4.4	16.4	-19.4	3.4 10^{-4}
$Pd(enH)Cl_3$	5.0	20.1	-9.5	9.3 10^{-5}
$Pd(Et_4dienH_2)Cl_3^+$	5.0	19.1	-12.4	1.4 10^{-4}
$Pd(dienH_2)Cl_3^+$	5.0	19.5	-8.9	3.5 10^{-4}
trans-$Pd(NH_3)_2Cl_2$	1.0	22.2(a)	-8.9(a)	3.7 10^{-6}(a)
	1.0	23.0	-4.9	6.9 10^{-6}
cis-$Pd(NH_3)_2Cl_2$	1.0	17.7(a)	-14.3(a)	4.8 10^{-4}(a)
	1.0	18.0	-11.2	14.0 10^{-4}
	5.0	18.5	-12.3	10.7 10^{-4}
$Pd(NH_3)Cl_3^-$	5.0	23.0	-7.4	2.3 10^{-6}

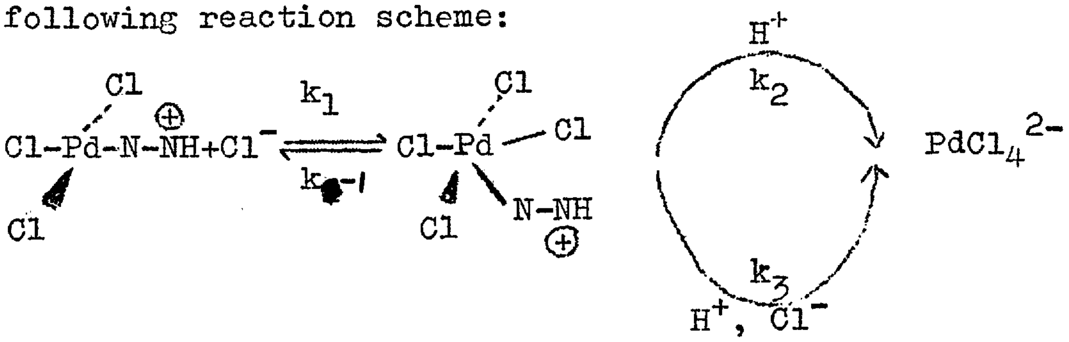
(a) Parameters for the $[Cl^-]$- independent reaction; all other parameters are for conditions such that the reactions are first order in $[Cl^-]$ and independent of $[H^+]$, the rate constants quoted being pseudo first order rate constants at $[Cl^-] = 1.0$ M.

Discussion

It is immediately apparent from the results that there exists a clear division between the behaviour of the non chelated and chelated complexes. The former exhibit the usual two term rate law$^{(35)}$ of equation (1) which is common to most planar d^8 metal complexes and can be interpreted as a mixture of nucleophilic attack by the solvent and the chloride ion on the metal ion. The absence of any effect upon the kinetics by varying the $[H^+]$, even though in some cases it was as low as 10^{-3} M., implies that the sole purpose of the hydrogen ion is to neutralise the released amine or ammonia and so ensure that the reaction goes to completion.

The chelated complexes, however, are quite different : two features of importance are the two stage nature of the reaction of Pd en Cl_2 and the dependence of this second stage on $[H^+]$. Although other chelated complexes show a similar dependence on $[H^+]$, this arises from the choice that the monodentate chelate has of either reforming the original complex i.e. become bidentate again, or else react with a proton and then rapidly dissociate from the complex completely. For a complex such as $Pd(enH)Cl_3$, which has a monodentate amine ligand with the uncomplexed nitrogen of the ethylenediamine being fully protonated at the high acidities used, this choice is obviously not open to it. The dependence of the rates on $[H^+]$ can not be due to a displacement of the dissociation equilibrium because even at low acidities where the rates are less than the limiting values the reactions still go to completion. Thus the dependence must be purely kinetic and so a transition state which contains one hydrogen ion more than the original reactant complex is involved. It should also be noted that when the hydrogen ion concentration is sufficiently high to produce the limiting rate the dependence of the rate on the chloride ion concentration is first order; when the hydrogen ion concentration is not so high the dependence on chloride is intermediate between first and second order apart from $[Pd(Et_4dienH_2)Cl_3]^+$ at μ = 5.0 M. which has an odd dependence on the chloride ion concentration.

It is possible to account for these facts with the following reaction scheme:



where $-\overset{+}{\text{N}}\text{-NH}$ is the monodentate polyamine with its non-coordinated N atom or atoms protonated. This reaction scheme leads to the rate law given in equation (11) below:

$$k_{obs} = k_1[\text{Cl}^-]\frac{\left\{\dfrac{k_2[\text{H}^+]}{k_{-1}} + \dfrac{k_3[\text{H}^+][\text{Cl}^-]}{k_{-1}}\right\}}{1 + \dfrac{k_2[\text{H}^+]}{k_{-1}} + \dfrac{k_3[\text{H}^+][\text{Cl}^-]}{k_{-1}}} \qquad \ldots \quad (11)$$

From studies(53) on the effect of different entering and leaving groups, and of the effect of different leaving groups on the entering group dependence, it was suggested that the five coordinate intermediate developed in the reaction of a Au(III) substrate was less stable than that occurring in the reactions with a Pt(II) substrate which in turn was less stable than the intermediate formed with a Rh(I) substrate. Indeed it was found that in the reaction(54) of amines such as pyridine with $[\text{C}_8\text{H}_{10}\text{RhCl Sb(p-tolyl)}_3]$ to give $[\text{C}_8\text{H}_{10}\text{Rh py Cl}]$ the formation and decomposition of the five coordinate intermediate were kinetically distinguishable steps whereas for Au(III) complexes the intermediate may be indistinguishable from the transition state. The reason for this order of stability may be due to the increase in the relative energy separation, as the oxidation state of the metal ion increases, between the (n-1)d and (n)S, and between the (n)S and (n) p orbitals which are needed to form a set of five equivalent orbitals for the trigonal bipyramidal intermediate(55).

The stability of the five coordinate intermediate, formed during the loss of the monodertate protonated amine in the last stage of the reaction of the chelated palladium(II) complexes, is such that, in order for the forward reaction to compete with the re-formation of the original four coordinate complex, attack by a hydrogen ion is necessary. It is possible that some stability for the intermediate can be derived from hydrogen bonding between a coordinated chloride ion and one of the hydrogen ions which is joined to a non-coordinated nitrogen atom. Thus the forward reaction can be regarded as electrophilic attack on the last coordinated nitrogen atom by a hydrogen ion. When the $[H^+]$ is insufficient to produce the limiting rate then, in order to account for the greater than first order dependence of the rate on $[Cl^-]$, some additional path must exist for the forward reaction. This additional path has some assistance from an additional chloride ion but the exact nature of this path is uncertain. It may be possible that instead of intramolecular hydrogen bonding between one of the hydrogen ions joined to a free nitrogen atom and a coordinated chloride, hydrogen bonding to a free chloride ion occurs resulting in the formation of an ion pair of the type $[Cl_4Pd\text{-}N\text{-}\overset{+}{N}H\ Cl^-]^{2-}$. This ion pair may be more susceptible to electrophilic attack by a hydrogen ion at the coordinated nitrogen atom; a measure of this susceptibility is given by the ratio k_3/k_2 , and the values derived for the different five coordinate complexes are discussed below.

Equation (11) can be rearranged to

$$\frac{1}{k_{obs}} = \frac{1}{k_1[Cl^-]\left\{k_2/k_{-1} + k_3[Cl^-]/k_{-1}\right\}[H^+]} + \frac{1}{k_1[Cl^-]} \quad .. \quad (12a)$$

and

$$\frac{k_{obs}/[Cl^-]}{k_1 - k_{obs}/[Cl^-]} = \frac{k_2[H^+]}{k_{-1}} + \frac{k_3[H^+][Cl^-]}{k_{-1}} \quad ... \quad (12b)$$

Thus from a variation of k_{obs} with either $[H^+]$ or $[Cl^-]$ at $\mu = 1.0$ M. it is possible to obtain estimates of the individual parameters k_1 , k_2/k_{-1} , and k_3/k_{-1} . The variation of k_{obs} with $[H^+]$ at $[Cl^-] = 1.0$ M. yields values of k_1 and $\left\{k_2/k_{-1} + k_3/k_{-1}\right\}$ whereas when $[H^+]$ is constant a plot of the left hand side of equation (12b) against $[Cl^-]$ yields values of k_2/k_{-1} and k_3/k_{-1} individually. The values $(k_2/k_{-1} + k_3/k_{-1})$ obtained in the two different ways from the data on the reaction of $Pd(enH)Cl_3$ were 0.88 and 0.86. For the reaction of $[Pd(Et_4dienH_2)Cl_3]^+$, at $\mu = 1.0$ M. the variation of k_{obs} with $[Cl^-]$ at a constant $[H^+]$ is first order so that $k_3 \ll k_2$. The two values of k_2/k_{-1} obtained from the variation of k_{obs} with $[H^+]$ and $[Cl^-]$ are 1.66 and 1.49 respectively. For the $[Pd(dienH_2)Cl_3]^+$ reaction, k_{obs} is first order in $[H^+]$ up to 1.0 M. with the result that k_1 can not be obtained. Instead a value of $k_1(k_2/k_{-1} + k_3/k_{-1})$ is obtained from equation(13).

$$k_{obs} = k_1[Cl^-]\left\{k_2/k_{-1} + k_3[Cl^-]/k_{-1}\right\}[H^+] \quad \ldots \qquad (13)$$

which is derived from equation (12a) by noting that for this system $\left\{k_2/k_{-1} + k_3[Cl^-]/k_{-1}\right\} \ll 1$. Using this equation the values of $k_1(k_2/k_{-1} + k_3/k_{-1})$ obtained from the variation of k_{obs} with $[H^+]$ or $[Cl^-]$ are both equal to $1.1.10^{-4}$ l.mole^{-1}sec.$^{-1}$. Table (10) shows the values

Table (10)

Values of the rate constants for the reactions of the complexes $PdLCl_3$ with hydrochloric acid according to equation (11)

Complex	T (°C)	K_1 ($M^{-1}sec.^{-1}$)	k_2/k_{-1} (M^{-1})	k_3/k_{-1} (M^{-2})	k_3/k_2 (M^{-1})
$Pd(enH)Cl_3$	40.0	$4.8.10^{-4}$	0.52	0.34	0.65
$Pd(dien\ H_2)Cl_3^+$	28.7	(6.10^{-4})	(0.05)	(0.14)	3.2
$Pd(Et_4dien\ H_2)Cl_3^+$	30.0	$8.6.10^{-4}$	1.5	<0.1	<0.1

The values in parentheses are estimated by assuming that k_1 for the $Pd(dien\ H_2)Cl_3^+$ ion is affected by ionic strength in the same way as k_1 for $Pd\ (Et_4dien\ H_2)Cl_3^+$

derived for these parameters.

The value of the parameter k_1 obtained for Pd(enH)Cl_3 is $4.8.10^{-4}$ l.mole.$^{-1}$sec.$^{-1}$ which compares with a value of $4.5.10^{-4}$ l.mole.$^{-1}$sec.$^{-1}$ obtained from studies at $\mu = 5.0$ M. Thus the reaction of this uncharged complex with chloride is relatively unaffected by a change in the ionic strength over this region. However, the value of k_1 obtained from the data at $\mu = 1.0$ M. for the reaction of $[Pd(Et_4dienH_2)Cl_3]^+$ is $8.6.10^{-4}$ l.mole.$^{-1}$sec.$^{-1}$ which compares with a value of $2.4.10^{-4}$ l.mole.$^{-1}$sec.$^{-1}$ obtained from studies at $\mu = 5.0$ M. Thus this positively charged complex reacts more slowly with chloride at the higher ionic strength. If it is assumed that the reaction of $[Pd(dienH_2)Cl_3]^+$ is similarly affected by the change in ionic strength, the values of the parameters given in parentheses are obtained. However, the value of k_3/k_2 is not depdendent on this assumption as it is obtained from the ratio of the slope and intercept of equation (13) for the variation of k_{obs} with $[Cl^-]$.

An inspection of the parameters in table (10) shows that the five coordinate complex $[Pd(Et_4dienH_2)Cl_4]$ is most susceptible to attack by H^+ relative to loss of chloride whereas $[Pd(dienH_2)Cl_4]$ is the least susceptible. $[Pd(enH)Cl_4]^+$ is more susceptible to attack by H^+, relative to loss of chloride, than is $[Pd(dienH_2)Cl_4]^-$, and it is also more susceptible to the combined effects of H^+ and Cl^- though the effect is somewhat smaller in the latter case. Because of the lack of a detailed understanding of the unusual mechanism of these reactions, any attempt to rationalise these trends would be rather premature.

The lack of any dependence of the rates upon the $[H^+]$ for the non-chelated complexes suggests that the five co-ordinate intermediate is much less stabilised, probably because the type of hydrogen bonding described for the chelated complexes is unavailable, and the forward reaction may very well not need any assistancefrom a hydrogen ion. Recent studies(49)(50) on the reaction of $Pd(NH_3)_4{}^{2+}$ with hydrochloric acid to form trans- $Pd(NH_3)_2Cl_2$ have shown that it is a two stage reaction with the rate constants for the individual steps obeying the usual two term rate law given by equation (1). It was also noted that the rates were unaffected by varying amounts of hydrogen ion. This difference in behaviour between the two types of complexes is not due to the inductive effect of the alkyl groups, which are necessarily present in thechelating ligands, since trans- $Pd(Et_2NH)_2Cl_2$ behaves in a similar manner to the other non-chelated complexes with its rate of substitution of the second amine ligand by chloride being unaffected by the variation of $[H^+]$. The inductive effect may, however, be responsible for the slower reaction of the diethylamine complex compared to the corresponding ammonia complex.

The lack of any kinetic data on the first stages of the reactions of the chelated complexes renders any detailed analysis impossible. One interesting observation is that the first stages are not driven to completion very easily which suggests, not unexpectedly, that the five coordinate intermediates, such as $PdenCl_3^-$, revert to the original complex far more readily than, for example, does the $Pd(enH)Cl_4^-$.

It is rather surprising that only two stages were detected for the $[Pd(dien)Cl]^+$ and $[Pd(Et_4dien)Cl]^+$ complexes. The very close similarity in the second stages of the reactions of these complexes to each other and to that of the $PdenCl_2$ complex would seem to indicate that it is the last coordinated nitrogen that is being displaced in these reactions. From the available data it is not possible to decide whether it is a terminal or central nitrogen atom that is the last to leave in the case of the triammines. No initial very fast reaction was observed and the first stages are both characterised by isosbestic points. It is not necessarily certain that the first stage corresponds to the slow reversible dissociation of the first coordinated nitrogen atom, followed by a rapid reversible dissociation of the second, since the dissociation of the first nitrogen might be rapid but thermodynamically very unfavourable. A comparison of the spectrum of $PdenCl_2$ with that of the product at the end of the first stage of the reaction of the triamines, shows them to be very similar, but, this is rather misleading as the spectroscopic changes during the first stage of the reaction of $PdenCl_2$ are not very significant, there being only an increase in absorbance.

The kinetic behaviour of the sample assumed to be <u>cis</u> - $Pd(NH_3)_2Cl_2$ is entirely consistent with this assignment; any <u>trans</u>- $Pd(NH_3)Cl_2$ present as an impurity would not affect the kinetics. However, it is still rather strange that the rate plots for the reaction of $[Pd(NH_3)Cl_3]^-$ obtained from <u>cis</u>- $Pd(NH_3)_2Cl_2$ are not better than those obtained from <u>trans</u>- $Pd(NH_3)_2Cl_2$.

In order to discuss the relative kinetic cis- and trans- effects of chloride and ammonia in the non-chelated complexes it would be advantageous to incorporate into the discussion the published results(49)(50) on the $Pd(NH_3)_4^{2+}$ system.

The trans- effect of a pair of ligands is usually determined by the ratio of the rate constants for reactions of two substrates having either one or the other of the two ligands in the position trans- to the leaving group. The cis effect is determined in a similar manner. As the rate constants are affected by the ionic strength of the medium, it would be better to use the results of Reinhardt and Sparkes(49) which were at $\mu = 1.0$ M. rather than those of Coe(50) et al which were at $\mu = 0.25$ M. However, Coe has pointed out the possibility that Reinhardt and Sparkes may have incorrectly assigned the values obtained for their rate parameters. In view of this uncertainty the results of Coe et al have been used. A complete summary of the kinetic parameters is given in table (11). Statistical effects are corrected for by dividing the rate constant by the number of equivalent leaving groups in the complex. The kinetic cis and trans effects of chloride vs. ammonia are given in table (12).

Table (11)

Summary of kinetic parameters for the reactions

$$[Pd(NH_3)_{4-x}Cl_x] + Y \longrightarrow [Pd(NH_3)_{3-x}Cl_xY] + NH_3$$

μ = 1.0 M.

			Y = Cl^-				Y = H_2O			
		(a)	(b)	(b)	(c)	(d)	(e)	(e)	(c)	(d)
	Complex	n	10^4k	$10^4k/n$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	10^4k	$10^4k/n$	$\Delta H^\ddagger$	$\Delta S^\ddagger$
1)	$Pd(NH_3)_4^{2+}$	4	471	118	20.3	0	13.7	3.4	17.4	-14
2)	$Pd(NH_3)_3Cl^+$	1	117	117	19.1	-4	10.9	10.9	24.4	+10
3)	<u>Cis</u>-$Pd(NH_3)_2Cl_2$	2	14.0	7.0	18.0	-11.2	4.8	2.4	17.7	-14.3
4)	<u>Trans</u>-$Pd(NH_3)_2Cl_2$	2	0.069	0.035	23.0	-5	0.037	0.019	22.2	-8.9
5)	$Pd^{(f)}(NH_3)Cl_3^-$	1	0.02	0.02	23.0	-7.4	-----	-----	----	----

(a) n is the number of equivalent leaving groups in the complex

(b) Values of rate constant at 25°C in $l.mole^{-1}sec.^{-1}$.

(c) Values in kcal/mole.

(d) Values in $cal.mole^{-1}deg^{-1}$

(e) Values of rate constant at 25°C in $sec.^{-1}$

(f) Values are for μ = 5.0 M.

Table (12)

Relative kinetic *cis*- and *trans*- effects of Cl vs. NH_3 as found in the reactions:

$$[Pd(NH_3)_{4-x}Cl_x] + Y \longrightarrow [Pd(NH_3)_{3-x}Cl_xY + NH_3$$

Leaving group is NH_3

	Entering group is Cl		Entering group is H_2O	
Reactions Considered	(a) *Trans*-effect	(a) *Cis*-effect	(a) *Trans*-effect	(a) *Cis*-effect
2/1	1.0	---	3.2	---
5/4	0.57	---	---	---
5/3	----	0.003	---	---
3/2	----	0.06	---	0.22

(a) Values are ratios of the rate constants listed in table (10)

From the results it can be seen that the relative kinetic trans- effect of Cl is greater than that of NH_3 , except when measured by reactions 5 and 4 for which the order is reversed, also, the relative kinetic cis effect of NH_3 is greater than that of Cl. The trans- effects for the Pd(II) complexes are spanned by a factor of 6, similarly the cis- effects are spanned by a factor of just over 70. This is in contrast to work(56) on Pt(II) substitution where it was found that for the replacement of chloride by water in Pt(II) ammine complexes, the relative kinetic trans- effects of Cl vs. NH_3 were spanned by a factor of about 4 (Cl > NH_3), and the cis- effects by a factor of about 3 (NH_3 > Cl).

An alternative approach is to consider the activation enthalpies. Thus, for chloride substitution, the cis- effect of NH_3 is greater than that of Cl by 5 kcal./mole when measured by reactions 5 and 3; however, it appears that the order is reversed when the cis- effect is measured by reactions 3 and 2. In this latter case the cis- effect of Cl is greater than that of NH_3 by 1 kcal/mole. Similarly, with water as the entering group the cis- effect of Cl is greater than that of NH_3 by over 6 kcal/mole. when measured by reactions 3 and 2. In the reactions of some Pt(II) complexes with NH_3, it was found that the cis- effect of ammonia was greater than that of Cl by only 1.6 k cal./mole(57). A comparison of the activation enthalpies for the two stages of the reaction of Pd en Cl_2 indicate that there may be a similar cis- effect operating here although it is not shown as clearly by the rate constants.

The trans- effect of Cl vs. NH_3 , as measured by the activation enthalpies, also reveals no regular pattern. When measured for chloride substitution as in reactions 2 and 1, the trans- effect of Cl is greater than that of NH_3 by 1 kcal/mole, whereas, when measured by reactions 5 and 4 there is no significant difference. There appears to be an inversion of the order when substitution by water, as in reactions 2 and 1, is considered. Here the trans- effect of NH_3 is greater than that of Cl by 7 kcal/mole.

Thus no regular trends, which can be associated with cis- and trans- effects are apparent. This may be partly due to the unusual parameters obtained for the reaction of $Pd(NH_3)_3Cl^-$: the values of $\Delta S^{\ddagger}$ for the reactions of the Pd(II) complexes in table (10) are all negative with the exception of the aquation of $Pd(NH_3)_3Cl^-$ which has a positive value. This would seem to suggest something odd about the reaction of this complex.

Although it is not possible to rationalise the data in terms of cis- and trans- effects, it is apparent that these transmitted effects can be just as great or greater in Pd(II) complexes as those found in Pt(II) complexes.

The relative importance of the [Cl$^-$] dependent path i.e. k_2/k_1 of equation (1), is approximately the same for the neutral diammine complexes but considerably less for the negatively charged mono-ammine complex. The occurrence of a [Cl$^-$] dependent path for the reaction of the $Pd(NH_3)Cl_3^-$ complex at μ = 1.0 M. is in contrast with the behaviour of $Pt(NH_3)Cl_3^-$ for which no [Cl$^-$] dependent path was observed in a study of its chloride exchange$^{(58)}$. The importance of the [Cl$^-$] dependent term increases when the ionic strength is raised from 1.0 M. to 5.0 M. This may be due to a large decrease in the activity of the solvent at the higher ionic strength.

No [Cl$^-$]-indpendent path was observed for any of the chelated complexes, this is explicable if the hydrogen bonding stabilising the five coordinate intermediate involves the incoming chloride ion and not one of those already co-ordinated, ion pairing to the free protonated end of the chelate providing a favourable path for introducing the chloride into the complex.

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