configuration corresponds to a tetragonally distorted octahedron. The d_{xy} and $d_{x^2-y^2}$ orbitals are expected to experience equal energy changes by such distortion, and it is noted that the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition (peak 3) is nearly at the same frequency in both the crystal and the solution. It is somewhat surprising that the tetragonal distortion from the octahedral is greater in aqueous solution, where the Pt(II) is expected to be bonded to axial H_2O ligands, than in the crystal. The feature that the anions are packed one directly over another along the symmetry axes of the crystal apparently causes the decrease in tetragonal distortion in the crystal.

The oscillator strength for peak 2 is about 0.4 to 0.2 that of those for peaks 3 and 4, respectively, which are doubtless singlet–singlet transitions. It appears therefore more satisfactory to attribute peak 2 and the corresponding peaks in the crystal spectra to a singlet–singlet transition. The singlet–triplet transitions, one of which may correspond to the barely discernible peak 1, are then at least an order of magnitude weaker.

It may be possible that the temperature dependence of the spectrum will offer a means to test the proposals in this paper. As thermal excitation of vibrations in the ground state are reduced, a band excited exclusively by the stretching modes should show a lower temperature dependence of intensity than one excited by the bending vibration. Bands should be sharpened and the differences between peaks in the z and the x–y polarization should increase somewhat. Plans are underway to attempt the measurement of these spectra down to liquid nitrogen temperatures.
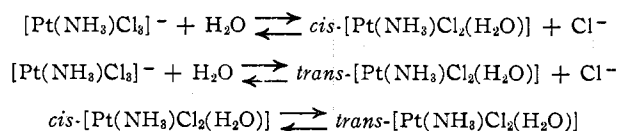

CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

Substitution Reactions of Trichloroammineplatinate(II) Ion and the *trans* Effect[1a,b]

BY MARY ANN TUCKER, CLIFFORD B. COLVIN, AND DON S. MARTIN, JR.

The acid and base hydrolyses for trichloroammineplatinate(II) ion have been followed spectrophotometrically. Both reactions are reversible in high chloride at pH <4. The six rate constants characterizing the three reactions at 20 and 25° have been evaluated.

$$[Pt(NH_3)Cl_3]^- + H_2O \rightleftharpoons cis\text{-}[Pt(NH_3)Cl_2(H_2O)] + Cl^-$$

$$[Pt(NH_3)Cl_3]^- + H_2O \rightleftharpoons trans\text{-}[Pt(NH_3)Cl_2(H_2O)] + Cl^-$$

$$cis\text{-}[Pt(NH_3)Cl_2(H_2O)] \rightleftharpoons trans\text{-}[Pt(NH_3)Cl_2(H_2O)]$$

The last reaction is considered to occur *via* the acid hydrolysis of each isomer to $cis\text{-}[Pt(NH_3)Cl(H_2O)_2]^+$. The assigned rate constants account for chloride-exchange rates. The significance of the results to the quantitative expression of the *trans* and *cis* effects is discussed.

Introduction

An extensive spectrophotometric study of the kinetics of the reversible acid and base hydrolysis reactions of the $[Pt(NH_3)Cl_3]^-$ ion has been completed. It has now been possible to evaluate individual reactivities for sterically different chloride ligands. Accordingly, the conclusions of Elleman, Reishus, and Martin,[2a,b] based on chemical and chloride isotopic exchange kinetics, have been revised and extended.
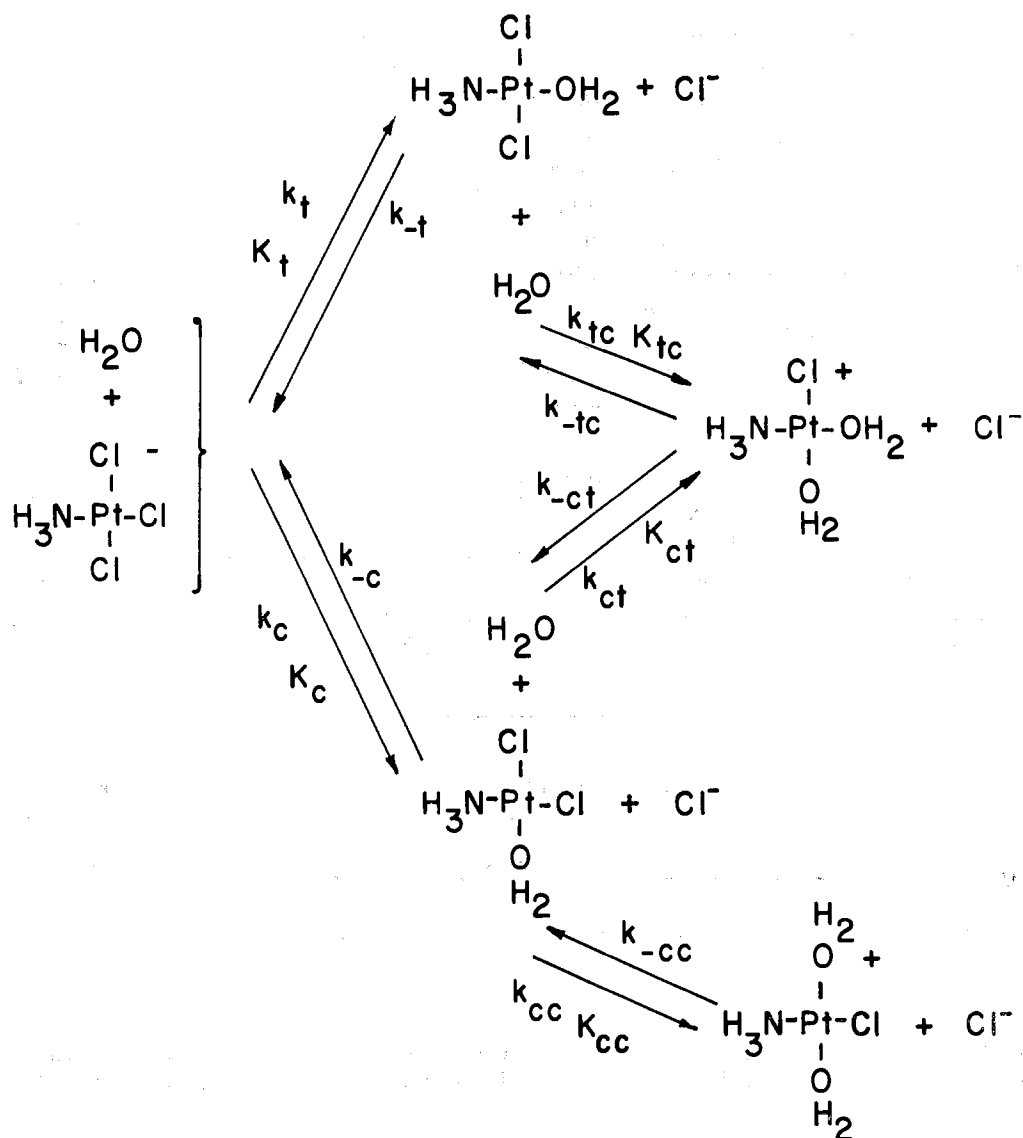
As a square-planar complex of platinum(II), [Pt-(NH_3)Cl_3]^- has two chemically different types of chloride ligands. The two chlorides, designated the "*cis*-chlorides," *cis* to the NH_3 are equivalent from symmetry. The "*trans*-chloride" is the single ligand *trans* to NH_3. A complete reaction scheme for all the possibilities of the successive double aquation (acid hydrolysis) is shown in Fig. 1 together with the designation of the pertinent rate constants and equilibrium quotients.

Since a large number of concentration variables must be considered, the symbols below have been selected to provide convenience in recognition and typographical economy. All the variables indicated are concentrations in moles/l. (M). A subscript 0 designates a condition at the initial time, a subscript ∞ designates an equilibrium condition, and a sub-

(1) (a) Contribution No. 1489. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission; (b) presented to the Inorganic Division, 145th National Meeting of the American Chemical Society, Sept. 12, 1963.

(2) (a) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **80**, 536 (1958); (b) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **81**, 10 (1959).

Cl
|
H₃N-Pt-OH₂ + Cl⁻
|
Cl

k_t / k_{-t}
K_t

H₂O
+
Cl⁻
|
H₃N-Pt-Cl
|
Cl

k_{tc} K_{tc}
k_{-tc}

Cl +
|
H₃N-Pt-OH₂ + Cl⁻
|
O
H₂

k_{-ct} / k_{ct} K_{ct}

H₂O
+
Cl
|
H₃N-Pt-Cl + Cl⁻
|
O
H₂

k_c / k_{-c}
K_c

k_{-cc}
k_{cc} K_{cc}

H₂
O +
|
H₃N-Pt-Cl + Cl⁻
|
O
H₂

Fig. 1.—Complete reaction scheme for the first and second acid hydrolyses of [Pt(NH₃)Cl₃]⁻.

Cl⁻	[Cl⁻]
[Pt(NH₃)Cl₃]⁻	[Cl₃⁻]
trans-[Pt(NH₃)Cl₂(H₂O)]	[t-(H₂O)]
trans-[Pt(NH₃)Cl₂(OH)]⁻	[t-(OH)⁻]
cis-[Pt(NH₃)Cl₂(H₂O)]	[c-(H₂O)]
cis-[Pt(NH₃)Cl₂(OH)]⁻	[c-(OH)⁻]
trans-[Pt(NH₃)Cl(H₂O)₂]⁺	[t-(H₂O)₂⁺]
cis-[Pt(NH₃)Cl(H₂O)₂]⁺	[c-(H₂O)₂⁺]

script r designates a condition in existence at the time that a hydrolysis or aquation reaction was reversed by the addition of HCl or KCl solutions.

Elleman, *et al.*,[2b] proposed that at 25° k_c = 3.6 × 10⁻⁵ sec.⁻¹ and K_c = 0.015 *M*. Although the extent of second aquation at equilibrium was shown to be slight so that $(K_{ct} + K_{cc})$ ≈ 4 × 10⁻⁵ *M*, it did apparently provide a mechanism for isotopic exchange. Also, it was especially significant that tagged chloride ion entered the [Pt(NH₃)Cl₃]⁻ rapidly in a freshly prepared solution of K[Pt(NH₃)Cl₃] before a significant quantity of cis-[Pt(NH₃)Cl₂(H₂O)] could be formed. To account for such exchange, it was proposed that k_t == 2.3 × 10⁻⁵ sec.⁻¹ with K_t << K_c. Grinberg, *et al.*,[3,4]

have expressed concern that the rate constant of the cis-chloride should be less than the value of 3.9 × 10⁻⁵ sec.⁻¹ for [PtCl₄]²⁻, in conflict with the cis effect which they have based on extensive kinetics data. Further, they have reported a rate constant of 6.0 × 10⁻⁵ sec.⁻¹ for the first-order (hydroxide-independent) replacement of a chloride ligand by hydroxide and they note such replacements for platinum(II) complexes generally occur only *via* acid hydrolysis which is followed promptly by the neutralization of the acidic proton of the H₂O ligand. They estimated from the initial aquation rate that the rate constant was approximately 6 × 10⁻⁵ sec.⁻¹, although the rate fell off so rapidly with time that a really firm value could not be established.

In view of the apparent uncertainties in the system the present investigation was undertaken. Because of concern that nonreversible reactions and possibly decomposition would influence results, especially in

(3) A. A. Grinberg and Yu. N. Kukushin, *Zh. Neorgan. Khim.*, **2**, 2360 (1957).

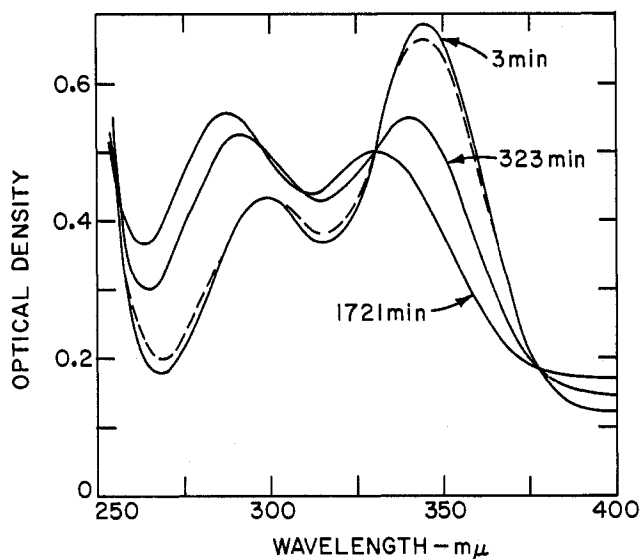(4) A. A. Grinberg and Yu. N. Kukushin, *ibid.*, **6**, 306 (1961).

Fig. 2.—Ultraviolet absorption spectrum of a solution of K[Pt(NH₃)Cl₃] during acid hydrolysis: $[Pt(NH_3)Cl_3]^-_0 = 6.00$ mM; cell length 1 cm.; 25.0°. Dashed curve is spectrum 23 hr. after reversal by the addition of KCl–Na₂SO₄ solution; $Pt_{tot} = 3.00$ mM; 2-cm. cell.

Fig. 3.—Optical density at 345 mμ during acid hydrolysis and reversal. Solid curves were calculated from the rate constants in Table II. For acid hydrolysis: $[Pt(NH_3)Cl_3]^-_0 = 6.00$ mM; cell length 1 cm.; 25.0°; $\mu = 0.318$ M. Dashed curve calculated with the assumption that $k_{ct} = k_{tc} = 0$. For the reversed reaction the volume was doubled by the addition of a KCl–Na₂SO₄ solution: cell length 2 cm.; $\mu = 0.318$ M; 25.0°; O, 0.080 M Cl⁻; ●, 0.160 M Cl⁻; calculated $[Pt(NH_3)Cl_2(H_2O)]_r = 2.19$ mM; $[Pt(NH_3)Cl_3]^-_r = 0.81$ mM.

basic solutions, it was planned to reverse both the aquation and base hydrolysis reactions by the establishment of high chloride concentrations at pH <4 to determine if the characteristic ultraviolet absorption spectrum of $[Pt(NH_3)Cl_3]^-$ reappeared. It was immediately evident that following base hydrolysis by 0.5 mole of OH⁻ per Pt, the starting complex was largely reformed within 10 min. at 25°. Following acid hydrolysis the original complex reformed slowly over many hours.

It may be concluded that one of the two possible isomers of $[Pt(NH_3)Cl_2(OH)]^-$ is formed predominantly in the basic solution. The high rate at which the $[Pt(NH_3)Cl_3]^-$ re-forms when the solution is acidified with HCl indicates the equilibrium quotient for the formation of the corresponding aquo isomer must be very small. This isomer will be assigned the *cis* configuration. Such assignment is in accordance therefore with the kinetic *trans* effect, with Grinberg's *cis* effect, and with the acid hydrolysis equilibrium systematics,[5] but has not really been given further confirmation.

In acid hydrolysis the *cis* isomer of $[Pt(NH_3)Cl_2(H_2O)]$ at first forms rapidly. Because of the small equilibrium constant K_c its concentration rapidly reaches a maximum value. The *trans* isomer forms slowly over a period of several hours. Since the equilibrium constant K_t is much larger, the *trans* isomer ultimately predominates, and the concentration of the *cis* isomer decreases from its maximum value. The $[Pt(NH_3)Cl_3]^-$ ion re-forms only slowly from this isomer when chloride concentrations are increased following an extended acid hydrolysis.

It has still not been possible to evaluate the complete set of rate constants designated in Fig. 1. However, the present work in combination with the earlier results
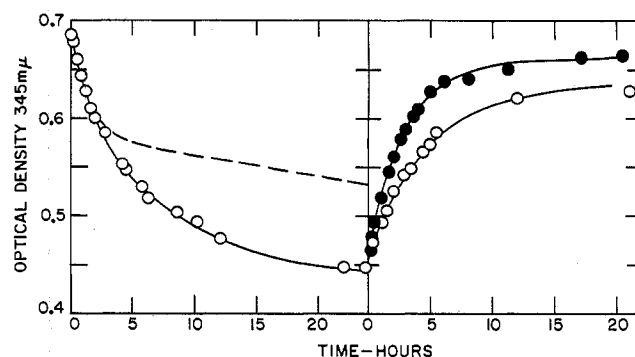
(5) F. Aprile and D. S. Martin, Jr., *Inorg. Chem.*, 1, 551 (1962).

does yield a number of these rate constants. Since the majority of earlier exchange experiments were conducted at 20°, the system is most completely characterized at that temperature.

Experimental

Materials.—K[Pt(NH₃)Cl₃] was prepared according to the procedure reported earlier.[2a] However, the platinum stock had been subjected to a fractional crystallization of K₂PtBr₆ which has been shown to reduce the Ir to a level of *ca.* 40 p.p.b.[6] The ultraviolet absorption spectrum of a freshly prepared solution of K[Pt(NH₃)Cl₃] agreed with that from the earlier work.

Equipment.—Reaction flasks were placed in thermostats which maintained the temperature to ±0.1°.

The ultraviolet absorption spectrum was scanned during the reaction by a Cary Model 14 recording spectrophotometer. For following the kinetics of the acid or base hydrolysis the optical density at 345 mμ, near the peak in the spectrum of $[Pt(NH_3)Cl_3]^-$ ion, was plotted *vs.* time. The conventional definition of optical density was used: O.D. $= \log I_0/I$, where I is the intensity of light passing through the sample cell and I_0 is the intensity of light through a matched cell containing the identical solvent solution. In the spectrophotometer the temperature was controlled to ±0.2° by the circulation of water from a thermostat through the walls of the sample chamber.

The IBM 7074 digital computer of the Iowa State University Computation Center was utilized for the numerical solution of the differential equations characterizing the kinetics and the isotopic exchange processes.

Procedures.—For acid hydrolysis the quantity of K[Pt(NH₃)-Cl₃] to give the desired concentration (2–8 mM) and of Na₂SO₄ for an ionic strength of 0.318 M were weighed into a 50-ml. volumetric flask. The reaction was started by adding H₂O which had been stored in the thermostat. A sample was immediately transferred from the flask to a silica spectrophotometer cell. The flask was then stored in the spectrophotometer cell compartment while the reaction was followed in the spectrophotometer. At intervals other samples were withdrawn from the flask. To reverse the reaction, a sample taken from the flask was diluted with an equal volume of a standard KCl and Na₂SO₄ solution at an ionic strength of 0.318 M. With this addition the ionic strength was substantially unchanged. A portion of the solution was transferred to a spectrophotometer cell with double the length of the original, and spectral changes were recorded as

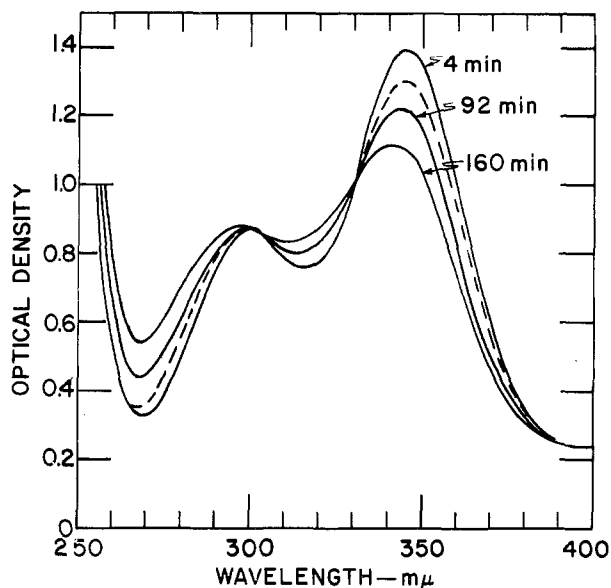(6) L. S. Jowanovitz, F. B. McNatt, R. E. McCarley, and D. S. Martin, Jr., *Anal. Chem.*, 32, 1270 (1960).

Fig. 4.—Ultraviolet absorption spectrum of a solution of K[Pt(NH₃)Cl₃] during base hydrolysis: $[Pt(NH_3)Cl_3]^-{}_0 = 6.00$ mM; $[OH^-]_0 = 3.00$ mM; 25.0°; 2-cm. cells; $\mu = 0.318\,M$. Dashed curve corresponds to spectrum 4 hr. after reversal by the addition of HCl solution.

H₂O ligands were replaced by the Cl⁻ which was then present in large excess. Figure 2 shows a few of the spectral scans during such an acid hydrolysis. Figure 3 shows the changes in the optical density at 345 mμ during both the acid hydrolysis and its reversal.

For basic hydrolysis the desired quantity of K[Pt(NH₃)Cl₃] was weighed into a 50-ml. volumetric flask. A solution of KCl and K₂SO₄ with [Cl⁻] = 0.100 M and ionic strength = 0.318 M was added to the mark. The desired quantity of standard 5 M NaOH was added from a micropipet so the volume was changed only slightly. The concentration of OH⁻ was in this way adjusted to some desired fraction of the total Pt, usually 0.2 to 0.5 so that the second hydrolysis would not be extensive. A portion of the solution was transferred to the spectrophotometer cells. Initially, the O.D. at 345 mμ dropped rapidly as the reaction proceeded. After the hydroxide was largely consumed, 5 M HCl was added from a micropipet to a portion of the solution in the thermostat flask to produce an acidic solution. The acidified solution was transferred to a spectrophotometer cell and the changes during the reverse reaction were followed. Figure 4 shows spectral scans of one of these solutions and Fig. 5 gives a plot of the O.D. at 345 mμ *vs.* time.

Treatment of Data

At the start the equilibrium data of Elleman, *et al.*,[2a] was taken to imply that

$$\frac{([t\text{-}(H_2O)]_\infty + [c\text{-}(H_2O)]_\infty)[Cl^-]_\infty}{[Cl_3{}^-]_\infty} =$$

$$K_c + K_t = 0.0144\,M\ \text{at}\ 25° \quad (1)$$

and

$$\frac{([t\text{-}(H_2O)_2{}^+]_\infty + [c\text{-}(H_2O)_2{}^+]_\infty)[Cl^-]_\infty}{[(t\text{-}H_2O)]_\infty + [c\text{-}(H_2O)]_\infty)} =$$

$$4 \times 10^{-5}\,M \quad (2)$$

Therefore, normally $([t\text{-}(H_2O)_2{}^+] + [c\text{-}(H_2O)_2{}^+]) \ll ([c\text{-}(H_2O)] + [t\text{-}(H_2O)])$. The titration curves of Elleman, *et al.*, for equilibrium solutions indicated
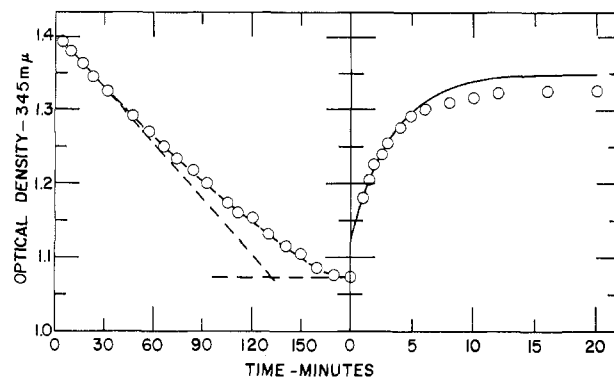

Fig. 5.—Optical density at 345 mμ during base hydrolysis of $[Pt(NH_3)Cl_3]^-$ and reversal. For the base hydrolysis: $[Pt(NH_3)Cl_3]^-{}_0 = 6.00$ mM; $[OH^-] = 3.00$ mM; cell length 2 cm.; 25.0°; $\mu = 0.318\,M$. For the reversed reaction 20 μl. of 5.00 M HCl was added to 20.0 ml. of the reaction solution. The solid curve was calculated from the parameters in Table II: $[Cl^-] = 0.105M$; cell length 2 cm.; 2.50°; $\mu = 0.318\,M$.

the acid dissociation constant for the predominant equilibrium species, *trans*-$[Pt(NH_3)Cl_2(H_2O)]$, *i.e.*

$$t\text{-}[Pt(NH_3)Cl_2(H_2O)] \rightleftharpoons H^+ + t\text{-}[Pt(NH_3)Cl_2(OH)]^- \quad (3)$$
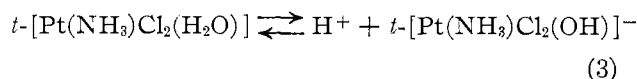
$$\frac{[t\text{-}(OH)^-][H^+]}{[t\text{-}(H_2O)]} = K_{at} = 10^{-7.5} \quad (4)$$

A similar equilibrium must exist for the *cis* isomer

$$c\text{-}[Pt(NH_3)Cl_2(H_2O)] \rightleftharpoons H^+ + c\text{-}[Pt(NH_3)Cl_2(OH)]^- \quad (5)$$
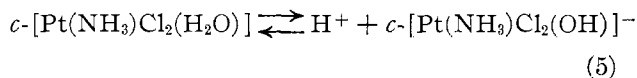
$$\frac{[c\text{-}(OH^-)][H^+]}{[c\text{-}(H_2O)]} = K_{ac} \quad (6)$$

In acidic solutions, pH <5, therefore $[t\text{-}(OH^-)] \ll [t\text{-}(H_2O)]$ and no evidence has appeared to indicate that a corresponding inequality did not apply to the *cis* isomers as well.

The spectrum of only $[Pt(NH_3)Cl_3]^-$ was known initially. It was therefore necessary to devise experiments whereby approximate values of some of the rate constants would be obtained without the spectra of product species. As approximate values of the rate constants were obtained, it then became possible to obtain approximate values of the molar extinction coefficients of the important species at 345 mμ. From such information minor terms in the rate expressions could be evaluated which in turn provided corrections for the previous values. With a set of rate constants, molar extinction coefficients, and starting concentrations, it then was possible to calculate complete O.D. *vs.* time curves for comparison with the observed curves.

If direct replacement by hydroxide is negligible but if the hydroxo and aquo species are in equilibrium according to reactions 3 and 5, the following differential equations, together with eq. 4 and 6, are expected to apply to the system represented by the scheme in Fig. 1.

$$\frac{d\{[c\text{-}(H_2O)] + [c\text{-}(OH)^-]\}}{dt} = k_c[Cl_3^-] -$$

$$k_{-c}[Cl^-][c\text{-}(H_2O)] - (k_{ct} + k_{cc})[c\text{-}(H_2O)] +$$

$$k_{-ct}[Cl^-][c\text{-}(H_2O)_2^+] + k_{-cc}[Cl^-][t\text{-}(H_2O)_2^+] \quad (7)$$

$$\frac{d\{[t\text{-}(H_2O)] + [t\text{-}(OH^-)]\}}{dt} = k_t[Cl_3^-] -$$

$$k_{-t}[Cl^-][t\text{-}(H_2O)] - k_{tc}[t\text{-}(H_2O)] +$$

$$k_{-tc}[Cl^-][c\text{-}(H_2O)_2] \quad (8)$$

Various approximate modifications of these equations apply to the different experimental conditions which are discussed under the separate sections.

Base Hydrolysis Reactions and Reversal.—In these experiments $K[Pt(NH_3)Cl_3]$ was dissolved in a high chloride solution and NaOH was added to give an initial $[OH^-] < [Pt(NH_3)Cl_3^-]$. With the assumption that no second hydroxide substitution occurred, eq. 7 and 8 may be modified to give

$$\frac{d\{[c\text{-}(OH)^-] + [c\text{-}(H_2O)]\}}{dt} =$$

$$k_c[Cl_3^-] - k_{-c}[Cl^-][c\text{-}(H_2O)] \quad (9)$$

$$\frac{d\{[t\text{-}(OH)^-] + [t\text{-}(H_2O)]\}}{dt} =$$

$$k_t[Cl_3^-] - k_{-t}[Cl^-][t\text{-}(H_2O)] \quad (10)$$

In these equations $[Cl^-]$ was substantially constant. The optical density for the solution may be expressed as

$$O.D. = l\{[Cl_3^-]\epsilon_{[Cl_3^-]}^{345} + [c\text{-}(H_2O)]\epsilon_{[c\text{-}H_2O]}^{345} +$$

$$[c\text{-}OH^-]\epsilon_{[c\text{-}OH^-]}^{345} + [t\text{-}(H_2O)]\epsilon_{[t\text{-}(H_2O)]}^{345} +$$

$$[t\text{-}OH^-]\epsilon_{[t\text{-}OH^-]}^{345}\} \quad (11)$$

where the ϵ's are the indicated molar extinction coefficients. Because of the high chloride, concentrations of the aquo species were much less than those of the hydroxo species, and the contribution of the terms from the aquo species can be neglected to a first approximation. Therefore the initial slope of the O.D. curve is approximately

$$\left(\frac{d(O.D.)}{dt}\right)_0 = l\left(\frac{d[c\text{-}(OH)^-]}{dt}\right)_0(\epsilon_{[c\text{-}(OH)^-]}^{345} - \epsilon_{[Cl_3^-]}^{345}) +$$

$$l\left(\frac{d[t\text{-}(OH)^-]}{dt}\right)_0(\epsilon_{[t\text{-}(OH)^-]}^{345} - \epsilon_{[Cl_3^-]}^{345}) =$$

$$l[Cl_3^-]_0[k_c(\epsilon_{[c\text{-}OH^-]}^{345} - \epsilon_{[Cl_3^-]}^{345}) + k_t(\epsilon_{[t\text{-}OH]}^{345} - \epsilon_{[Cl_3^-]}^{345})]$$

$$(12)$$

It is apparent from Fig. 5 that the substitution proceeded rapidly until the hydroxide was consumed. As the free OH^- was consumed the optical density approached a limiting value, $(O.D.)_{lim}$, and subsequent changes occurred only very slowly. At this time

$$[c\text{-}OH^-]_{lim} + [t\text{-}(OH)^-]_{lim} = [OH^-]_0 \quad (13)$$

With the additional assumption

$$[t\text{-}(OH)^-]/[c\text{-}(OH)^-] = k_t/k_c \quad (14)$$

the $(O.D.)_{lim}$ can be written

$$(O.D.)_{lim} - (O.D.)_0 =$$

$$l[OH^-]_0 \left(\frac{k_c(\epsilon_{[c\text{-}(OH)^-]}^{345} - \epsilon_{[Cl_3^-]}^{345})}{(k_c + k_t)} + \right.$$

$$\left. \frac{k_t(\epsilon_{[t\text{-}(OH)^-]}^{345} - \epsilon_{[Cl_3^-]}^{345})}{(k_c + k_t)}\right) \quad (15)$$

The extinction coefficients can be eliminated between eq. 12 and 15 to give eq. 16 from which $(k_t + k_c)$ is calculated from the observable quantities.

$$(k_c + k_t) = \frac{[OH^-]_0[d(O.D.)/dt]_0}{[Cl_3^-]_0[(O.D.)_{lim} - (O.D.)_0]} \quad (16)$$

Equation 14 will be valid for the early part of the reaction and will be true for all times if $K_{ac} = K_{at}$. However, readjustment of the relative hydroxide species occurs slowly and is not serious over the short time of the experiments. The base hydrolysis was carried out with different $[OH^-]_0/[Cl_3^-]_0$ ratios from 0.2 to 0.5.

Shortly after the hydroxide ion had been consumed and before a significant readjustment of the concentrations of cis- and trans-$[Pt(NH_3)Cl_2(OH)]^-$ could occur by the slow acid hydrolysis reactions, the pH of the solutions was dropped to <4 by the addition of HCl from a micropipet. The chloride concentration change and the volume change by this addition were negligible but virtually all the hydroxo ligands were converted to H_2O.

In eq. 9 and 10 the predominant term immediately became $k_{-c}[Cl^-][c\text{-}(H_2O)]$. The cis isomer was rapidly converted to $[Pt(NH_3)Cl_3]^-$ and the initial slope of the optical density following the reversal was

$$\left(\frac{d[O.D.]}{dt}\right)_r = l(\epsilon_{[c\text{-}(H_2O)]}^{345} - \epsilon_{[Cl_3^-]}^{345})\left(\frac{d[c\text{-}(H_2O)]}{dt}\right)_r \approx$$

$$l(\epsilon_{[c\text{-}(H_2O)]}^{345} - \epsilon_{[Cl_3^-]}^{345})(-k_{-c})[Cl^-][c\text{-}(H_2O)]_r \quad (17)$$

Following a brief rapid change, the optical density changed only slowly as the acid hydrolysis equilibrium of the trans-chloride was established. The optical density change of the initial rapid portion should be

$$\Delta(O.D.) = -l(\epsilon_{[c\text{-}(H_2O)]}^{345} - \epsilon_{[Cl_3^-]}^{345})[c\text{-}(H_2O)]_r \quad (18)$$

so an initial estimate for k_{-c} is given by eq. 19

$$k_{-c} = \left(\frac{d(O.D.)}{dt}\right)_r/\Delta(O.D.)[Cl^-] \quad (19)$$

Note that if at the start of this reversal $[t\text{-}(H_2O)]_r \ll [c\text{-}(H_2O)]_r \approx [OH]_0$ eq. 17 gives a first estimate of $\epsilon_{[c\text{-}H_2O]}^{345}$. Also if $k_c \gg k_t$ an estimate of K_c can be obtained from $(k_c + k_t)$ and k_{-c}, since

$$K_c = k_c/k_{-c}; \quad K_t = k_t/k_{-t} \quad (20)$$

Accordingly, a first estimate can also be made for K_t from eq. 1.

Acid Hydrolysis Reaction.—When $[Pt(NH_3)Cl_3]^-$ is

dissolved in H_2O, the aquo species formed in acid hydrolysis are sufficiently weak acids that negligible quantities of the hydroxo species exist. Since the second aquation equilibrium quotient, eq. 2, is so small, negligible amounts of diaquo species are formed. Under these conditions eq. 7 and 8 can be approximated in the following way.

$$\left(\frac{d[c\text{-}(H_2O)]}{dt}\right) = k_c[Cl_3^-] - k_{-c}[Cl^-][c(H_2O)] -$$
$$\frac{k_{ct}k_{-tc}[c\text{-}(H_2O)]}{(k_{-ct} + k_{-tc})} + \frac{k_{tc}k_{-ct}[t\text{-}(H_2O)]}{(k_{-ct} + k_{-tc})} \quad (21)$$

and

$$\left(\frac{d[t\text{-}(H_2O)]}{dt}\right) = k_t[Cl_3^-] - k_{-t}[Cl^-][t\text{-}(H_2O)] -$$
$$\frac{k_{tc}k_{-ct}[t\text{-}(H_2O)]}{(k_{-ct} + k_{-tc})} + \frac{k_{ct}k_{-tc}[c\text{-}(H_2O)]}{(k_{-ct} + k_{-tc})} \quad (22)$$

with

$$[Cl^-] = [Cl^-]_0 + [t\text{-}(H_2O)] + [c\text{-}(H_2O)] \quad (23)$$

and

$$[Cl_3^-] = [Cl_3^-]_0 - [t\text{-}(H_2O)] - [c\text{-}(H_2O)] \quad (24)$$

The optical density is given by the equation

$$O.D. = l\{[Cl_3^-]_0\epsilon_{[Cl_3^-]}^{345} + [c\text{-}(H_2O)](\epsilon_{[c\text{-}(H_2O)]}^{345} -$$
$$\epsilon_{[Cl_3^-]}^{345}) + [t\text{-}(H_2O)](\epsilon_{[t\text{-}(H_2O)]}^{345} - \epsilon_{[Cl_3^-]}^{345})\} \quad (25)$$

In the reversal of the acid hydrolysis by the addition of a solution of KCl and Na_2SO_4 to the original solution, a maximum concentration of 0.318 M KCl could be added, and lower concentrations of KCl with additions of Na_2SO_4 to maintain the ionic strength could be employed to evaluate the chloride dependence. From the experiment shown in Fig. 5 it is apparent that the replacement of any *cis*-aquo ligand is completed in a very few minutes. The replacement of the *trans*-aquo ligand occurs slowly, and the slow component of the curve, O.D. *vs.* time, can be extrapolated accurately for evaluation of its slope at the reversal time. The slope of this component at the reversal time is

$$\left(\frac{d(O.D.)}{dt}\right)_r = l(\epsilon_{[t\text{-}(H_2O)]}^{345} - \epsilon_{[Cl_3^-]}^{345})\left(\frac{d[t\text{-}(H_2O)]}{dt}\right)_r \quad (26)$$

At high chloride the dominant term in eq. 22 is $-k_{-t}$·$[Cl^-][t\text{-}(H_2O)]$ and the slowly changing component of the optical density at the instant of reversal is

$$(O.D.)_r = (O.D.)_0 + l[t\text{-}(H_2O)]_r(\epsilon_{[t\text{-}(H_2O)]}^{345} - \epsilon_{[Cl_3^-]}^{345}) \quad (27)$$

Therefore an initial estimate for k_{-t} is obtained by eliminating the molar extinction coefficients between eq. 26 and 27.

$$k_{-t} = \frac{(d(O.D.)/dt)_r}{[(O.D.)_0 - (O.D.)_r][Cl^-]} \quad (28)$$

It was therefore possible to calculate an initial value of k_{-t} without having the extinction coefficients, and with this value and K_t, k_t could be estimated from eq. 20. The value of ϵ_t could be evaluated from the O.D. of the acid hydrolysis steady-state solution together with the equilibrium concentrations that were calculated from K_t and K_c and the $\epsilon_{[c\text{-}(H_2O)]}$ available from the base hydrolysis experiments. The value of $\epsilon_{[c\text{-}(H_2O)]}$, incidently, was consistent with the initial fast component in the acid hydrolysis reversal.

Isotopic Exchange of Chloride Ligands.—A final satisfactory set of rate constants must account for the earlier exchange kinetics of Elleman, *et al.*[2b]

Even if the concentrations of *cis*- and *trans*-[Pt-$(NH_3)Cl(H_2O)_2]^+$ are negligibly small, there still are six chemical forms of chloride which must be considered for the treatment of isotopic exchange. These six forms together with the symbols used for the concentration and specific activity of each form are given in Table I.

TABLE I

Symbols for the Concentration of Cl^{36} and the Specific Activity in the Chemical Forms of Chlorides which Are Present in Appreciable Amounts for Consideration of the Isotopic Exchange Experiments of Elleman, *et al.*[2b]

Chemical form (in italics)	Concn. of activity, counts/min. l.	Specific activity, counts/min. mole
Cl^-	s	$S_s = s/[Cl^-]$
$\begin{array}{c}Cl\\ \| \\ H_3N\text{—}Pt\text{—}Cl \\ \| \\ Cl\end{array}$	u_1	$S_1 = u_1/[Cl_3^-]$
$\begin{array}{c}Cl\\ \| \\ H_3N\text{—}Pt\text{—}Cl \\ \| \\ Cl\end{array}$	u_2	$S_2 = u_2/2[Cl_3^-]$
$\begin{array}{c}Cl\\ \| \\ H_3N\text{—}Pt\text{—}OH_2 \\ \| \\ Cl\end{array}$	u_3	$S_3 = u_3/2[t\text{-}(H_2O)]$
$\begin{array}{c}H_2O\\ \| \\ H_3N\text{—}Pt\text{—}Cl \\ \| \\ Cl\end{array}$	u_4	$S_4 = u_4/[c\text{-}(H_2O)]$
$\begin{array}{c}H_2O\\ \| \\ H_3N\text{—}Pt\text{—}Cl \\ \| \\ Cl\end{array}$	u_5	$S_5 = u_5/[c\text{-}(H_2O)]$

The differential equations for the appearance of radioactive Cl^{36} in the ligands, based on the reaction scheme in Fig. 1, have been written as eq. 29–34.

$$\frac{du_1}{dt} = -(k_c + k_t)[Cl_3^-]S_1 + k_{-c}[c\text{-}(H_2O)][Cl^-]S_4 +$$
$$k_{-t}[t\text{-}(H_2O)][Cl^-]S_s \quad (29)$$

$$\frac{du_2}{dt} = -2(k_c + k_t)[\text{Cl}_3{}^-]S_2 + 2k_{-t}[t\text{-}(\text{H}_2\text{O})][\text{Cl}^-]S_3 +$$

$$k_{-c}[c\text{-}(\text{H}_2\text{O})][\text{Cl}^-](S_5 + S_3) \quad (30)$$

$$\frac{du_3}{dt} = 2k_t[\text{Cl}_3{}^-]S_2 - 2k_{-t}[t\text{-}(\text{H}_2\text{O})][\text{Cl}^-]S_3 +$$

$$\frac{k_{tc}k_{-ct}}{(k_{-tc} + k_{-ct})}[t\text{-}(\text{H}_2\text{O})][S_s - S_3] -$$

$$\frac{2k_{tc}k_{-ct}}{(k_{-tc} + k_{-ct})}[t\text{-}(\text{H}_2\text{O})]S_3 +$$

$$\frac{k_{ct}k_{-tc}}{(k_{-tc} + k_{-ct})}[c\text{-}(\text{H}_2\text{O})](S_s + S_5) \quad (31)$$

$$\frac{du_4}{dt} = k_c[\text{Cl}_3{}^-]S_1 - k_{-c}[c\text{-}(\text{H}_2\text{O})[\text{Cl}^-]S_4 +$$

$$\frac{k_{ct}k_{-ct}}{(k_{-tc} + k_{-ct})}[c\text{-}(\text{H}_2\text{O})](S_s - S_4) -$$

$$\frac{k_{ct}k_{-tc}}{(k_{-tc} + k_{-ct})}[c\text{-}(\text{H}_2\text{O})]S_4 +$$

$$\frac{k_{tc}k_{-ct}}{(k_{-tc} + k_{-ct})}[t\text{-}(\text{H}_2\text{O})]S_s \quad (32)$$

$$\frac{du_5}{dt} = k_c[\text{Cl}_3{}^-]S_2 - k_{-c}[c\text{-}(\text{H}_2\text{O})][\text{Cl}^-]S_5 +$$

$$k_{cc}[c\text{-}(\text{H}_2\text{O})](S_s - S_5) - \frac{k_{ct}k_{-tc}}{(k_{-ct} + k_{-tc})}[c\text{-}(\text{H}_2\text{O})]S_5 +$$

$$\frac{k_{tc}k_{-ct}}{(k_{-ct} + k_{-tc})}[t\text{-}(\text{H}_2\text{O})]S_3 \quad (33)$$

$$I = u_1 + u_2 + u_3 + u_4 + u_5 + s \quad (34)$$

where I is the total Cl^{36} concentration (counts/min. 1.). These equations contain the premise that the concentration of diaquo species is negligible. Also it is assumed that chloride enters a complex only by replacement of an aquo ligand and there is no second-order process for the direct substitution of a chloride ligand by a chloride ion.

Numerical Solution of Rate Equations.—With a set of rate constants eq. 21 and 22 were solved numerically for the initial conditions of each acid hydrolysis experiment and reversal by the Runge–Kutta method.[7] Increments as small as 0.01 hr. were used in critical regions and in general the increments were small enough that by their doubling no calculated concentrations were changed by as much as 1%. Then with a set of molar extinction coefficients the O.D. at 345 mμ was calculated by eq. 25 and plotted for comparison to the observed curves.

In the application of the Runge–Kutta method to eq. 9 and 10 which apply for base-hydrolysis, eq. 4 and 6 together with the acid dissociation constants for H_2O had to be satisfied at each point. The evaluation of $[\text{H}^+]$ at each point required the solution of a fourth degree equation which was accomplished by the Richmond[8] method.

(7) J. B. Scarborough, "Numerical Mathematical Analysis," 4th Ed., Johns Hopkins Press, Baltimore, Md., 1958, pp. 314–319.

For conditions corresponding to the Cl^- exchange experiments, eq. 29–34 were also solved numerically by the Runge–Kutta method[7] for trial sets of rate constants. From these numerical solutions the specific activities, corresponding to the fractions which had been separated and counted, were calculated for comparison. Equations 29–34 could be combined with eq. 21 and 22 to give the various specific activities even though chemical equilibrium with respect to acid hydrolysis had not been established. Such was the case in some of the critical exchange experiments.

Adjustments in the rate constants and molar extinction coefficients were made to improve subjectively the fit of a large number of calculated optical density and exchange curves with those determined experimentally. The evaluated quantities were highly interdependent and whereas an adjustment of one quantity might improve the fit to a portion of one curve, it might also prove deleterious to that of another.

Results

The rate constants, molar extinction coefficients, and equilibrium quotients which have been inferred from the equilibrium studies and kinetics data at 20 and 25° are collected in Table II. The solid curves of Fig. 3, which represent a typical experiment, correspond to the O.D. calculated from the parameters in Table II. If only the first acid hydrolyses, characterized by k_c, k_{-c} and k_t, k_{-t}, were considered, i.e., if the last two terms were omitted from each of eq. 21 and 22, the curve shown by the dashed line was computed for the O.D. in the acid hydrolysis reaction. There were appreciable changes in this dashed curve for optical density over 3 days, whereas the solution was substantially at a steady state in about 24 hr. at 25°. It was therefore concluded that isomerization was occurring by an alternate path. The logical mechanism for this isomerization is *via* the formation of the *cis*-$[\text{Pt(NH}_3)\text{Cl(H}_2\text{O})_2]^+$ which is a common acid-hydrolysis product of both the *cis*- and *trans*-monoaquo isomers. If negligible concentrations of *cis*-$[\text{Pt(NH}_3)\text{Cl(H}_2\text{O})_2]^+$ are formed, the isomerization reactions are first order, and the first-order rate constants, corresponding to $k_{tc}[k_{-ct}/(k_{-ct} + k_{-tc})]$ and $k_{ct}[k_{-tc}/(k_{-ct} + k_{-tc})]$, which were required to fit the experimental acid hydrolysis curves are included in Table II. These two constants are not independent, for the principle of microscopic reversibility requires the relation

$$k_{tc}k_{-ct}/k_{ct}k_{-tc} = K_c/K_t \quad (35)$$

For the base hydrolysis reactions the molar extinction coefficients are not given unambiguously for the two $[\text{Pt(NH}_3)\text{Cl}_2(\text{OH})]^-$ species and the O.D. for the base hydrolyses, illustrated by Fig. 5, was not calculated. As indicated by eq. 16, $(k_t + k_c)$ is determined from the initial slope of the O.D. curve and the difference between the initial and the limiting O.D.'s. In a

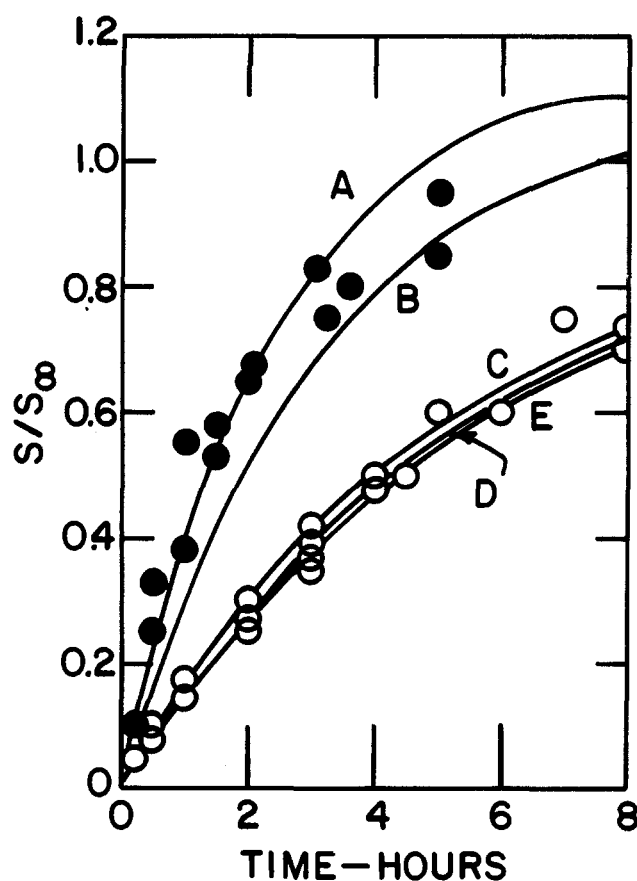(8) H. W. Richmond, *J. Math. Soc.* (London), **19**, 31 (1944).

Fig. 6.—Isotopic exchange experiments of Elleman, *et al.*[2b] The specific activity of separated fraction *vs.* time in equilibrium solution: $[Pt(NH_3)Cl_3^-] = 9.15$ mM; *cis* + *trans*-$[Pt(NH_3)Cl_2$-$(H_2O)] = 7.45$ mM; $[Cl^-] = 17.45$ mM; $20.0°$; $\mu = 0.318$ M; ●, S/S_∞ for $[c\text{-}(H_2O)] + [t\text{-}(H_2O)] = (u_3 + u_4 + u_5)/(2[t\text{-}(H_2O)] + 2[c\text{-}(H_2O)])I$; ○, S/S_∞ for $[Pt(NH_3)Cl_3]^- = (u_1 + u_2)/3[Cl_3^-]I$.

	Calculated curve of S/S_∞	$k_{-ct}/(k_{-ct} + k_{-tc})$	k_{cc}, sec.
A	$[c\text{-}(H_2O)] + [t\text{-}(H_2O)]$	0.06	0.1 and 0.5
B	$[c\text{-}(H_2O)] + [t\text{-}(H_2O)]$	0.08	0.1
C	$[Cl_3^-]$	0.06	0.5
D	$[Cl_3^-]$	0.08	0.1
E	$[Cl_3^-]$	0.06	0.1

number of experiments the ratio $[OH]_0/[Cl^-]_0$ was varied from 0.2 to 0.5 and consistent values for $(k_c + k_t)$ were indicated. It is believed therefore that second hydrolysis was not extensive and did not interfere with the determination of this rate constant sum. Initially, *trans*-and *cis*-$[Pt(NH_3)Cl_2(OH)]^-$ form in the ratio $k_t:k_c$. However, when hydroxide is largely consumed, appreciable concentrations of the $[Pt$-$(NH_3)Cl_2(H_2O)]$ isomers occur. If K_{at} and K_{ac} of eq. 4 and 6 are not equal, there will be a slow change in the *trans*:*cis* ratio. The concentrations of all species were computed with the assumption $K_{at} = K_{ac}$. Addition of acid at 120 min. for the experiment of Fig. 5 converted the hydroxo ligands to aquo ligands. The solid curve represents the O.D. curve from the concentration of species which were calculated to exist at the end of the base hydrolysis. A tenfold change in K_{ac} in either direction did not alter the calculated curve substantially. The rate constant k_{-c} was chosen to give a good fit to the initial slope. The fit at times

Molar extinction coefficient (25°, 345 mμ)

	ϵ, moles^{-1} l. cm.$^{-1}$
$[Pt(NH_3)Cl_3]^-$	115
cis-$[Pt(NH_3)Cl_2(H_2O)]$	71
trans-$[Pt(NH_3)Cl_2(H_2O)]$	57

Equilibrium quotients

	20°	25°
K_c, mM^{-1}	1.10	1.31
K_t, mM^{-1}	13.0	13.1

Rate constants ($\times 10^5$)

	20°	25°
k_c, sec.$^{-1}$	3.06	5.6
k_{-c}, M^{-1} sec.$^{-1}$	2690	4300
k_t, sec.$^{-1}$	0.40	0.63
k_{-t}, M^{-1} sec.$^{-1}$	30.55	48.
$k_{tc}k_{-ct}/(k_{-ct} + k_{-tc})$, sec.$^{-1}$	0.43	0.75
$k_{ct}k_{-tc}/(k_{-ct} + k_{-tc})$, sec.$^{-1}$	5.56	7.5
k_{tc}, sec.$^{-1}$	7.2[a]	
k_{ct}, sec.$^{-1}$	5.9[a]	
k_{cc}, sec.$^{-1}$	(2.8)	

[a] Based on a value of $k_{-ct}/(k_{-ct} + k_{-tc}) = 0.06$ obtained from the exchange studies.

longer than 7 min. was rather poor, and this feature is believed to result from the formation of small amounts of the second hydrolysis product *cis*-$[Pt(NH_3)Cl$-$(OH)_2]^-$ which upon acidification would be partially converted to *trans*-$[Pt(NH)_3Cl_2(H_2O)]$.

The isotopic exchange of the chloride ligands of the $[Pt(NH_3)Cl_2(H_2O)]$ species is especially sensitive to the actual rate constants, k_{ct} and k_{tc}, so the earlier exchange experiments have permitted their evaluation. In Fig. 6 is shown the determination of the S/S_∞ ratio for both the $[Pt(NH_3)Cl_3]^-$ and the combined *cis*- and *trans*-$[Pt(NH_3)Cl_2(H_2O)]$ fractions. The points were taken from several experiments that had been repeated for the same conditions. The free chloride in the solution was sufficiently low that the two fractions were comparable in magnitude. The calculated curve for the $[Pt(NH_3)Cl_2(H_2O)]$ fraction was quite sensitive to the value of $[k_{-ct}/(k_{-ct} + k_{-tc})]$ and calculations based on values of 0.06 and 0.08 are shown in the figure. A value of 0.06 ± 0.02 was selected which permits the evaluation of k_{ct} and k_{tc}, which have been included in Table II. The S/S_∞ function for $[Pt(NH_3)Cl_3]^-$ was not especially sensitive to the value of this ratio as indicated in Fig. 6, and the experiments did not provide a critical evaluation of k_{cc}. The results indicate only that it cannot be an order of magnitude larger than the estimated value in Table II. Times of half-exchange for the chloride ligands of $[Pt(NH_3)Cl_3]^-$ with free chloride, calculated from the rate constants of Table II for a variety of concentration conditions listed in Table III, agree very satisfactorily with the observed quantities.

Discussion

The information gained in this work strikingly demonstrates the kinetic aspects of the *trans* effect. Thus the
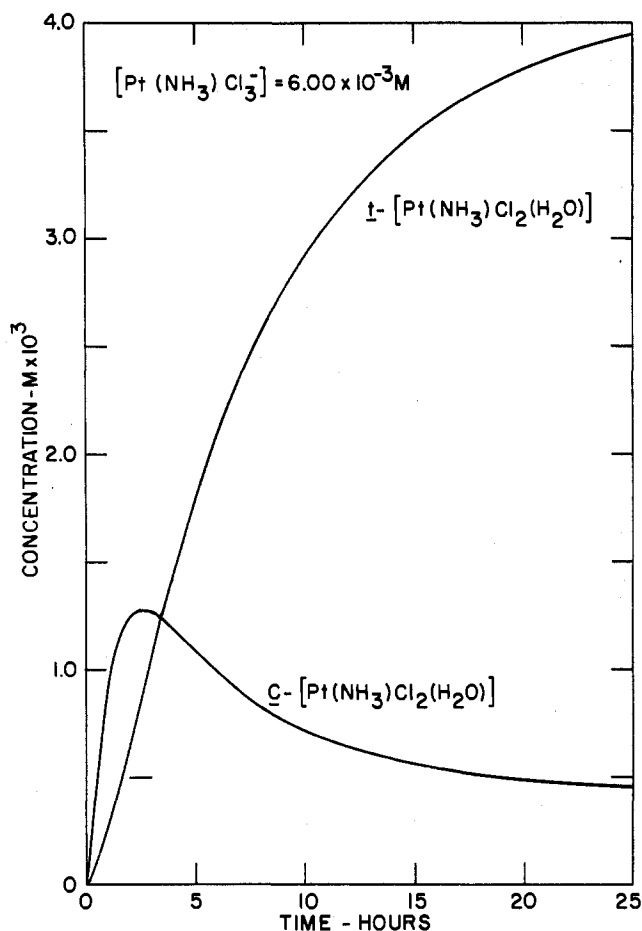
Fig. 7.—Calculated concentration of the isomers of [Pt(NH₃)-Cl₂(H₂O)] during acid hydrolysis.

Fig. 8.—Isotopic exchange experiment of Elleman, *et al.*,[2b] for freshly prepared solution of K[Pt(NH₃)Cl₃]: $[Pt(NH_3)Cl_3]^-{}_0$ = 16.6 mM; $[Cl]^-{}_0$ = 5.00 mM; 20.0°; μ = 0.318 M; $[k_{-ct}/(k_{-ct} + k_{-tc})]$ = 0.06; k_{cc} = 14 × 10⁻⁵ sec.⁻¹; curve B. $[k_{-ct}/(k_{-ct} + k_{-tc})]$ = 0.06, 0.08, k_{cc} = 2.8 × 10⁻⁵ sec.⁻¹, curve A.

TABLE III

EXCHANGE BETWEEN $[Pt[NH_3]Cl_3]^-$ AND Cl^- IN AGED SOLUTIONS

Temp., °C.	$[Pt(NH_3)Cl_3]^-{}_0$, mM	$[Cl]^-{}_0$, M	$[Pt(NH_3)Cl_2(H_2O)]_\infty$, m$M$		Time of half-exchange for $[Pt(NH_3)Cl_3]^-$, hr.	
			trans	cis	Obsd.	Calcd.
20.0 ± 0.2	16.6	0.01	6.85	0.596	4.0-5.1	4.4
	16.6	0.268	0.858	0.075	13.0	14.3
	8.3	0.268	0.377	0.033	14.5	15.9
	4.15	0.01	2.05	0.178	9	8.2
25.0 ± 0.2	16.6	0.01	6.90	0.69	3.2	2.9
	8.3	0.134	0.746	0.074	7.2	8.0

isomer formed most rapidly is the thermodynamically unstable one. The concentrations calculated for each isomer are shown in Fig. 7. The concentration of the *cis* isomer, which initially forms most rapidly, passes through a maximum at 2.6 hr. and eventually falls to about one-tenth of that for the *trans* isomer, which forms more slowly. A considerable quantity of the *trans* isomer is formed *via* the formation of the *cis* isomer and subsequently the second acid hydrolysis. As a consequence of this feature the curve of (O.D.∞ — O.D.) deviates only very slightly from a single exponential as is apparent from Fig. 3. In the earlier work,[2a,b] therefore, it was concluded incorrectly that the acid hydrolysis of only one of the two types of chloride was being observed spectrophotometrically. A critical experiment involved isotopic exchange of the chloride lig-
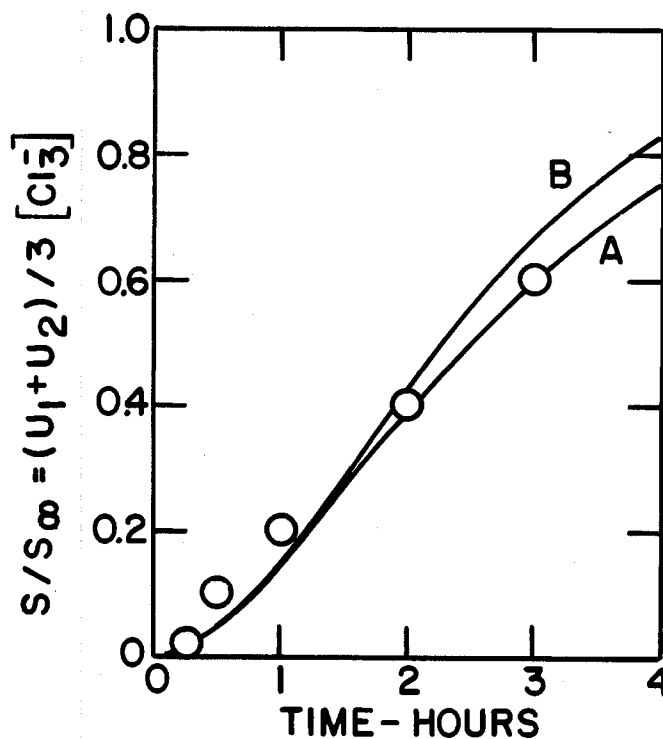
ands of $[Pt(NH_3)Cl_3]^-$ with free chloride in a freshly prepared solution. The single acid hydrolysis reaction was too slow to account for the observed rapid rise of Cl^{36} in $[Pt(NH_3)Cl_3]^-$. However, with the *cis* isomer forming so rapidly a faster exchange occurs. In Fig. 8 for such an experiment it can be seen that the specific activity found in the $[Pt(NH_3)Cl_3]^-$ fraction agrees quite satisfactorily with the solid curves. These curves were calculated on the basis that exchange occurred only *via* the acid hydrolysis reactions of Fig. 1 and the rate constants of Table II.

The kinetic *trans* effect for the acid hydrolysis of $[Pt(NH_3)Cl_3]^-$, represented by the ratio k_c/k_t, is somewhat less than 10. It is perhaps surprising that it is so small, for it represents rather a minimum value that can be useful for synthetic work, and the *trans* effect has proven so valuable in preparative work and structure assignments   Of course, different rate constant ratios may apply with second-order reactions, but the first-order acid hydrolysis proves to be the rate-determining step in a number of substitution reactions for platinum(II).[9]

With this work the equilibrium quotients and the rate constants for the complete set of the chloroammine complexes of platinum(II) are now available, and the values for 25° have been included in Table IV. The systematics for this interesting system are now apparent. Logarithms of the equilibrium quotients divided by the number of equivalent chlorides, *i.e.*,

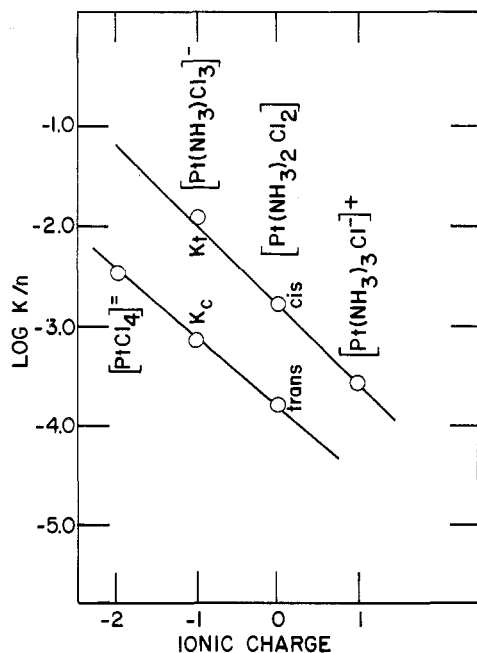(9) F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, 3, 48 (1961).

Fig. 9.—Dependence of the acid hydrolysis equilibrium quotients for the chloroammine complexes of Pt^{II} upon ionic charge.

$\log K/n$, for each of the first aquation reactions have been plotted in Fig. 9 against the ionic charge on the complex. The six points fall along two approximately parallel lines. The general acid hydrolysis reaction is represented by the reaction

$$[LPt^{II}Cl]^{z} + H_2O \longrightarrow [LPt^{II}OH_2]^{z+1} + Cl^- \quad (36)$$

where z is the ionic charge and L is the ligand *trans* to the replaced chloride.

TABLE IV
EQUILIBRIUM QUOTIENTS AND RATE CONSTANTS FOR THE ACID HYDROLYSIS OF THE CHLOROAMMINEPLATINUM(II) COMPLEXES

Complex		Equil. quotient, $M \times 10^5$ First	Second	Rate constants, sec.$^{-1} \times 10^5$ First	Second
$[PtCl_4]^{-2}$		1500	50	3.9	3.3
$[Pt(NH_3)Cl_3]^-$	*trans*	1300⎫		0.62	$(12.5)_{tc}{}^a$
	cis	130⎭	4	5.6	$(8)_{ct}{}^a$
cis-$[Pt(NH_3)_2Cl_2]$		330	40	2.5	3.3
trans-$[Pt(NH_3)_2Cl_2]$		32	<2	9.8	<5
$[Pt(NH_3)_3Cl]^+$		27		2.6	...

^{a} Based on the $k_{-ct}/(k_{-ct} + k_{-tc})$ of 0.06 determined at 20°.

For each point on the lower line L is a chloride ligand and on the upper line L is an NH_3. Along each line the ionic charge increases as a *cis*-chloride is replaced by NH_3. An increase of *ca.* 1 kcal. occurs in the free energy change of reaction 36 for each such increase in charge; although quite possibly other factors than charge, *e.g.*, π-bonding, influence this energy. Hence an additional free energy of *ca.* 1.5 kcal. is required for the aquation of a chloride which is *trans* to a chloride in reaction 36 over that required for a complex with the same z but with its replaced chloride *trans* to NH_3. This 1.5 kcal. can be attributed to the reduced repulsion between two chloride ligands in the starting complex resulting from the larger separation in the *trans* arrange-

ment. In the strictly electrostatic model for the complexes, which ignores covalent bonding, this repulsion is described merely as the ionic repulsion of the negative charges of the ions. With any covalent bonding model such repulsions must be described more subtly, but they do still play some important role. For example, Chatt and Wilkins[10] have noted that if two pairs of different ligands are to compete for the bonding orbitals in the square-planar arrangement, the *cis* isomer will give the stronger bonded system. They cite this effect to account for the greater stability of *cis* - dichlorobis(triethylphosphine)platinum(II) over the *trans* isomer. A similar conclusion can be reached from the ultraviolet spectrum of dichlorodiammine-platinum(II) complexes[11] in which the peaks corresponding to transitions from nonbonding d-orbitals into the antibonding orbital are shifted to shorter wave lengths for the *cis* isomer. However, the *trans* isomer is the more stable of the two, ΔH° for isomerization amounting to 3 kcal.[12] Here, apparently, the more favorable disposition of the chloride ligands more than outweighs the more stable bonds of the *cis* isomer.

From the set of rate constants the kinetics may be formulated quantitatively as separate *trans* and *cis* kinetic effects. All six of the first acid hydrolysis rate constants for 25° are given to within 20% by the simple formula

$$k/n = 1.0 \times 10^{-5} \text{ sec.}^{-1} \times (0.5)^m \times (2.4)^p \quad (37)$$

where n is the number of equivalent chlorides in the complex (a statistical factor), m is the number of NH_3 *trans* to the replaced Cl^-, *i.e.*, 0 or 1, and p is the number of NH_3 *cis* to the replaced chlorides, *i.e.*, 0, 1, or 2. The charge on the ion apparently has no primary effect on these rate constants. Presumably a dissociative mechanism does not apply and the transition state likely consists of a trigonal bipyramid coordination figure in which the *trans* ligand, the replaced chloride, and the entering H_2O occupy equatorial positions. It appears that for the acid hydrolysis of the chloride–ammine systems the *cis* neighbor has somewhat a greater influence on the kinetics than the *trans* neighbor. Thus, in any theory concerning the kinetic directive effects by such groups, which are at best weakly *trans* directive, more attention should be given to the *cis* effect.

Undoubtedly a major factor with the strong *trans* directors is, as Chatt, *et al.*,[13] and Orgel[14] have proposed, the withdrawal of electrons toward the *trans* ligand into the π-type bonds so the Pt orbitals become more available for bonding to the fifth ligand in the transition state. Such excess negative charge on the electron-withdrawing group will also serve to act repulsively with other ligands. The strongest such in-

(10) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 525 (1956).

(11) J. Chatt, G. A. Gamlen, and L. E. Orgel, *ibid.*, 486 (1958).

(12) I. I. Chernyaev, V. A. Palkin, R. A. Baranova, and N. N. Kuzmina, *Zh. Neorgan. Khim.*, **5**, 1428 (1960).

(13) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4456 (1955).

(14) L. E. Orgel, *J. Inorg. Nucl. Chem.*, **2**, 137 (1956).

teractions will be with ligands bonded at 90° to the π-electron-withdrawing group. There are two such 90° neighbors in the trigonal bypyramid transition state for the replacement of the *trans* ligand, but three such neighbors in the replacement of a *cis* ligand in the transition state. Therefore, the electron withdrawal may deactivate the transition state in *cis* substitution. Thus the ethylene in the $[Pt(C_2H_4)Cl_3]^-$ ion of Zeise's salt virtually labilizes the *trans*-chloride but reduces the rate of acid hydrolysis of the *cis*-chloride by a factor of 0.15.[15] A negative ion, such as chloride, is therefore

(15) S. J. Lokken and D. S. Martin, Jr., *Inorg. Chem.*, **2**, 562 (1963).

especially effective in *cis* deactivation in comparison to its rather weak *trans* activation. Hence the ligand repulsions which are important in the equilibrium *trans* effect can be considered to exert a strong influence on the kinetics also.

Finally, it seems appropriate to comment that the great utility of the *trans* effect has focused attention upon differences in rates which are frequently rather modest. It is certainly an ambitious and formidable requirement for the models of bonding in the coordination complexes, which are admittedly crude, that they predict differences of the order of 0.4 kcal./mole in activation energies of the respective reactions.

The Luminescence of Thallium(I) Halo Complexes

BY RUSSELL E. CURTICE AND ALLEN B. SCOTT

Excitation and emission spectra of solutions of KCl, KBr, and KI containing thallium(I) have been obtained by means of a spectrophotofluorometer. The emission spectra of the chloride and bromide solutions were analyzed using previously determined dissociation constants for the halo complexes of thallium. For coordination number $n = 0, 1, 2, 4$, emission peaks lie at 370, 435, 435, and 450 mμ, respectively, for $TlCl_n^{1-n}$ and at 370, 440, 475, and 495 mμ, respectively, for $TlBr_n^{1-n}$.

Introduction

When a small amount of a thallium(I) halide is added to a solution of an alkali halide, new absorption and emission bands, which are not characteristic of the alkali halide itself, are observed. Investigations of the ultraviolet absorption spectra of alkali halide solutions containing thallium(I) halide by Fromherz and Lih,[1] and of the luminescence spectra by Pringsheim and Vogels,[2] clearly indicated that the absorption and luminescence are due to complex ions of the type TlX_n^{1-n}.

The thallium-activated alkali halide single crystal phosphors exhibit ultraviolet absorption spectra which are markedly similar to the corresponding aqueous solutions. Because of this parallel, Fromherz[3] and Hilsch[4] concluded that the absorption and luminescence of the crystal phosphors should also be attributed to complex centers within the crystal.

Evidence that thallium(I) halo complexes exist in solution is manifold. Scott and Hu[5,6] have determined the dissociation constants and molar absorptivities for TlCl and $TlCl_2^-$. Scott, Dartau, and Sapsoonthorn[7] have reported the dissociation constants and molar absorptivities for TlBr, $TlBr_2^-$, and $TlBr_4^{3-}$. Kul'ba

(1) H. Fromherz and K. H. Lih, *Z. physik. Chem.*, **A153**, 321 (1931).
(2) P. Pringsheim and H. Vogels, *Physica*, **7**, 225 (1940).
(3) H. Fromherz, *Z. Physik*, **68**, 233 (1931).
(4) R. Hilsch, *Proc. Phys. Soc.* (London), **49** (extra part), 40 (1937).
(5) K. H. Hu and A. B. Scott, *J. Am. Chem. Soc.*, **77**, 1380 (1955).
(6) A. B. Scott and K. H. Hu, *J. Chem. Phys.*, **23**, 1830 (1955).
(7) A. B. Scott, R. G. Dartau, and S. Sapsoonthorn, *Inorg. Chem.*, **1**, 313 (1962).

and Mironov[8,9] indicate that TlI, TlI_2^-, and TlI_4^{3-} exist in KI solutions containing TlI.

Recently Avramenko and Belyi[10] and Brauer and Pelte[11] have investigated the luminescence spectra KCl–TlCl and KBr–TlBr solutions. Avramenko and Belyi attributed the 430 mμ emission of the chloride solutions to TlCl and $TlCl_4^{3-}$ and the 470 mμ emission of the bromide solutions to TlBr, $TlBr_3^{2-}$, and possibly $TlBr_4^{3-}$. On the other hand, Brauer and Pelte concluded that the broad luminescence band of the chloride solutions is due to the overlap of three symmetric bands. These bands are supposedly due to Tl^+, TlCl, and $TlCl_2^-$ with band maxima at 368, 395, and 440 mμ, respectively. They indicate that analogous results should occur in the bromide solutions; however, they did not assign a definite band to any of the bromide complexes.

Experimental

The solutions were prepared using doubly-recrystallized analytical grade salts. The concentration of potassium halide and thallium(I) halide ranged from zero to saturation. For many of the solutions three types of spectrum were measured. Optical absorption measurements were made by means of a Beckman

(8) F. Y. Kul'ba and V. E. Mironov, *Russ. J. Inorg. Chem.*, **2** (part 6), 78 (1957).
(9) F. Y. Kul'ba and V. E. Mironov, *ibid.*, **3** (part 6), 68 (1958).
(10) V. G. Avramenko and M. U. Belyi, *Bull. Acad. Sci. USSR, Phys. Ser.*, **24**, 737 (1960).
(11) P. Brauer and D. Pelte, *Z. Naturforsch.*, **17a**, 875 (1962).