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Kinetics of Ammonation of the Chloro-Ammine Series of Platinum(II) Complexes *

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Spectrophotometric evaluation of the rate constants for the replacement of chloride ligands in the complete series of chloro-ammine complexes of platinum(II) are reported. These second order rate constants for the series extended over at least a fifty-fold range at 25°C. There appears to be no large effect of the ionic charge on the rates, and the rate constants can be fairly well systematized according to the neighbors cis *and* trans *to the leaving chloride ligand.*

Introduction

Earlier papers[1] from this Laboratory have described the kinetics for the replacement of chloride ligands by H_2O in aqueous solutions and the kinetics for the isotopic exchange with free chloride ion for the complete chloride-ammine series of platinum(II) complexes. The kinetics of each of these complexes with ammonia have also been followed by a number of these workers. In so far as we can determine, the kinetics for the replacement of chloride by ammonia has not been previously reported for some of these complexes. In our reporting for these systems, we have also included results for the entire series in order to provide a complete picture; although some of the systems have been treated by other workers as will be mentioned.

In general, ammonia concentrations have been sufficiently high to be considered constant, *i.e.*, conditions for pseudo first order kinetics applied. However, except for the species, $Pt(NH_3)_3Cl^+$, successive replacement of more than one chloride ligand was possible. The replacement of Cl^- ligand by NH_3 appeared complete in every instance under these conditions, *i.e.*, the reverse reaction or the equilibrium between chloride and ammonia did not need to be considered. The replacement of chloride ligands by H_2O is a competitive process however. The H_2O ligands are sufficiently acidic that at the high pH of the NH_3 solutions they are converted to hydroxo ligands. Ammonia apparently does not replace the OH^- groups.

Experimental Section

Preparation of each of the complexes has been described previously.[1] A spectrophotometric technique has been used in which the spectra and their changes were recorded by means of a Cary Model 14 spectrophotometer in the ultraviolet region of 400 to 200 mμ. Spectra for each member of the chloro-ammine complexes had been recorded quickly after their compounds had dissolved in 0.1 to 0.318 *M* Cl^- solutions. It was generally possible to evaluate the rates of reactions from the initial slopes of the plots of absorbance *vs.* wave length.

Somewhat different procedures were required for the different complexes. For the anionic species, $PtCl_4^{2-}$ and $Pt(NH_3)Cl_3^-$, for which aquation was most serious, the weighed salts were dropped into standardized solutions of KCl and NH_3 which were thermostated at reaction temperatures. Aliquots of these solutions were quickly transferred to jacketed cells in the spectrophotometer. For *cis*- and *trans* $Pt(NH_3)_2Cl_2$, which dissolved slowly, solutions of the complex in 0.318 *M* KCl were prepared. The reaction was started by adding freshly standardized NH_3 solution at reaction temperature, and the solution was transferred into a cell in the thermostated cell compartment. Spectra were scanned repetitively after the start of the reaction; or the absorbance, A, at one or two wave lengths was recorded as a function of time. Plots of A *vs.* time were linear in the first few minutes of the runs so $(dA/dt)_0$ could be evaluated rather accurately. From these slopes was subtracted the initial rate of change of A *vs.* time when solutions of equal complex concentration reacted with KOH. This procedure subtracted the initial changes due to the aquation reactions, and their contribution to the slopes did not, in any of the cases, exceed 20 percent of the slope in the NH_3 solutions.

Each complex in the series except $Pt(NH_3)Cl_3^-$ yielded a single product as a consequence of the initial ammonation, and spectra for each of these products were available. The initial rate of change in

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(1) *a.* L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., *J. Am. Chem. Soc.*, *77*, 2965 (1955). *b.* T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., *J. Am. Chem. Soc.*, *80*, 536 (1958). *c.* T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., *J. Am. Chem. Soc.*, *81*, 10 (1959). *d.* J. W. Reishus and D. S. Martin, Jr., *J. Am. Chem. Soc.*, *83*, 2457 (1961). *e.* R. J. Adams and D. S. Martin, Jr., « Advances in the Chemistry of the Coordination Compounds », S. Kirschner, Editor, Mac Millan Co., New York, 1961, p. 579. *f.* F. Aprile and D. S. Martin, Jr., *Inorg. Chem.*, *1*, 551 (1962). *g.* M. A. Tucker, C. B. Colvin and D. S. Martin, Jr., *Inorg. Chem.*, *3*, 1373 (1964).

the absorbance at wave length, λ, due to the ammonation reaction is given by the expression

$$\left(\frac{dA^{\lambda}_{am}}{dt}\right)_0 = R_0 l(\varepsilon_2 - \varepsilon_1) \qquad (1)$$

where: ε_2 and ε_1 are the molar absorptivities of the first ammonation product and starting complex, respectively. 1 is the cell length. R_0 is the initial rate of reaction. The second order rate constant was then calculated from the expression

$$R_0 = k_{NH_3}[NH_3][Pt]_0 \qquad (2)$$

The wave length for the absorbance measurements was chosen to give large changes in the absorbance for optimum precision. The wave lengths used are indicated in *Table I* which also gives the range of concentrations covered and the average values of k_{NH_3} obtained for each complex. In general, each rate constant was an average based on 4 to 8 experiments.

The complex, $Pt(NH_3)Cl_3^-$, can add one ammonia to form either *cis* or *trans*-$Pt(NH_3)_2Cl_2$ so equation (1) must be modified in the following way:

$$\left(\frac{dA^{\lambda}_{am}}{dt}\right)_0 = (R_{tr})_0 l(\varepsilon_{tr} - \varepsilon_1) + (R_{cis})_0 l(\varepsilon_{cis} - \varepsilon_1). \qquad (3)$$

$(R_{tr})_0$ and $(R_{cis})_0$ and therefore the corresponding second order rate constants can be evaluated from the initial slopes at two different wave lengths. A wave length of 345 mμ, where $Pt(NH_3)Cl_3^-$ has a maximum and both *cis*-and *trans*-$Pt(NH_3)_2Cl_2$ have low molar absorptivities, was chosen for one wave-length. A wave length of 300 mμ, where *cis*-$Pt(NH_3)_2Cl_2$ has a maximum, was used for the other.

Results and Discussion

The second order ammonation rate constants together with their standard deviations from the sets of measurements for each of the chloroammine-complexes of platinum(II) at the temperatures studied are presented in Table I. The uncertainities in the rates indicated by the standard deviation appear consistent with applications of the spectrophotometric method to systems with competing and successive reactions. Values of the rate constants which have been reported by Grinberg and his co-workers[2-4] are included in the table for comparison. It appears that there is a fiftyfold variation in these ammonation rate constants among the group of complexes. Enthalpies of activation, which range from 10 to 18 kcal are generally a few kcal lower than the values for the aquation reactions of the corresponding chloride. Entropies of activation have sizable negative values which are rather characteristic of the ligand replacement reactions of platinum(II).[5]

For $PtCl_4^{2-}$ our rate constants agree very satisfactorily with those of Grinberg and Smolenskaya.[2] For $Pt(NH_3)Cl_3^-$ they measured the total reaction, determining the NH_3 consumed in the reaction by titration. From the spectrophotometric observations it was apparent that the $Pt(NH_3)Cl_3^-$ formed predominantly the *cis* isomer of $Pt(NH_3)_2Cl_2$; for a large peak at 300 mμ, characteristic of the *cis*-isomer, was observed to grow into the spectrum. The fact, that reaction is used in the practical synthesis of the *cis* isomer, does not preclude the extensive formation of the *trans* isomer since any of this *trans*-$Pt(NH_3)_2Cl_2$, which forms, reacts some 30 times faster with NH_3 to give the $Pt(NH_3)_3Cl^+$. However, the rate constant for the chloride *trans* to NH_3 in $Pt(NH_3)Cl_3^-$ appears to be not more than 10 - 15% as great as that for the chloride cis to NH_3. Since the rate of the *trans*-chloride is so low and must be obtained by the difference of large numbers, it is not given at all accurately in these experiments and the indicated rate constant did not exceed its standard deviation. It appears that the reactivity ratio for the *cis* and the *trans* chlorides must be as great as found for the aquation process[1g]. However, the value of 1.2×10^{-4} M^{-1} sec^{-1} for the *trans*-chloride at 25° is much larger than the value indicated by the systematics in equation 4 below. The sum of the two rate constants from the spectrophotometric method agrees very well with the overall rate constant of Grinberg and Smolenskaya.[2]

The rate constant for *cis*-$Pt(NH_3)_2Cl_2$ was lower than for any other except the *trans* chloride in $Pt(NH_3)Cl_3^-$. Its activation enthalpy was highest although it was partially compensated by a high activation entropy. On the other hand, the *trans*-$Pt(NH_3)_2Cl_2$ reacted the most rapidly by far of all the complexes, and its reaction possesses the lowest activation enthalpy. This reaction was so fast that half-times for the process amounted to only 10 - 15 minutes, and consequently the rate constants suffered in accuracy. Our values appear to be substantially higher than those reported by Grinberg *et al.*[4] This behavior resembles the reaction of *trans*-$Pt(NH_3)_2Cl_2$ with the chloride ion where the second order rate constants for ligand exchange is 10 times larger than for any other of these complexes.

There is a moderate entering group effect indicated between Cl^- and NH_3, probably attributable to charge on the chloride. $Pt(NH_3)_3Cl^+$ has the second highest second order rate constant for exchange, whereas for ammonation it is the $Pt(NH_3)Cl_3^-$. Again, for $Pt(NH_3)_3Cl^+$, our rate constant is significantly higher than that of Grinberg *et al.*[4]

The reaction rates appear to be consistent with the normal mechanism for the ligand substitution process of platinum(II) complexes, which is considered to be an association mechanism involving a nucleophilic attack by the entering group and a trigonal bipyramid intermediate.[6, 7] No evidence appeared for

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(2) A. A. Grinberg and D. B. Smolenskaya, *Zh. Neorg. Khim.*, *6*, 95 (1961).

(3) A. A. Grinberg and D. B. Smolenskaya, *Zh. Neorg. Khim.*, *6*, 103 (1961).

(4) A. A. Grinberg, S. S. Borsakova, I. N. Kukaskin, V. E. Mironov, L. E. Nikolskaya, D. B. Smolenskya and G. A. Sagisultanova, *Svensk. Kem. Tidskrift.*, *73*, 199 (1961).

(5) U. Belluco, R. Ettore, F. Basolo, R. G. Pearson and A. Turco, *Inorg. Chem.*, *5*, 591 (1966).

Table I. Second Order Rate Constants for the Reaction of the Chloro-Ammine-Platinum(II) Complexes with NH_3. Ionic Strength Adjusted to 0.318 *M* by the Addition of KCl.

Complex	Wave Length Utilized mμ	Con. Range of Complex m*M*	Conc. Range of NH_3 *M*	$10^4 \times k_{NH_3}$ M^{-1} sec^{-1} 15.0°	20.0°	25.0°	35.0°	ΔH* kcal mole^{-1}	ΔS* cal deg. mole^{-1}
$PtCl_4^{2-}$	390	2 - 10	0.05-1.05	1.5±.1		3.7±.3	9.0±.3	16	—22
						4.2 [a]	10.7 [a]		
$Pt(NH_3)Cl_3^-$	345	4 - 8	0.15-.53	*cis* -		9.9±.9	25±1.4	16	—18
				trans -		1.2±1.2	3.3±1.5	17.5	—18
				Total	7.3 [b]	11.4 [b]	26.1 [b]		
cis-$Pt(NH_3)_2Cl_2$	300	1.3	0.10-.90	0.61±.03		1.9±.06	4.8±.3	18	—15
trans-$Pt(NH_3)_2Cl_2$	315	0.5	0.10-.20		45±3	57±3	111±8	10	—33
						29 [c]			
$Pt(NH_3)_3Cl^+$	265	3.0	0.2-.84		2.9±.1	5.4±.1	13±.4	17	—15
						3.7 [c]			

[a] Reference 2. [b] Reference 3. [c] Reference 4.

an *anomalous* mechanism involving dimeric transition states sometimes found for the ligand replacement reactions of platinum(II)[8]; although the concentration ranges which could be tested were somewhat limited by molar absorptivities and solubilities.

It has been noted that the first order aquation rate constants at 25°C for this series of complexes[1g] were given very well by the simple expression:

$$k_{H_2O}/n = C(M)^m(P)^p \qquad (4)$$

where: n = the number of equivalent chlorides; m = the number of NH_3 ligands *trans* to the leaving Cl^- ligand, *i.e.* either 0 or 1; p = the number of NH_3 *cis* to the leaving Cl^- ligand, *i.e.* either 0, 1 or 2. M = 0.5, P = 2.4, C = 1.0×10^{-5} sec^{-1}.

Coe, Hussain and Malik[9] have commented on limitations of this formula in that: (*i*) it does not account for a charge effect of the entering group, (*ii*) it does not consider ionic strength effects, and (*iii*) it correlates rate constants or activation free energies rather than enthalpies of activation. Whereas we concur with a number of their comments and reservations, we believe the formula does provide a useful systematization. Hopefully, the charge effects may become evident as sufficient information is accumulated. There are still only very limited ionic strength studies, and in at least some cases we have tested, the aquation reactions have appeared relatively independent of moderate ionic strength changes. For this set rate of constants the ionic strength was high and constant (.318*M*). Usually, rate constants are known with considerably higher accuracies than the activation enthalpies which require differences in the rate constants. Consideration of the k's is then the more profitable.

Coe *et al.*[9] also pointed out that the aquation rate constants would be given by the expression:

$$k_{H_2O}/n = C(A)^a(B)^b, \qquad (5)$$

where: a = the number of NH_3 *trans* + the number of Cl^- *cis* to the leaving chloride; b = the number of Cl^- *trans* + the number of NH_3 *cis* to the leaving chloride; A = 0.8; B = 1.75 and C, 1.0×10^{-5} sec^{-1}.

In equation (4) the m and p are independent parameters. However, in equation (5) the parameters a and b must satisfy the relation $a+b=3$. Hence, in equation (5) A and B are not independent, and from the ratios of rate constants only the ratio of A/B can be evaluated. Under the conditions where $M\approx1/P$ applies in equation (4), as was observed, an equation of the form of (5) will apply as well. In addition to providing a numerical correlation of the rates, the equation (4) has emphasized the importance of the *cis* neighbor in influencing ligand substitution reaction rates in the platinum system which have very frequently been attributed to a « *trans*-effect ».

Accordingly, we have tested equation (4) for the values of k_{NH_3}/n given in Table I for 25°. All but the one for the replacement of the chloride *trans* to NH_3 in $Pt(NH_3)Cl_3^-$ are given to about 10% by this expression when $M=(1/5)$, $(P)=5$ and $C=1.0\times10^{-4}M^{-1}$sec^{-1}. This formula predicts a value of about $0.2\times10^{-4}M^{-1}$sec^{-1} rather than $1.2\times10^{-4}M^{-1}$sec^{-1} which was observed. A much lower value than $1.2\times10^{-4}M^{-1}$sec^{-1} is probably not outside the realm of possibility in view of the uncertainty in this constant which must be evaluated in the presence of the more rapid ammonation of the *cis*-chlorides. This formula indicates that, as with aquation, the presence of a *cis* ammonia is about equal to the effect of a *trans* chloride, *i.e.* $1/M=P$. However, the ammonation reactions are much more sensitive to effects of these neighbors as evidenced by $1/M=P=5$ in comparison to the values $1/M=2.0$, $P=2.4$. This greater sensitivity is perhaps a consequence of the lower activation enthalpy so that the neighbors exert a relatively greater influence in the transition state. The results emphasize that in the preparation of *cis*-$Pt(NH_3)_2Cl_2$ from $Pt(NH_3)Cl_3^-$, which is perhaps the most frequently quoted example of the *trans* effect, the success of the synthesis is attributable to a combined *cis* and *trans* effect.

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(6) C. H. Langford and H. B. Gray, « Ligand Substitution Processes » (Benjamin, Ney York, 1965) Chapter 2.

(7) F. Basolo and R. G. Pearson, « Mechanisms of Inorganic Reactions », (2nd Ed. Wiley, New York, 1967) Chapter 5.

(8) D. S. Martin, Jr., *Inorg. Chim. Acta Reviews*, *1*, 87 (1967).

(9) J. S. Coe, M. O. Hussain and A. A. Malik, *Inorg. Chim. Acta*, *2*, 67 (1968).