Contribution from the Chemistry Department,
King's College, London, W.C.2, United Kingdom

The Kinetics of Some Reactions of Tetra-amminepalladium(II) and Chlorotriamminepalladium(II) Ions in Acid Solution

J. S. Coe, M. D. Hussain, and A. A. Malik

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Rate constants and activation parameters have been determined for the aquation and chloride substitution reactions of $Pd(NH_3)_4^{2+}$ *and* $Pd(NH_3)_3Cl^+$ *in acid solution. The commonly encountered two-term rate law,* $k_{obs} = k_{H_2O} + k_{Cl}[Cl^-]$, *is found to apply for these reactions. In the light of these and other published data the concepts of* cis- *and* trans-*effects in* Pd^{II} *and* Pt^{II} *chloro-ammine systems are discussed critically.*

Introduction

Comparatively little is known about ligand substitution reactions of Pd^{II} complexes. Where direct comparison is possible it appears that complexes of Pd^{II} react much more rapidly than those of Pt^{II}. Thus, the replacement of chloride in *trans*-$Pd(PEt_3)_2$(o-tolyl)Cl by pyridine is about 10^5 times faster than the corresponding reaction of the Pt^{II} complex.[1a] A similar factor is involved in comparing the rates of replacement of SCN^- in $[M(dien)SCN]^+$ by pyridine,[1b] where M = Pt or Pd and dien = diethylenetriamine. It has also been shown[1c] that in some reactions of bis(acetylacetonato)palladium(II) the order of nucleophilic reactivity of a series of ligands is the same as that found in reactions with many Pt^{II} substrates. The reactions of sterically hindered Pd^{II} complexes,[1d] however, appear to resemble those of Co^{III}.

Another feature of the comparison between the chemistry of Pt^{II} and Pd^{II} is the fact that, in the case of complexes with monodentate ligands, the Pd^{II} analogue of a given Pt^{II} complex is often unknown or difficult to obtain pure. This fact is probably related mainly to the differences in kinetic behaviour of the two elements and is illustrated by the difficulties experienced[1e] in obtaining pure samples of *cis*-$Pd(NH_3)_2Cl_2$ and *cis*-$Pd(NH_3)_2Br_2$ due to the rate of isomerisation of these complexes. (It also appears to be difficult to obtain good *crystals* of *cis*-$Pt(NH_3)_2Cl_2$).[1f]

Very recent reports of kinetic studies on Pd^{II} complexes include that of Poë and Vaughan,[2] discussed more fully below, and that of Reinhardt and Sparkes,[16] to which brief reference is made at the end of the present paper.

Experimental Section

Materials. Sodium perchlorate was recrystallised from water, evaporated repeatedly with acetone and dried at 130°.

AR Sodium chloride and reagent grade ammonium perchlorate were used.

trans-Dichlorodiamminepalladium(II) (from Johnson, Matthey & Co.) was used without purification.

Anal. % Found Pd, 50.4; Cl, 33.5; N, 13.3. % Calcd. Pd, 50.41; Cl, 33.51; N, 13.00.

Tetra-amminepalladium(II) chloride monohydrate was prepared by the method of Drew *et al.*[15]

Anal. % Found Pd, 40.7; Cl, 27.3; N, 21.5. % Calcd. Pd, 40.44; Cl, 26.88; N, 21.24.

Tetra-amminepalladium(II) perchlorate was prepared by adding the calculated amount of silver perchlorate required to precipitate chloride ion from the tetra-ammine chloride. The product was crystallised out after filtering the precipitated silver chloride.

One sample was analysed and gave the following percentage composition: Pd, 28.5; ClO_4^-, 53.6; N, 15.0 (% calcd. Pd, 28.55; ClO_4^-, 53.23; N, 14.99). This sample was used to establish the O.D. concentration dependence at 297 mμ. Further samples gave identical calibration curves.

Instruments. Unicam SP 800 and Perkin Elmer spectrophotometers were used (usually without thermostatic control) to obtain overall pictures of spectral changes occurring during reactions.

A Unicam SP 500 spectrophotometer with thermostatic control was used for all measurements from which rate constants were calculated.

Kinetics. Separate solutions of reagents were thermostated at the temperature under investigation and then mixed rapidly. A sample of the mixture was then transferred to a thermostated cell (1 cm. or 4 cm. path) and optical densities at a given wavelength were measured at intervals.

(A) Aquation of the tetra-amminepalladium(II) ion

Results. On mixing aqueous $Pd(NH_3)_4(ClO_4)_2$ with aqueous perchloric acid spectral changes of the type shown in Figure 1 were observed over a period of about 1 hr. at 25°C. Solutions of $Pd(NH_3)_4(ClO_4)_2$ were found to obey Beer's law at 297-300 mμ.

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(1) (a) F. Basolo, J. Chatt, H. B. Gray, R. G. Pearson, and B. L. Shaw, *J. Chem. Soc.*, 2207 (1961); (b) F. Basolo, H. B. Gray, and R. G. Pearson, *J. Am. Chem. Soc.*, *82*, 4200 (1960); (c) R. G. Pearson and D. A. Johnson, *J. Am. Chem. Soc.*, *86*, 3983 (1964); (d) W. H. Baddley and F. Basolo, *J. Am. Chem., Soc.*, *86*, 2075 (1964); (e) J. R. Durig and B. R. Mitchell, *Appl. Spectros.*, *21*, 221 (1967); (f) G. H. W. Milburn and M. R. Truter, *J. Chem. Soc.*, (A), 1609 (1966).

(2) A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta*, *1*, 255 (1967).

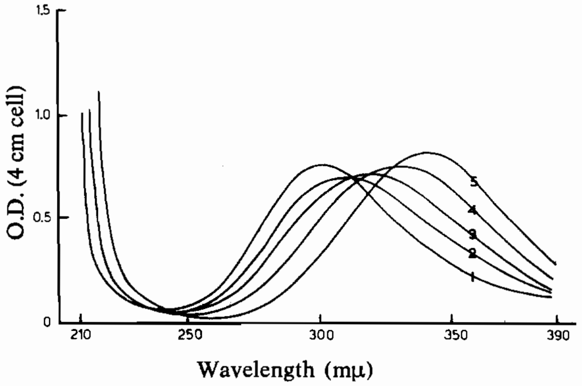


Figure 1. Spectral study of the reaction of 0.001 *M* $Pd(NH_3)_4(ClO_4)_2$ with 0.01 *M* $HClO_4$. Curves 1-5 show spectra 0.5, 5, 10, 20 and 90 minutes respectively after mixing the reagents.

Measurements of O.D. at 297 mμ were taken over a period of 2-30 mins. immediately after mixing the complex solution with perchloric acid. In some experiments $NaClO_4$ or NH_4ClO_4 was added and in others free ammonia was present in the palladium solution before adding excess perchloric acid. In each case the initial gradient of the curve showing O.D. against time, $\left[\frac{d(O.D.)}{dt}\right]_0$, was determined and the quantity k_{min} calculated, where

$$k_{min} = -\frac{1}{(O.D.)_0}\left[\frac{d(O.D.)}{dt}\right]_0$$

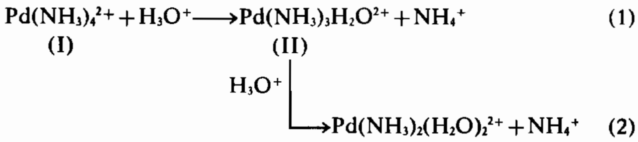
Values of k_{min} at three temperatures are given in Table I.

Table I. Rate constants and activation parameters for the reaction $Pd(NH_3)_4^{2+} + H_2O \longrightarrow Pd(NH_3)_3H_2O^{2+} + NH_3$

	$10^4k_{min}sec^{-1}$	$10^4k_{H_2O}sec^{-1}$	Temp. °C
	16.7	—	35
	5.2	13.7	25
	—	7.7	20
	1.8	4.8	15
ΔH^* kcal./mole	19.1	17.4	
ΔS^* cal./deg./mole	—9	—14	

Some reaction mixtures were allowed to stand until no further spectral changes were observed. In other cases excess chloride ion was added to reaction mixtures in the early stages of reaction. Addition of chloride resulted in rapid spectral changes to give spectra similar to those observed during the course of the reaction of $Pd(NH_3)_4^{2+}$ with HCl (see below). A number of preliminary experiments (in which O.D. values were measured at 300 mμ) showed that values of k_{min} were constant within experimental error for a variety of acid concentrations and ionic strengths up to 0.25 *M*, and for initial complex concentrations from 0.0005 *M* to 0.003 *M*. The presence of free ammonia in the palladium solution before acidifying appeared not to affect the value of k_{min}.

Discussion. The overall reactions occurring when aqueous $Pd(NH_3)_4(ClO_4)_2$ is acidified with $HClO_4$ must be stoichiometrically of the type:



$$\underset{(I)}{Pd(NH_3)_4^{2+}} + H_3O^+ \longrightarrow \underset{(II)}{Pd(NH_3)_3H_2O^{2+}} + NH_4^+ \qquad (1)$$

$$\xrightarrow{H_3O^+} Pd(NH_3)_2(H_2O)_2^{2+} + NH_4^+ \qquad (2)$$

The general picture of spectral changes exemplified in Figure 1 is that expected for a process involving at least two consecutive reactions with comparable rates.

If, before acidification, solutions of $Pd(NH_3)_4^{2+}$ salts contain appreciable amounts of $Pd(NH_3)_3H_2O^{2+}$ ions due to the equilibrium (3),

$$Pd(NH_3)_4^{2+} + H_2O \leftrightharpoons Pd(NH_3)_3H_2O^{2+} + NH_3 \qquad (3)$$

then our initial gradient values will be a measure of the rates of reactions (1) and (2) occurring in parallel. However, some of our initial palladium solutions contained excess NH_3 and, in these, it is unlikely that significant amounts of $Pd(NH_3)_3H_2O^{2+}$ were present. As values of k_{min} were found to be independent of the initial concentration of free ammonia, it seems that all our measurements refer to the single process:

$$Pd(NH_3)_4^{2+} + H_2O \longrightarrow Pd(NH_3)_3H_2O^{2+} + NH_3 \qquad (4)$$

the rate of which is expected to be first order in $Pd(NH_3)_4^{2+}$ and independent of ionic strength, as observed.

A more detailed analysis of our O.D./time curves was not undertaken owing to the difficulty of determining extinction coefficients for the species $Pd(NH_3)_n(H_2O)_{4-n}^{2+}$. Thus, the values of k_{min} are not rate constants for reaction (4) but only minimum values of such constants. In fact k_{min} is related to the pseudo 1st order rate constant (k_{H_2O}) for reaction (4) by,

$$k_{min} = \left(1 - \frac{\varepsilon_3}{\varepsilon_4}\right) k_{H_2O}$$

where ε_3 and ε_4 are the extinction coefficients at 297 mμ of $Pd(NH_3)_3H_2O^{2+}$ and $Pd(NH_3)_4^{2+}$ respectively. As the ratio $\varepsilon_3/\varepsilon_4$ is not likely to vary much with temperature, the values of k_{min} may be used to calculate activation parameters for reaction (4). These parameters are shown in Table I together with k_{H_2O} values obtained as described below. For the two temperatures (25° and 15°C) at which both k_{min} and k_{H_2O} have been determined, the ration $\varepsilon_3/\varepsilon_4$ has the value 0.62 in each case. Thus, $\varepsilon_3 \simeq 125$ as $\varepsilon_4 = 200$.

One final point concerns the ultimate extent of the replacement of NH_3 by H_2O in these reactions. Comparison of the spectra of our reaction mixtures at infinite time with spectra of solutions believed to contain Pd mainly in the form

(a) $Pd(NH_3)_2(H_2O)_2^{2+}$ (ref. 3)

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(3) B. Chakravarty and D. Banerjea, *J. Inorg. and Nucl. Chem.*, *16*, 288 (1961).

or (b) $Pd(H_2O)_4^{2+}$ (refs. 4-8)

showed similarity to the former. Comparisons of this kind are not very conclusive as concentrations of the species (a) and (b) are not known with certainty and spectra of their solutions are likely to be affected by, for example, the presence of NH_4^+ ions. One further piece of evidence is that our final reaction mixtures were converted back to solutions of $Pd(NH_3)_4^{2+}$ on addition of excess ammonia. This behaviour is found with $Pd(NH_3)_2(H_2O)_2^{2+}$ but not with $Pd(H_2O)_4^{2+}$, which precipitates hydroxo species.[3,4] Our conclusion is, therefore, that the aquation of $Pd(NH_3)_4^{2+}$ in the presence of excess acid probably proceeds rapidly only as far as the replacement of two ammonia molecules. Whether the final product, $Pd(NH_3)_2(H_2O)_2^{2+}$ has the *cis*- or *trans*-configuration is not known.*

(B) Reaction of the tetra-amminepalladium(II) ions with chloride

Results. A number of preliminary measurements[9] was made at 25°C by mixing aqueous $Pd(NH_3)_4Cl_2$ with excess HCl and following the change in O.D. at 300 mμ over a period of 30-40 mins. From initial gradients of O.D./time curves we obtained a series of rate constants, k_{obs}, fitting an equation of the form

$$k_{obs} = k_{H_2O} + k_{Cl}[Cl^-]$$

at a given ionic strength.

The value of k_{Cl} was found to decrease by a factor of about 10 when the ionic strength was increased from 0.01 *M* to 0.25 *M*.

More detailed investigations were carried out using solutions of $Pd(NH_3)_4(ClO_4)_2$ containing free ammonia, in place of the tetra-ammine chloride, and varying independently the concentrations of added chloride ion and acid. In this way it was hoped practically to eliminate from the initial palladium solutions such species as $Pd(NH_3)_3H_2O^{2+}$ and $Pd(NH_3)_3Cl^+$, which could be formed as a result of equilibria (3) and (5).

$$Pd(NH_3)_4^{2+} + Cl^- \rightleftharpoons Pd(NH_3)_3Cl^+ + NH_3 \qquad (5)$$

(That these species may normally be present in detectable concentration in ammonia free solutions is indicated by the small spectral changes, intensities and positions of maxima, resulting from the addition of ammonia to aqueous solutions of $Pd(NH_3)_4(ClO_4)_2$ or $Pd(NH_3)_4Cl_2$ [9]). The method of measuring initial gradients was also discarded in favour of the procedure described below.

The general changes in spectrum with time are shown in Figure 2 for a typical reaction mixture containing $Pd(NH_3)_4(ClO_4)_2$, $HClO_4$, $NaClO_4$ and HCl or NaCl. In all reaction mixtures studied the chloride ion concentration was more than 20 times that of the palladium complex.

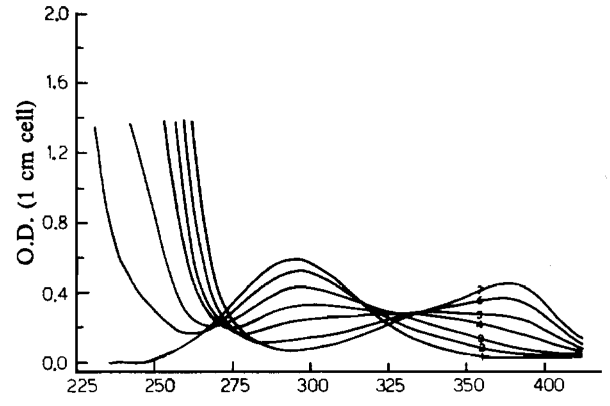

Figure 2. Spectral study of the reaction of 0.003 *M* $Pd(NH_3)_4(ClO_4)_2$ with 0.10 *M* Cl^-. $[H^+] = 0.05$ *M*, $\mu = 0.25$ *M*. Curves 1-7 show spectra at a series of time intervals after mixing, from 0.5 to 20 minutes.

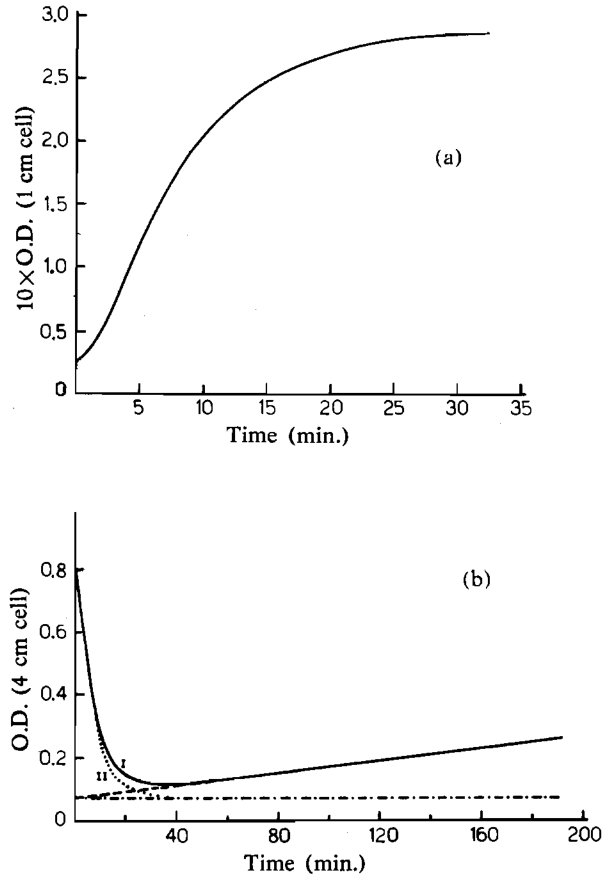

Figure 3. Variation of O.D. with time for the reaction of $Pd(NH_3)_4^{2+}$ with Cl^- at 25°. $[Cl^-] = 0.10$ *M*, $[H^+] = 0.05$ *M*, $\mu = 0.25$ *M*. (a) Measurements at 376 mμ $[Pd(NH_3)_4^{2+}] = 0.002$ *M*. (b) Measurements at 297 mμ $[Pd(NH_3)_4^{2+}] = 0.001$ *M*. (I) Experimental curve. (II) Corrected curve.

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(4) S. E. Livingstone, *J. Chem. Soc.*, 5091 (1957).

(5) D. H. Templeton, G. W. Watt, and C. S. Garner, *J. Am. Chem. Soc.*, *65*, 1608 (1943).

(6) A. K. Sundaram and E. B. Sandell, *J. Am. Chem. Soc.*, *77*, 855 (1955).

(7) H. A. Droll, B. P. Block, and W. C. Fernelius, *J. Phys. Chem.*, *61*, 1000 (1957).

(8) C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon (1962).

(9) A. A. Malik, Ph. D. thesis, University of London (1965).

(*) It appears, however, from some recent experiments (by J. R. Lyons) in this laboratory that appreciable amounts of *cis*-$Pd(NH_3)_2(H_2O)_2^{2+}$ may be present. If concentrated solutions of $Pd(NH_3)_4(ClO_4)_2$ are allowed to stand for several days with perchloric acid and then Cl^- ions added, rapid precipitation occurs to give a substance showing infrared bands characteristic of *cis*-$Pd(NH_3)_2Cl_2$. Similar results are obtained by adding Br^- or I^- instead of Cl^-, and the products in each case appear, from infrared evidence, to be *cis*-isomers.

A notable feature of the curves of the type shown in Figure 2 is the appearance of an isosbestic point after 6-10 minutes. The positions of such isosbestic points were studied carefully and were found to vary slightly (between about 336 mμ and 342 mμ) with the total chloride ion concentration in the reaction mixture. Detailed studies were carried out on the variation of O.D. with time at three wavelengths, 297 mμ, 376 mμ and the isosbestic point corresponding to the chloride concentration in the mixture. The measurements at 376 mμ gave O.D./time curves of the type shown in Figure 3a. A very slow decrease in O.D., detectable only after several hours, followed the initial increase. Values of O.D.$_{max}$ in these experiments were directly proportional to initial complex concentrations and were taken as infinity readings for plots of log-(OD$_\infty$–OD$_t$) against time. The latter were linear over at least 80% of the reaction except for some deviation near the beginning. Devations from linearity were smaller the higher the chloride ion concentration in the reaction mixture. Measurements at wavelengths in the range 336-342 mμ also gave good linear plots of log-(OD$_\infty$–OD$_t$) against time over at least 80% of the reaction. The treatment of the results of O.D. measurements at 297 mμ was complicated by the difficulty of determining infinity values—due to a slow linear increase in O.D. following the initial sharp decrease. Results of a typical experiment are shown in Figure 3b. When reaction mixtures were allowed to stand for 1-2 days the O.D. values at 297 mμ reached high values. Extrapolation to zero time of the rising linear parts of curves of the type shown in Figure 3b gave intercepts that were directly proportional to the initial palladium concentrations and corresponded closely to values of O.D. at 297 mμ for solutions of *trans*-$Pd(NH_3)_2Cl_2$ in aqueous media of similar composition to that used in reaction mixtures but without excess chloride added. These intercepts were taken as infinity readings. The O.D. values measured over the initial period of the reaction were then "corrected" by subtracting the small linear increase represented by the extrapolated portion of the curve (see Figure 3b). Using data obtained in this way, plots of log(OD$_t$–OD$_\infty$) against time were good straight lines over at least 80% of the reaction, with some deviation at the beginning.

Table II. Values of pseudo 1st order rate constants ($10^4k_{obs}sec^{-1}$) from O.D./time data in the reactions of $Pd(NH_3)_4^{2+}$ with Cl^-
(A) [complex] = 0.001 *M*; [H$^+$] = 0.05 *M*; μ = 0.25 *M*

Values from measurements of O.D. at 297 mμ and 376 mμ

	297 mμ			376 mμ		
[Cl$^-$]	15°	25°	35°	15°	25°	35°
0.25	12.5	42.5	128	11.2	37.7	123
0.20	10.7	35.9	108	9.33	32.5	106
0.15	8.37	30.2	92.3	7.50	27.0	90.0
0.10	6.37	24.1	72.8	5.67	21.3	71.7
0.05	—	17.7	52.5	3.83	15.7	51.7

Values from measurements of O.D. at wavelenghts (λ) in the region 366-342 mμ

λ(mμ)	[Cl$^-$]	15°	20°	25°
336	0.20	34.7	63.4	110
337	0.15	27.3	49.7	86.0
338.5	0.10	20.0	35.0	61.7
342	0.05	12.0	21.7	37.7

(B) [complex] = 0.001 *M*; [Cl$^-$] = 0.05 *M*; μ = 0.25 *M*
Measurements at 376 mμ and 25°C

[H$^+$]	$10^4k_{obs}sec^{-1}$
0.20	15.0
0.15	15.2
0.10	15.4
0.05	15.7

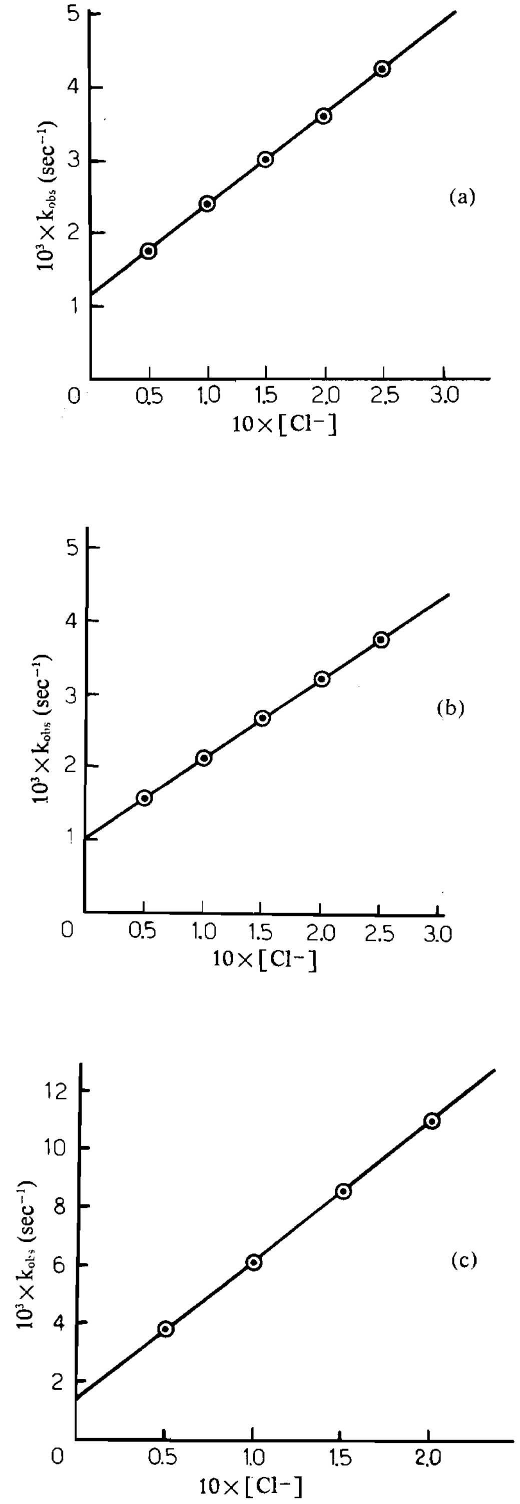

Figure 4. Values of k_{obs} (25°) as a function of [Cl$^-$] from measurements at (a) 297 mμ, (b) 376 mμ, (c) 336-342 mμ.

Table III. Intercepts ($k_{H_2O}sec^{-1}$) and gradients ($k_{Cl}\,M^{-1}\,sec^{-1}$) of curves showing k_{obs} against $[Cl^-]$. Ionic strength = 0.25 *M*

	Measurement at:					
	297 mμ		376 mμ		A value in the range 336-342 mμ	
Temp. °C	$10^4k_{H_2O}$	10^4k_{Cl}	$10^4k_{H_2O}$	10^4k_{Cl}	$10^4k_{H_2O}$	10^4k_{Cl}
35	34.7	373	36.0	350	—	—
25	11.7	123	10.1	112	13.7	471
20	—	—	—	—	7.7	279
15	2.2	40.6	2.0	36.8	4.8	153

Gradients of log plots obtained from the measurements at various wavelengths were used to calculate the pseudo 1st order rate constants given as k_{obs} values in Table II. For reactions at a given ionic strength and temperature, the k_{obs} values obtained from O.D. measurements at a given wavelength showed good linear dependence on the chloride ion concentration, as shown by the examples in Figure 4. Values of k_{obs} were, however, independent of hydrogen ion concentration.

Intercepts at $[Cl^-]=0$ and gradients of curves of the type shown in Figure 4 are given as k_{H_2O} and k_{Cl} values respectively in Table III.

Interpretation and assessment of results

The results outlined in the previous section can be interpreted in terms of a reaction scheme of the type

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{slow} D \qquad (6)$$

where k_1 and k_2 correspond to the 1st order rate constants calculated from measurements at the isosbestic point (k_1) and at 297 mμ and 376 mμ (k_2). According to this interpretation k_1 should be greater than k_2 but not so great as to make the step A→B too fast for detection in comparison with the step B→C. Owing to the small variation in the position of the isosbestic point with $[Cl^-]$ it must also be supposed that the nature of either B or C or both varies slightly as the chloride ion concentration changes. Also, to explain the results of O.D. measurements at 297 mμ, species D must have a large extinction coefficient at that wavelength although its concentration during the early stages of the reaction can be regarded as negligible.

Using the standard formulae[10] for the variation of concentration with time for the species A, B and C in reaction of the above type it can be shown easily that the quantity $(OD_\infty - OD_t)$ for measurements at a given wavelength is given by

$$(OD_\infty - OD_t) = a_2e^{-k_2t} - a_1e^{-k_1t}$$

where a_1 and a_2 are constants in terms of k_1, k_2 and the extinction coefficients at the appropriate wave-

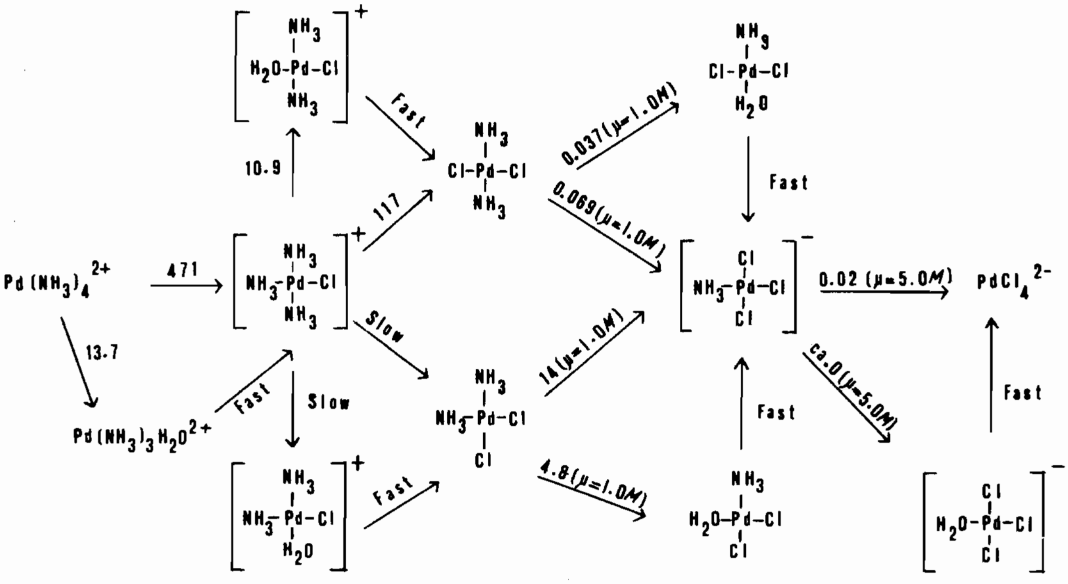

Figure 5. Reactions resulting from the addition of chloride ion to solutions containing $Pd(NH_3)_4^{2+}$ under acid conditions. Except where otherwise stated, numbers adjacent to the arrows are our values of 10^4k (in sec^{-1} or $M^{-1}\,sec^{-1}$ units as appropriate) at 25° and $\mu=0.25\,M$. Values of rate constants for $\mu=1.0\,M$ and $5.0\,M$ are from Poë and Vaughan,[2] and refer to aqueous media containing a small percentage of ethanol.

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(10) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd Ed., Wiley, p. 166 (1961).

lengths of the species A, B and C. (If B and C have an isosbestic point, a_2 becomes zero). Thus,

$$\ln(OD_{\infty}-OD_t) = \ln a_2 - k_2 t + \ln\left(1 - \frac{a_1}{a_2} e^{-(k_1-k_2)t}\right) \qquad (7)$$

The last term on the right hand side of (7) will be negligible at sufficiently large values of t and plots of $\ln(OD_{\infty}-OD_t)$ against t should tend to straight lines of gradient $-k_2$ within experimentally accessible times if k_1 and k_2 are not too similar in magnitude. Furthermore, in the present case, as k_1 and k_2 include a term in $[Cl^-]$, the deviation from linearity of the log plots should become smaller as the chloride ion concentration is increased—as observed. The two values of k_{obs} deduced from measurements of O.D. at both 297 mμ and 376 mμ on a given reaction mixture should be equal. Inspection of Table II shows that there is fair agreement between the two sets of values. Those obtained from measurements at 297 mμ may be the less reliable owing to uncertainties in determining OD_{∞} values (see above).

If (see (6)) we identify A as $Pd(NH_3)_4^{2+}$, B as $Pd(NH_3)_3Cl^+$ and C as a mixture of *cis*- and *trans*-$Pd(NH_3)_2Cl_2$, and remember that the values of k_{obs} can be expressed as $(k_{H_2O}+k_{Cl}[Cl^-])$, the details of the reactions occurring when $Pd(NH_3)_4^{2+}$ is mixed with chloride in acid solution can be discussed with reference to Figure 5, in which the results of Poë and Vaughan[2] are included. It is assumed that in all cases the replacement of H_2O by Cl^- is a fast reaction, as in the case of similar Pt^{II} complexes.[11] Evidence for this in the case of the species $Pd(NH_3)_3(H_2O)^{2+}$ is given above, and it seems likely to be so for the other aquo species shown in Figure 5 in view of the simple two-term form of the expression for k_{obs}. One major point of interest concerns the course of the reactions following the formation of $Pd(NH_3)_3Cl^+$. Poë and Vaughan[2] found that the reactions of *cis*- and *trans*-$Pd(NH_3)_2Cl_2$ with HCl are slow at 25° and occur at quite different rates to form $Pd(NH_3)Cl_3^-$, so isomerisation of the starting materials cannot occur rapidly under their conditions. Our conditions are very similar in that hydrogen and chloride ions are present in large excess in the reaction mixtures, and differ from those of Poë and Vaughan mainly in respect of ionic strength. (There is also a small difference in solvent composition). It should therefore be possible, in principle, to determine whether the ion $Pd(NH_3)_3Cl^+$ undergoes chloride substitution to give *cis*- or *trans*-$Pd(NH_3)_2Cl_2$ or both. The spectra of our reaction mixtures show the appearance of a low intensity ($\varepsilon \simeq 200$) product peak with a maximum in the region 376-378 mμ. This peak could be due to either *cis*- or *trans*-$Pd(NH_3)_2Cl_2$ (or both), with maxima at 376 mμ and 380 mμ respectively.[2] There is no clear evidence in any of our kinetic experiments for the appearance of a shoulder at 290 mμ ($\varepsilon = 1500$)[2] due to *cis*-$Pd(NH_3)_2Cl_2$. In a few kinetic experiments in which low (ca. 10^{-4} *M*) palladium concentrations were used, features of the spectra of reaction mixtures in the region below 270 mμ were discernable (Figure 6).

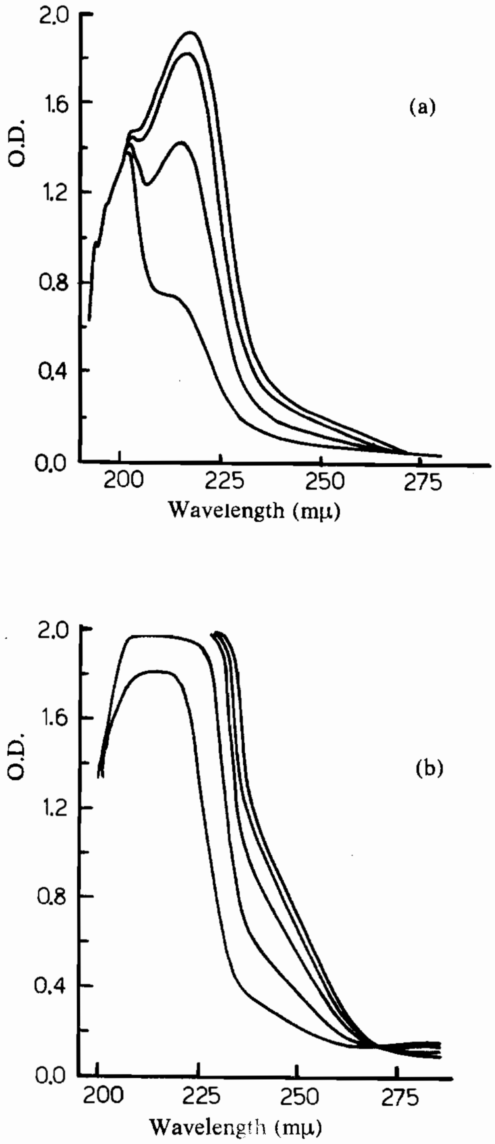

Figure 6. Spectral study of the reaction of 0.0001 *M* $Pd(NH_3)_4(ClO_4)_2$ with 0.25 *M* Cl^-. $[H^+]=0.20$ *M*, $\mu=0.25$ *M*; (a) 1 cm. cell, (b) 4 cm. cell.

These show the presence of a shoulder in the product spectrum at ca. 250 mμ, which is characteristic of *trans*-$Pd(NH_3)_2Cl_2$.[2] However, the spectrum of *cis*-$Pd(NH_3)_2Cl_2$ has a shoulder of about the same intensity at 260 mμ.[2] We conclude from all the spectral evidence that the *main* product in the reaction of $Pd(NH_3)_3Cl^+$ with Cl^- is *trans*-$Pd(NH_3)_2Cl_2$. The kinetic evidence also supports this conclusion. If *cis*-$Pd(NH_3)_2Cl_2$ were formed in significant amount we should expect to find marked evidence in our runs for the formation of $PdNH_3Cl_3^-$. (Chloride substitution in *trans*-$Pd(NH_3)_2Cl_2$ is too slow[2] at 25° to be detectable in our experiments). That at least a small quantity of *cis*-$Pd(NH_3)_2Cl_2$ is formed is suggested by two observations, First, the slow increase in O.D. at 297 mμ following the initial sharp decrease (Figure 3b) could be due to Second, the slight variation in isosbestic points mentioned above could result from the formation of *cis*-products of substitution reactions of *cis*-$Pd(NH_3)_2Cl_2$.

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[11] D. Banerjea, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.*, 79, 4055 (1957).

and *trans*-dichlorodiammines in proportions depending upon the total chloride ion concentration. (If this were so the observed pseudo 1st order rate constants for the reaction of $Pd(NH_3)_3Cl^+$ would still be of the form $(k_{H_2O}+k_{Cl}[Cl^-])$, but both k_{H_2O} and k_{Cl} would be composite and the ratio [*cis*-isomer]|[*trans*-isomer] in the product would be chloride dependent.)

General discussion

As a basis for the discussion of *cis*- and *trans*-effects in chloro-ammine complexes of Pd^{II} and Pt^{II}, kinetic data for various reactions have been summarised in Table IV. It is usual to compare the *trans*-effects of a given pair of ligands by calculating the ratio of rate constants for reactions of two substrates having one or other of the two ligands in the position *trans*- to the leaving group. The *cis*-effect may be determined similarly. If this procedure is applied to the data in Table IV, the *trans*- and *cis*-effects of chloride as compared with ammonia are obtained, as shown in Table V.

Table IV. Summary of kinetic parameters for the reactions:

$$\text{(A)}\quad [Pd(NH_3)_{4-x}Cl_x]+X \longrightarrow [Pd(NH_3)_{3-x}Cl_xX]+NH_3$$

$$\text{(B)}\quad [Pt(NH_3)_{4-x}Cl_x]+Y \longrightarrow [Pt(NH_3)_{4-x}Cl_{x-1}Y]+Cl^-$$

(Charges on complex ions have been omitted for clarity). Values of rate constants (k) are in $M^{-1}\,sec^{-1}$ (X or Y = Cl^-) or sec^{-1} (X or Y = H_2O or NH_3) units for the reactions at 25°C. ΔH^* values are in kcal./mole. ΔS^* values are in cal./deg./mole. n = Number of equivalent leaving groups in the substrate

(A)		X = Cl^-			X = H_2O				
Substrate	n	$10^4\frac{k}{n}$	ΔH^*	ΔS^*	$10^4\frac{k}{n}$	ΔH^*	ΔS^*	μ (*M*)	Ref.
(a) $Pd(NH_3)_4^{2+}$	4	118	20.3	0	3.4	17.4	−14	0.25	This work
(b) $Pd(NH_3)_3Cl^+$	1[a]	117	19.1	− 4	10.9	24.4	+10	0.25	
(c) *cis*-$Pd(NH_3)_2Cl_2$	2	7.0	18.0	−11.2	2.4	17.7	−14.3	1.0	
(d) *trans*-$Pd(NH_3)_2Cl_2$	2	0.035	23.0	− 4.9	0.019	22.2	− 8.9	1.0	(2)
(e) $PdNH_3Cl_3^-$	1	0.02	23.0	− 7.4	—	—	—	5.0	

(B)	n	Y = Cl^-			Y = H_2O			Y = NH_3		
		$10^5\frac{k}{n}$	ΔH^*	ΔS^*	$10^5\frac{k}{n}$	ΔH^*	ΔS^*	$10^4\frac{k}{n}$	ΔH^*	ΔS^*
(1) $Pt(NH_3)_3Cl^+$	1	7			2.6	18	−18	3.7		
(2) *trans*-$Pt(NH_3)_2Cl_2$	2	39			4.9	20	−11	14.5		
(3) *cis*-$Pt(NH_3)_2Cl_2$	2	1.5			1.25	20	−14	—	—	—
(4) $PtNH_3Cl_3^-$	2[b]				2.8	18	[d]	5.7	14.4	−24
(5) $PtNH_3Cl_3^-$	1[c]				0.62	[d]	[d]	—	—	—
(6) $PtCl_4^{2-}$	4				1.0	21	− 8	1.0_5	16	−21
	μ:	0.318 *M*			0.318 *M*					
	Ref.:	(13)			(12) and references cited therein			(14)		

[a] Leaving group is NH_3 *trans*- to Cl^-. [b] Leaving group is Cl^- *cis*- to NH_3. [c] Leaving group is Cl^- *trans*- to NH_3. [d] ΔH^* and ΔS^* are respectively 19 and −15 from rate data for reactions (4) and (5) occurring together.

Thus, for different pairs of substrates and different entering groups, the *trans*-effects ($Cl^-:NH_3$) for the Pd^{II} complexes are within a factor of 5-6 of each other. A factor of slightly less than 4 spans the *trans*-effects in the Pt^{II} complexes. A similar situation arises for the *cis*-effects in the Pt^{II} complexes (factor slightly greater than 3), but for the Pd^{II} complexes a factor of about 70 is found. This last figure is rather unexpected in view of the comparative consistency found for the most part in Table V. However, with the present limited information, any discussion of *cis*- and *trans*-effects in Pd^{II} and Pt^{II} chloro-ammine complexes must remain highly qualitative. Tucker *et al.*[12] state that for the aquation reactions of Pt^{II} chloro-ammine systems the *cis*- neighbour has somewhat greater influence on the kinetics than the *trans*- neighbour. The statement appears to be based on the fact that the formula $k/n=1.0\times10^{-5}\times(0.5)^m\times(2.4)^p$ represents reasonably well (*i.e.* to within 20%) the rate constants for the aquation reactions (m and p are the numbers of NH_3 groups *trans*- and *cis*- respectively to the leaving Cl^-, and n is the number of equivalent leaving groups in the substrate). The argument is not altogether convincing because other formulae for k/n may be devised and, on the basis of the same kind of reasoning, would lead to different conclusions (*e.g.* for the same set of rate constants, the values k/n are given to within less than 20% by the formula $k/n=1.0\times10^{-5}\ sec^{-1}\times(0.8)^a(1.75)^b$, where a = number of *trans*-NH_3 groups + number of *cis*-chlorides, and b = number of *cis*-NH_3 groups + number of *trans*-chlorides. This result would then lead to the more complicated conclusion that *cis*-NH_3 and *trans*-Cl have about the same effect, and that this is greater than the effect of *trans*-NH_3 or *cis*-Cl. The data for the Pt^{II}

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(12) M. A. Tucker, C. B. Colvin and D. S. Martin, *Inorg. Chem.*, *3*, 1373 (1964).
(13) F. Aprile and D. S. Martin, *Inorg. Chem.*, *1*, 551 (1962).
(14) A. A. Grinberg, *Russ. J. Inorg. Chem.*, *4*, 683 (1949).

Table V. *trans*- and *cis*-effects of chloride as compared with ammonia. Values are ratios of rate constants for the reactions listed in Table IV

Entering group	Reactions of Pd^{II} complexes (Leaving group NH_3)				Reactions of Pt^{II} complexes (Leaving group Cl^-)						
	trans-effect		*cis*-effect		*trans*-effect			*cis*-effect			
	(b)/(a)	(e)/(d)	(c)/(b)	(e)/(c)	(2)/(1)	(6)/(5)	(4)/(3)	(3)/(1)	(4)/(2)	(5)/(3)	(6)/(4)
H_2O	3.2	—	0.22	—	1.9	1.6	2.2	0.48	0.57	0.5	0.36
Cl^-	1.0	0.57	0.06	0.003	5.6	—	—	~0.2	—	—	—
NH_3	—	—	—	—	3.9	—	—	—	0.4	—	0.18

reactions in Table V support this conclusion, *i.e.* the *trans*-effect ($Cl > NH_3$) $\simeq$ *cis*-effect ($NH_3 > Cl$) $\simeq 2$.

The whole question of discussing *cis*- and *trans*-effects in terms of ratios of rate constants as given in Table V raises at least three difficulties.

(i) When the two ligands being compared differ in charge, the effect of changing the ligand necessarily includes the effect of changing the charge on the substrate. It would be useful if that part of the total effect due to changing the charge could be estimated separately from the other factors. Possibly the effect of charge can be estimated by considering the ratios k_{Cl}/k_{H_2O} for a series of substrates. In the case of the Pd^{II} complexes, k_{Cl}/k_{H_2O} at 25° decreases fairly regularly by a factor of 3-4 through reactions (a) to (d) (Table IV(A)), although the ratios are different (by a factor of nearly 2) for (c) and (d), each of which has a substrate of zero charge. The values of k_{Cl}/k_{H_2O} for the Pt^{II} reactions (1)-(3) (Table IV(B)) vary irregularly, however, so that no simple charge effect can be discerned. Furthermore, any arguments based upon values of k_{Cl}/k_{H_2O} ratios are open to objections (ii) and (iii) below.

(ii) The effect of ionic strength may be marked. It is not sufficient to compare two rate constants determined under conditions of equal ionic strength, for the two reactions to which the constants refer may be unequally affected by this factor. Our preliminary experiments indicate that rate constants for the chloride substitutions in $Pd(NH_3)_4^{2+}$ may decrease by a factor of 10 as μ is increased from 0.01 *M* to 0.25 *M*. The results of Poë and Vaughan[2] show that k decreases by a factor of about 1.5 for the reaction of *cis*-$Pd(NH_3)_2Cl_2$ with Cl^- when μ is increased from 1.0 *M* to 0.5 *M*, and decreases by a factor of 5-6 for aquation of the same complex.

It is difficult to estimate in general the magnitude of ionic strength effects in the reactions of Pd^{II} and Pt^{II} chloro-ammines as experimental date are almost non-existent and the problem is not at the moment accessible to theoretical treatment in the range of ionic strengths often used in these experiments.

(iii) The ratio of the two rate constants determined at the same temperature will vary with temperature, unless the reactions to which they refer have equal ΔH^* values. As an alternative to rate constant data, values of activation parameters may be used in comparing kinetic aspects of a series of reactions. For example, Poë and Vaughan[2] pointed out that, for the chloride substitution reactions (e) and (c) (Table IV(A)), the *cis*-effect of NH_3 is *greater* than that of Cl^- to the extent of 5 kcal./mole. However, for reactions (d) and (b) the *cis*-effect of NH_3 appears to be *less* than that of Cl^- to the extent of 1 kcal./mole and 6 kcal./mole respectively in the chloride substitution and aquation reactions. Similar calculations using other values of ΔH^* and ΔS^* in Table IV seem to reveal no regular pattern that can be associated with *cis*- and *trans*-effects either for Pt^{II} or for Pd^{II} complexes. The data are, however, rather limited. Most of the reactions for which ΔH^* and ΔS^* values are listed in Table IV are aquations. It may be that the appearance of a regular pattern is disguised by the untypical behaviour of H_2O as an entering group. The value of ΔS^* for the aquation of $Pd(NH_3)_3Cl^+$ is particularly odd in being positive, whereas for all the other aquation reactions of Pd^{II} and Pt^{II} complexes listed the ΔS^* values are negative in the range -8 to -18 e.u.

Our general conclusion is that attempts to rationalise the present published kinetic data in terms of *cis*- and *trans*-effects of the ligands are not very profitable in the case of Pd^{II} and Pt^{II} chloroammine systems.

In a very recent publication Reinhardt and Sparkes[16] have reported their results on the chloride substitution and aquation reactions of $Pd(NH_3)_4^{2+}$. It appears that our conclusions differ significantly from theirs in that they consider the first step of reactions (8) to be slower than the second step.

$$Pd(NH_3)_4^{2+} \xrightarrow{k'_A} Pd(NH_3)_3Cl^+ \xrightarrow{k'_B} \textit{trans}\text{-}Pd(NH_3)_2Cl_2 \qquad (8)$$

(Where, using the nomenclature of Reinhardt and Sparkes, k'_A and k'_B represent observed pseudo 1st order rate constants.) Our experiments were carried out at $\mu = 0.25$ *M*, whereas most of theirs refer to conditions of unit ionic strength. However, at 25°, for $[Cl^-] = 0.25$ *M* and $\mu = 0.25$ *M*, our values of $10^4 k'_B$ (42.5 and 37.7 sec^{-1}, see Table II) are close to the value of $10^4 k'_A$ (*i.e.* 42.2 sec^{-1}) given by Reinhardt and Sparkes for $[Cl^-] = 0.24$ *M* and $\mu = 0.24$ *M* at the same temperature (see their Table II). It appears, therefore, that our differences are mainly in the interpretation of our respective results, rather than in the actual magnitudes found for the rate constants. In support of our interpretation we make the following points:

(i) The overall spectral changes in our experiments (as exemplified in Figure 2) show clearly the appearance after a short interval of isosbestic points in the region 336-342 mμ. It is not easy to see how these

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(15) H. D. K. Drew, F. W. Pinkard, G. H. Preston and W. Wardlaw, *J. Chem. Soc.*, 1895 (1932).
(16) R. A. Reinhardt and R. K. Sparkes, *Inorg. Chem.*, *6*, 2190 (1967).

results could be explained on the interpretation given by Reinhardt and Sparkes.

(ii) It seems possible to give a reasonable interpretation of their results, however, if the values assigned to k'_A and k'_B are interchanged. Thus according to Figure 2, measurements of O.D. at 355 mμ would be expected to yield values of k'_B rather than k'_A *i.e.* values close to our results from measurements at 376 mμ. Furthermore, if the values of k_{A2} and k_{B2} are interchanged, the dependence on ionic strength predicted by the Davies relation (neglecting the small linear term in μ) is confirmed, *i.e.* values of

$[(\log k_{A2})+\mu^{1/2}/(1+\mu^{1/2})]$ and of $[(\log k_{B2})+2\mu^{1/2}/(1+\mu^{1/2})]$

remain constant within experimental error. (l.c. their Table II).

We reserve further comment until we have seen their supplementary material, which was not given in the paper.

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