

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
EMORY UNIVERSITY, ATLANTA, GEORGIA**A Kinetic Study of the Replacement of a Chloride Ion in the *trans*-Dichlorotetraammineplatinum(IV) Cation by Ammonia**BY RONALD C. JOHNSON AND EUGENE R. BERGER¹

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The rate law for the replacement of one chloride ion in *trans*-Pt(NH₃)₄Cl₂²⁺ by NH₃ in aqueous NH₃-NH₄ClO₄ solutions at 22.5° is $d[\text{Pt}(\text{NH}_3)_5\text{Cl}^{3+}]/dt$ (moles l.⁻¹ sec.⁻¹) = $1.21[\text{trans-Pt}(\text{NH}_3)_4\text{Cl}_2^{2+}][\text{Pt}(\text{NH}_3)_4^{2+}][\text{NH}_3]$; $\Delta H^* = 6$ kcal./mole and $\Delta S^* = -37$ e.u. In unbuffered ammonia solutions side reactions are important. Evidence is reported which invalidates an earlier kinetic study in dilute aqueous ammonia.

Introduction

Zvyagintsev and Shubochkina have studied the rate of reaction 1 and a variety of similar reactions.²



They reported the rate law at 25.0° to be $d[\text{Pt}(\text{NH}_3)_5\text{Cl}^{3+}]/dt$ (moles l.⁻¹ sec.⁻¹) = $2.50 \times 10^{-4}[\text{trans-Pt}(\text{NH}_3)_4\text{Cl}_2^{2+}][\text{NH}_3]$, and found the rate to be unaffected by the addition of Pt(NH₃)₄²⁺. A variety of substitution reactions of similar Pt(IV) compounds have been studied³⁻⁶ and in these cases a first-order dependence on a Pt(II) catalyst was observed.

The earlier study of reaction 1 was made by titration of unreacted NH₃ in the reaction mixture as a function of time. The ammonia dependence was evaluated from kinetic runs at several ammonia concentrations. Since *trans*-Pt(NH₃)₄Cl₂²⁺ is a weak acid (pK = 11.3⁵), its concentration in solution would be pH dependent; therefore, variations in NH₃ concentration produce changes in the $[\text{trans-Pt}(\text{NH}_3)_4\text{Cl}_2^{2+}]/[\text{Pt}(\text{NH}_3)_5\text{NH}_2\text{Cl}_2^+]$ ratio which should influence the observed kinetics. The earlier workers did not comment on this effect.²

We have studied the kinetics of reaction 1 using a spectrophotometric method in order to determine the pH dependence and to check whether Pt(II) catalysis can be found.

Experimental

Materials.—*trans*-Dichlorotetraammineplatinum(IV) chloride, Pt(NH₃)₃Cl(NO₃)₃, and Pt(NH₃)₄Cl₂ were prepared by published procedures.⁷⁻⁹ The products were characterized by platinum and chloride analysis and ultraviolet spectra. The concentrations of solutions of *trans*-Pt(NH₃)₄Cl₂²⁺ were determined from their absorbance at 259 mμ, where the molar absorptivity was observed to be 680. Concentrations of Pt(NH₃)₄²⁺ solutions were determined by titration with Ce(IV) in H₂SO₄ acid solution containing chloride ion as a catalyst. Solutions of NaClO₄ were prepared

from reagent grade Na₂CO₃ and HClO₄. All other compounds were reagent grade chemicals.

Kinetic Measurements.—The bulk of the kinetic data was taken on a Cary Model 14 spectrophotometer having thermostated cell holders. The temperature of the reaction mixtures was controlled within ±0.1°. The product of the reaction in the ammine buffers used (largely Pt(NH₃)₄NH₂Cl²⁺) has an absorbance maximum at 315 mμ; at this wave length the absorbance of the products is over four times as intense as that of the reactants. Kinetic measurements were made both by scanning from 350 to 250 mμ at intervals and by recording the absorbance at 315 mμ vs. time. Reaction mixtures were prepared by mixing appropriate amounts of stock solutions of *trans*-Pt(NH₃)₄Cl₂²⁺, Pt(NH₃)₄Cl₂, NaClO₄ or NaNO₃, dilute aqueous NH₃, and a NH₃-NH₄ClO₄ or NH₃-NH₄NO₃ buffer. No precautions were taken to avoid exposure of the reaction mixtures to light. The majority of the experiments were run at $[\text{NH}_3]/[\text{NH}_4^+] = 1.24$. At 25° the measured pH of the stock NH₃-NH₄ClO₄ buffer diluted to $[\text{NH}_3] = 0.464$ M and $[\text{NH}_4^+] = 0.375$ M was 9.6. Several preparations of *trans*-Pt(NH₃)₄Cl₂²⁺ and Pt(NH₃)₄Cl₂ were used in the studies. Agreement between rate constants from the different preparations was within ±3%.

In all kinetic runs $[\text{NH}_3]/[\text{Pt(IV)}] > 47$; therefore pseudo-first-order kinetics were observed. First-order rate constants were calculated from ten-point Guggenheim¹⁰ plots using a least-squares technique. Linear plots for data including three or more half-lives were obtained in all runs. Third-order constants were calculated by dividing the observed rate constants by concentrations of Pt(NH₃)₄²⁺ and NH₃.

Measurements in Dilute Ammonia.—The spectra of *trans*-Pt(NH₃)₄Cl₂²⁺ and Pt(NH₃)₅Cl³⁺ were measured in 0.0463 and 0.370 M aqueous ammonia. The changes in the spectrum of *trans*-Pt(NH₃)₄Cl₂²⁺ dissolved in dilute ammonia were observed at intervals until a constant spectrum was obtained. The effect of Pt(NH₃)₄²⁺, NaClO₄, and changes in $[\text{NH}_3]$ on the rate of change of the spectrum was also determined. These measurements were made on a Beckman DU modified with a Gilford absorbance indicator. Spectral changes were observed at 318 mμ.

Results

A summary of rate data is presented in Table I. The data suggest that rate law 2 is obeyed at 22.5°, ionic strength 0.38, and pH 9.6. The data indicate

$$d[\text{Pt}(\text{NH}_3)_5\text{Cl}^{3+}]/dt \text{ (moles l.}^{-1} \text{ sec.}^{-1}) = 1.21[\text{trans-Pt}(\text{NH}_3)_4\text{Cl}_2^{2+}][\text{Pt}(\text{NH}_3)_4^{2+}][\text{NH}_3] \quad (2)$$

that the rate of reaction in the absence of Pt(NH₃)₄²⁺ catalyst must be very slow. The rate of reaction increases as the $[\text{NH}_3]/[\text{NH}_4^+]$ ratio is lowered, indicating H⁺ catalysis. The H⁺ dependence is much

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less than first order. The rate of the reaction is markedly altered by changes in the ionic strength of the solution. Nitrate- and perchlorate-containing solutions give similar results. The temperature dependence of the rate constants yields $\Delta H^* = 6$ kcal./mole and $\Delta S^* = -37$ e.u.

TABLE I
RATE DATA^a

[Pt(NH ₃) ₄] ²⁺ × 10 ³ M	[NH ₃], M	[NH ₄ ⁺], M	μ^b	10 ³ <i>k</i> _{obsd.} sec. ⁻¹	<i>k</i> , M ⁻² sec. ⁻¹
22.5°					
4.7	0.464	0.375	0.375	2.64	1.21
2.35	0.464	0.375	0.375	1.32	1.21
1.17	0.464	0.375	0.375	0.63	1.16
4.7	0.232	0.188	0.38	1.33	1.22
4.7	0.116	0.094	0.38	0.70	1.28
4.7	0.464	0.375	0.375	2.58 ^c	1.18
4.7	0.444	0.188	0.38	2.38	1.14
4.7	0.432	0.94	0.38	2.23	1.10
4.7	0.232	0.188	0.188	0.69	0.63
4.7	0.232	0.188	0.57	2.08	1.90
4.4	0.170	0.231	0.462 ^d	0.98 ^e	1.31
4.4	0.170	0.231	0.231 ^d	0.64 ^e	0.86
29.8°					
2.35	0.464	0.375	0.375	1.65	1.51
4.7	0.232	0.188	0.38	1.75	1.61
39.3°					
2.35	0.464	0.375	0.375	2.39	2.24
4.7	0.232	0.188	0.38	2.51	2.30

^a [*trans*-Pt(NH₃)₄Cl₂]²⁺ = 1.74 × 10⁻³ M. ^b μ due to NH₄ClO₄ and NaClO₄. ^c [*trans*-Pt(NH₃)₄Cl₂]²⁺ = 1.16 × 10⁻³ M. ^d μ due to NH₄NO₃ and NaNO₃. ^e [*trans*-Pt(NH₃)₄Cl₂]²⁺ = 2.10 × 10⁻³ M.

A spectrum of a reaction mixture after reaction was known to be complete was identical with that of Pt(NH₃)₅Cl(NO₃)₃ in the NH₃-NH₄ClO₄ buffer when corrections for the absorbance of the Pt(NH₃)₄Cl₂ catalyst were made. This and the fact that Pt(NH₃)₅Cl³⁺ can be prepared in good yield under conditions similar to our reaction conditions indicate that our spectral measurements were a measure of reaction 1.

It is known that both *trans*-Pt(NH₃)₄Cl₂²⁺ and Pt(NH₃)₅Cl³⁺ hydrolyze in basic solution⁵ and that Pt(NH₃)₅Cl³⁺ reacts with chloride ion in the presence of Pt(NH₃)₄²⁺ to regenerate starting material.³ Rate data are available for these reactions; reasonable estimates of the rates of these reactions in pH 9.6 solutions containing Pt(NH₃)₄²⁺ suggest that they are quite slow with respect to the reaction being studied.

Studies in unbuffered solutions containing 0.046 to 0.37 M NH₃ indicate that reactions in addition to (1) occur. The absorbance at 318 m μ of a solution initially 3.70 × 10⁻³ M in *trans*-Pt(NH₃)₄Cl₂²⁺ and 0.0463 M in NH₃ was 0.64. The absorbance decreased to a minimum of 0.58 in 1 hr. and then increased to a maximum of 1.90 in 161 hr. This absorbance decreased on standing, but the change was very slow. The spectrum of the reaction mixture after 161 hr. does suggest that some Pt(NH₃)₅Cl³⁺ is present. The absorbance at 318 m μ of a 1.23 × 10⁻³ M solution of Pt(NH₃)₅Cl³⁺

in 0.0463 M NH₃ was found to be 1.407; this corresponds to 4.23 for a 3.70 × 10⁻³ M solution. The behavior of *trans*-Pt(NH₃)₄Cl₂²⁺ in more concentrated ammonia solutions was similar to that reported at 0.046 M. It was found that the rate of absorbance change was increased by additions of Pt(NH₃)₄²⁺ or NaClO₄ and by increases in NH₃ and [Pt(NH₃)₄-Cl₂]Cl₂ concentration.

Discussion

The first-order rate dependence of reaction 1 in NH₃-NH₄⁺ buffers on concentrations of the initial Pt(IV) complex, the entering ligand, and a Pt(II) catalyst is in line with a number of other kinetic studies on replacement of Cl⁻ in *trans*-Pt(NH₃)₄Cl₂²⁺ and *trans*-Pt(en)₂Cl₂²⁺.^{3-6,11} Therefore it seems probable that the mechanism for reaction 1 is similar to that previously proposed for other platinum(II)-catalyzed reactions. The rate law indicates that the activated complex has the composition Cl(NH₃)₄PtClPt(NH₃)₅⁴⁺, and the observed product suggests it has Pt-Cl-Pt bridging. The low activation enthalpy and the large negative activation entropy observed for reaction 1 are consistent with activation parameters observed in other platinum(II)-catalyzed substitution reactions.^{5,12}

The marked dependence of the rate of reaction 1 on the ionic strength of the solution can be interpreted as a primary salt effect. The Debye-Hückel theory as applied to the observed rate law for reaction 1 predicts a marked rise in reaction rate as the ionic strength of the reaction mixture is increased.

The [H⁺] dependence of the rate of reaction 1 in NH₃-NH₄ClO₄ buffers can be rationalized in terms of the weak acid behavior of *trans*-Pt(NH₃)₄Cl₂²⁺. At pH 9.6 about 98% of the reacting Pt(IV) complex should be present as Pt(NH₃)₄Cl₂²⁺ and only 2% as Pt(NH₃)₃NH₂Cl₂⁺. The observed H⁺ catalysis suggests that Pt(NH₃)₄Cl₂²⁺ reacts more rapidly than Pt(NH₃)₃NH₂Cl₂⁺ in the Pt(II)-catalyzed reaction. Since so little of the amido complex is present in our studies, a fourfold decrease in [H⁺] would be expected to decrease the rate by only 8%, if one assumes that the amido complex does not react at all. A 10% decrease was observed. This agreement is surprisingly good, for the rate changes are not much larger than experimental error.

Rate data have been reported on the reverse of reaction 1.¹² The reverse reaction is first order in [Pt(NH₃)₅-Cl³⁺], [Pt(NH₃)₄²⁺], and [Cl⁻]. The rate constant is 2.0 × 10⁻³ M⁻² sec.⁻¹ at 30.0° in 0.0055 M HClO₄ in which the ionic strength (provided by NaCl) was 0.32 M. At 30.0° and an ionic strength of 0.32 M, reaction 1 has a rate constant of 1.31 M⁻² sec.⁻¹. The hydrogen ion dependence of reaction 1 suggests that *trans*-Pt(NH₃)₄Cl₂²⁺ is the reactive species in the rate studies at pH 9.6. Therefore there seems to be no reason why the observed rate data for reaction 1 should not also apply in acidic solution. If this is true,

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then the equilibrium constant for reaction 1 can be calculated. The probable value is 7×10^2 ; this corresponds to a free energy change of -4 kcal./mole. Values of ΔH , -12 kcal./mole, and ΔS , -34 e.u., for reaction 1 were calculated from the activation parameters for the forward and reverse reactions.

Studies on the reaction of *trans*-Pt(NH₃)₄Cl₂²⁺ and NH₃ in dilute unbuffered NH₃ indicate that the products include 50% or less Pt(NH₃)₅Cl³⁺. Moreover, the change in absorbance at 318 m μ of reaction mixtures does not give linear first- or second-order kinetic plots. Sufficiently detailed studies to ascertain the nature of the products of the reaction were not performed. However, it seems clear that the previous kinetic study on this system² at best reflects the total rate of two or more concurrent or consecutive processes. The most probable side reaction is hydrolysis (eq. 3). Kinetic

$$\text{trans-Pt(NH}_3)_4\text{Cl}^{2+} + \text{OH}^- \rightarrow \text{trans-Pt(NH}_3)_4\text{ClOH}^{2+} + \text{Cl}^- \quad (3)$$

data on reaction 3 at 25° in the pH range 10–11 are not available, but examination of related data does suggest hydrolysis would compete with the slow replacement of chloride by ammonia (in the absence of Pt(NH₃)₄²⁺).^{5,13}

Zvyagintsev and Shubochkina also reported rate data on other reactions of dihalotetraammine complexes with ammonia and pyridine.² In view of the present study all of these data need review. The reactions with pyridine are less likely to be subject to a competing hydrolysis reaction, since the pyridine reactions are faster and pyridine is a much weaker base than ammonia. However, if their data are accurate, it still seems likely that a platinum(II)-catalyzed process will provide an alternate route to products.

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Metal Chelates of Triethylenetetraminehexaacetic Acid¹

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Potentiometric studies of the interaction between the decadentate chelating agent triethylenetetraminehexaacetic acid (TTHA) and various metal ions are described. Evidence is given for the formation of Th(IV) chelates having a 1:1 ratio of Th(IV) to ligand, Cu(II), Co(II), Ni(II), and La(III) chelates with 1:1 and 2:1 molar ratios of the respective metal ions to ligand, and chelates containing 1:1, 2:1, and 3:1 molar ratios of Mg(II) and Ca(II) ions to ligand. Formation constants are calculated and probable coordinate bonding of the 1:1, 2:1, and 3:1 chelates is deduced.

One of the objectives of coordination chemists has been to synthesize chelating agents which have the highest possible affinities toward metal ions. A survey of published stability constants in collections such as the tables of stability constants by Sillén and Martell² reveals that the achievement of high stability has been developed about as far as seems possible with the synthesis and investigation of ethylenediaminetetraacetic acid and a number of analogous compounds and derivatives.

It has been noted, however, that some of the metal chelates of diethylenetriaminepentaacetic acid are considerably more stable than those of EDTA, especially for the more highly charged ions. It would seem, therefore, that further extension of the EDTA structure

to the analogous substituted tetramine, the decadentate ligand triethylenetetraminehexaacetic acid shown in formula I, is of interest because of the possibility of further increasing the affinity of the ligand for metal ions of +3 and +4 charge. Further, because of the presence of ten coordinating groups, this ligand would provide some interesting possibilities for the formation of polynuclear complexes with metals of lower charge or relatively low coordination number. A potentiometric investigation of the interaction between TTHA and various metal ions was therefore carried out to determine the nature and extent of these reactions. The metal chelates of Ca(II), Mg(II), Cu(II), Co(II), Ni(II), La(III), and Th(IV) ions were studied in varying ratios of metal ion to ligand.

While this work was in progress Grimes, *et al.*,³

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