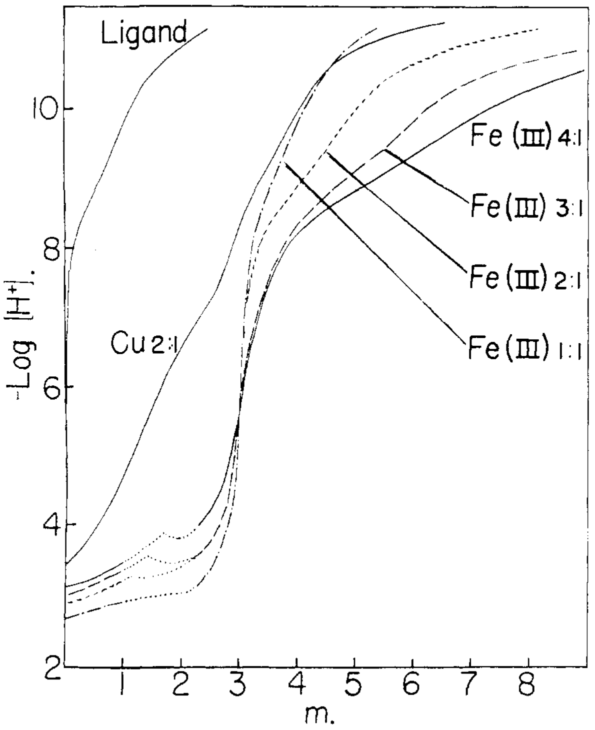

Fig. 5.—Potentiometric titration of *o*-hydroxyphenylglycine at 25° and 0.1 μ (KNO_3) in the absence of metal ions and in the presence of various amounts of Cu(II) and Fe(III) nitrates. Numbers indicate molar ratio of ligand to metal. Abscissa, *m*, represents moles of base added per mole of metal.

analogous to XIII. This effect is seen in the absorption spectra by a decrease in extinction coefficient of the Fe(III) chelate above *p*H 11.

The significant difference in the Fe(III) complexes of I and IIIa brought out by the titration and spectrophotometric data is the much greater stability of the former, in accordance with the fact that the IIIa chelate does not form until a relatively high *p*H is attained.

The absorption spectrum of the copper chelate of IIIa is quite similar to that of the corresponding EHPG chelate. In the ultraviolet region there is an absorption band at 238.5 mμ which increases in intensity with an increase in *p*H. This is apparently due to the copper phenolate linkage which is formed as the *p*H increases. There is also a band at 213 mμ at very low *p*H which disappears at and above the inflection point and which probably is due to the presence of the free phenolic group in acid solution.

In the visible region the similarity between the copper chelates of EHPG and IIIa are quite striking and the effects observed as a result of participation of the phenolic groups in complex formation are the same for both compounds.

Like EHPG, the ultraviolet spectra of α,α'-ethylenediiminodi-*o*-cresol (II) and of 2-(*o*-hydroxyphenyl)-glycine (IIIa) show a band at about 277 mμ (with ϵ of about 2000 per cresol group) which shifts at high *p*H to give a phenolate band at 292–6 mμ with ϵ of about 3000 per cresol group. In all three compounds the spectra indicate that the ionization of the phenol group is not complete until the *p*H is over 12. In the case of 2-(*o*-methoxyphenyl)-glycine (IIIb, not shown), this variation of spectra with *p*H does not occur, and the 273 mμ band remains at the same intensity (ϵ 2000) over the whole *p*H range.

Comparison of the ultraviolet spectra of II and IIIa with the spectra of their iron chelates indicates that no significant changes are introduced by combination with the metal ion. This is roughly in accord with the titration data, which indicate that a stable chelate between the Fe(III) ion and the ligand is not formed except perhaps at rather high *p*H.

Worcester, Mass. Framingham, Mass.

[Contribution No. 587 from the Institute for Atomic Research and Department of Chemistry, Iowa State College. Work was Performed in the Ames Laboratory of the U. S. Atomic Energy Commission]

The Acid Hydrolysis (Aquation) of the Trichloroammineplatinate(II) Ion

By Thomas S. Elleman, John W. Reishus and Don S. Martin, Jr.

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The acid hydrolysis of $[Pt(NH_3)Cl_3]^-$ in aqueous solution has been studied by spectrophotometric and potentiometric titration techniques in the temperature range of 0 to 35°. For the first hydrolysis: $[Pt(NH_3)Cl_3]^- + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} [Pt(NH_3)Cl_2(H_2O)] + Cl^-$, k_1 is 3.6×10^{-5} sec.$^{-1}$ and k_{-1} is 2.5×10^{-3} l. moles^{-1} sec.$^{-1}$ at 25°. $\Delta H_1^\ddagger$ is 18.9 kcal. and $\Delta H_{-1}^\ddagger$ is 16.8 kcal. The existence of a second acid hydrolysis has been demonstrated: $[Pt(NH_3)Cl_2(H_2O)] + H_2O \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} [Pt(NH_3)Cl(H_2O)_2]^+ + Cl^-$. Approximate values, $K_2 = k_2/k_{-2} = 4 \times 10^{-5}$ mole/l. and $k_{-2} = 0.2$ l. mole^{-1} sec.$^{-1}$ at 24° were indicated.

Introduction

In an earlier publication[1] it was shown that the tetrachloroplatinate(II) ion undergoes a reversible acid hydrolysis reaction in aqueous solution for which rate constants and an equilibrium constant were presented. A similar aquation has been observed for *cis*-$[Pt(NH_3)_2Cl_2]$ and $[Pt(en)Cl_2]$, (en is ethylenediamine) by Banerjea, Basolo and Pear-

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[1] L. F. Grantham, T. S. Elleman and D. S. Martin, Jr., This Journal, 77, 2965 (1955).

son.[2] However, they found that aquation was not observable for *trans*-$[Pt(NH_3)_2Cl_2]$ or for $[Pt(NH_3)_3Cl]^+$.

The present paper concerns a study of the kinetics and equilibrium behavior of aqueous systems containing $K[Pt(NH_3)Cl_3]$. The aquation process, in which a chloride is reversibly replaced by H_2O, provides a means for the isotopic exchange of chloride ligands with chloride ion in the solution. This work was undertaken to supplement a study of such isotopic exchange which is to be reported later.

With the $[Pt(NH_3)Cl_3]^-$ system special consideration needs to be given to the possible nonequivalence of the chlorides in the well-recognized square planar complexes. Thus in the reaction

$$[Pt(NH_3)Cl_3]^- + H_2O \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} [Pt(NH_3)Cl_2(H_2O)] + Cl^- \quad (1)$$

the replaced Cl^- might be either *cis* or *trans* to the NH_3. Since the replacement of Cl^- by NH_3 to give predominantly the *cis*-$[Pt(NH_3)_2Cl_2]$ is often cited as a classic example of the *trans*-effect, which was reviewed by Quagliano and Schubert,[3] one expects the *cis*-chloride to be the more labile. However, the possibility exists that a mixture of the isomers may form. Also, in case of a second aquation

$$[Pt(NH_3)Cl_2(H_2O)] + H_2O \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} [Pt(NH_3)Cl(H_2O)_2]^+ + Cl^- \quad (2)$$

a *cis*- or a *trans*-isomer may result. According to a summary given by Chatt, *et al.*,[4] NH_3 and H_2O do not differ greatly in their *trans*-directing effects which are relatively weak. If the *trans*-directing effect of NH_3 is greater than that of H_2O, following the order given by Chatt, *et al.*, the *cis*-$[Pt(NH_3)Cl(H_2O)_2]^+$ would predominate even if it were formed from the *cis*-$[Pt(NH_3)Cl_2(H_2O)]$.

Experimental

Materials.—$K[Pt(NH_3)Cl_3]$ was prepared from the $K_2[PtCl_4]$ starting material.[1] To attain a satisfactory purity, the final salt was crystallized from a concentrated solution which contained no excess chloride. An involved procedure was required to attain these conditions.

The preparation utilized suggestions of Lebedinskii and Golovnya.[5] $K_2[PtCl_4]$ was first converted to *cis*-$[Pt(NH_3)_2Cl_2]$ by refluxing with 5% ammonium acetate. The crystallized *cis*-$[Pt(NH_3)_2Cl_2]$ was refluxed for *ca.* 2 hr. with concd. HCl in the presence of some reduced platinum metal catalyst. After the mixture was cooled, unreacted *cis*-$[Pt(NH_3)_2Cl_2]$ and catalyst were removed by filtration. $[Pt(NH_3)_4]Cl_2$ was added to precipitate the golden salt $[Pt(NH_3)_4][Pt(NH_3)Cl_3]_2$. After they were washed, the golden crystals were mixed with a freshly prepared, concentrated solution of a stoichiometric quantity of $K_2[PtCl_4]$ and heated for a short time to precipitate the $[Pt(NH_3)_4]^{++}$ from the golden salt as the highly insoluble Magnus green salt, $[Pt(NH_3)_4][PtCl_4]$. The resulting solution of $K[Pt(NH_3)Cl_3]$ was evaporated to dryness under reduced pressure below 45° to avoid deposition of Pt metal. The crystals were taken up in a small volume of warm water and recrystallized in an ice-bath. They were washed finally with alcohol and ether and dried at 60°. Typical analyses of freshly dried crystals were: K = 10.8, Pt = 54.6, Cl = 31.2, 28.4, NH_3 = 5.1; calculated K = 10.9, Pt = 54.5, Cl = 29.6, NH_3 = 4.8.

Analyses for chloride were made gravimetrically as AgCl, after platinum had been plated out of a basic solution. Platinum was determined gravimetrically by electroplating on Pt-electrodes from an H_2SO_4 solution containing a trace of nitrate. The potassium and ammonium ion in the solution were determined by the use of the sodium tetraphenylboron reagent, following the procedure of Gloss.[6]

Analyses indicated that in the laboratory atmosphere the crystals slowly added approximately one H_2O per mole. However it was shown that the H_2O did not replace ligands on the platinum.

The sodium tetraphenylboron was purchased from the Hach Chemical Company. It was dissolved and filtered to prepare the precipitating reagent.

For ion-exchange separations, Dowex-1 anion-exchange resin, screened 20/50 mesh (inches), was employed. Other reagents met ACS specifications. Water from the laboratory distilled water tap was redistilled from alkaline permanganate.

Equipment.—Solutions were thermostated in a water-bath whose temperature was controlled to ±0.1°. A refrigerating coil in the bath permitted controlled temperatures down to 0°.

*p*H measurements were made with a Beckman model "G" *p*H meter, with electrode model 1190-80, calibrated with a standard buffer at *p*H 4 or 7.

Ultraviolet spectra were scanned with a Cary recording spectrophotometer, model 12. For following kinetics, the absorbance of a solution, A, at a fixed wave length, was followed as a function of time by a Beckman model DU spectrophotometer. The conventional definition of absorbance is used: $A = \log I_0/I$, where I is the intensity of light passing through the solution cell and I_0 is the intensity of light passing through solvent in an equivalent cell.

Behavior of $K[Pt(NH_3)Cl_3]$ Solutions.—It was observed that when $K[Pt(NH_3)Cl_3]$ dissolves in H_2O at room temperature, the *p*H of the solution falls and slowly approaches a value of 4.5 to 5.0. A simultaneous change in the ultraviolet spectrum occurs, and the titer of the solution by base increases. These changes ensue over a period of several hours and they are reversed by the addition of KCl. Such behavior is consistent with the reversible replacement of a chloride ligand by a water molecule if the aquo-ligand is a weak acid which can dissociate to give H^+ and $[Pt(NH_3)Cl_2(OH)]^-$. If an NH_3 were replaced by H_2O, the addition of Cl^- would yield $[PtCl_4]^=$. The presence of $[PtCl_4]^=$ is not detectable in the solution, although tests showed that the presence of 1% $[PtCl_4]^=$ gave discernible changes in the ultraviolet spectrum. Apparently, NH_3 is not replaced.

A number of solutions of $K[Pt(NH_3)Cl_3]$ in water were prepared in which Na_2SO_4 was added to give an initial ionic strength of 0.318 mole/l. The solutions were allowed to stand in a constant temperature bath to attain a steady-state condition; usually a period of one to seven days was allowed. The temperature range was 0 to 35°. Samples were withdrawn, and the equivalents of acid present were determined by the procedure which was used for the study of $[PtCl_4]^=$.[1] A typical titration curve is shown in Fig. 1. In this figure the blank titer has been subtracted. If the degree of second aquation described by equation 2 were negligible, the equivalents of base gave the amount of $[Pt(NH_3)Cl_2(H_2O)]$ in the solution, which also was equal to the chloride ion. Most titrations were carried out with an initial platinum complex concentration of 0.0166 *M;* however, a few were made at a concentration of 0.00415 *M* to test the consistency of the equilibrium constant for the system.

The kinetics of the aquation was conveniently followed spectrophotometrically. The absorbance at 343 mμ of a 0.0166 *M* $K[Pt(NH_3)Cl_3]$ solution, containing Na_2SO_4 to give an ionic strength of 0.318 mole/l., was followed with the Beckman DU spectrophotometer until the steady state was attained. It was assumed that the only significant platinum species were $[Pt(NH_3)Cl_3]^-$ and $[Pt(NH_3)Cl_2(H_2O)]$. The concentrations could then be calculated as

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[2] D. Banerjea, F. Basolo and R. G. Pearson, THIS JOURNAL, **79**, 4055 (1957).

[3] J. V. Quagliano and L. Schubert, *Chem. Revs.*, **50**, 201 (1952).

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

[5] V. V. Lebedinskii and V. A. Golovnya, *Izvest. Sektora Platiny i Drug. Blagorod. Metal Inst. Obshchei i Neorg. Khim. Akad. Nauk S.S.S.R.*, **20**, 95 (1947).

[6] G. H. Gloss, *Chemist Analyst* (Baker Chem. Co.), **42**, 50 (1953).

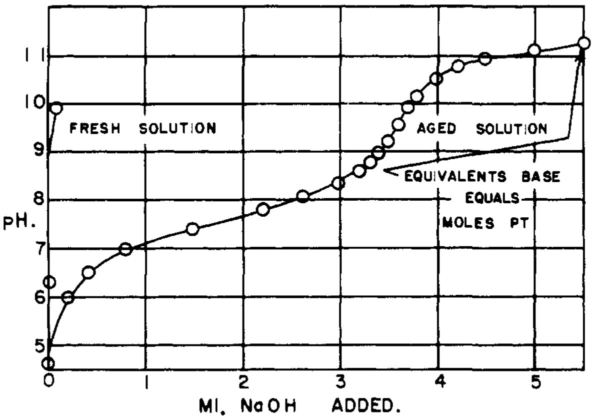

Fig. 1.—Titration curve of an aged solution of 0.0166 *M* $K[Pt(NH_3)Cl_3]$; Na_2SO_4 added to give ionic strength of 0.318 mole/l.

a function of time from the absorbance of the initial $K[Pt(NH_3)Cl_3]$ solution and from the absorbance of the equilibrium state.

$[Pt(NH_3)Cl_2(H_2O)]$ Solutions.—Since $[Pt(NH_3)Cl_2(H_2O)]$ species is uncharged, it was possible to prepare solutions of this compound which were relatively free from $[Pt(NH_3)Cl_3]^-$ and Cl^- by the use of an anion-exchange resin. The formation of the aquo-species was favored by dilution, so approximately 10^{-3} molar solutions of $K[Pt(NH_3)Cl_3]$ were aged to establish the steady state. This solution was then passed at a rate of about 5 ml./min. through a 1.5 cm. × 40 cm. column filled with Dowex-1 anion-exchange resin in the sulfate form. The ultraviolet spectrum of such an effluent solution is shown in Fig. 2 which also includes the spectrum of $[Pt(NH_3)Cl_3]^-$ for comparison.

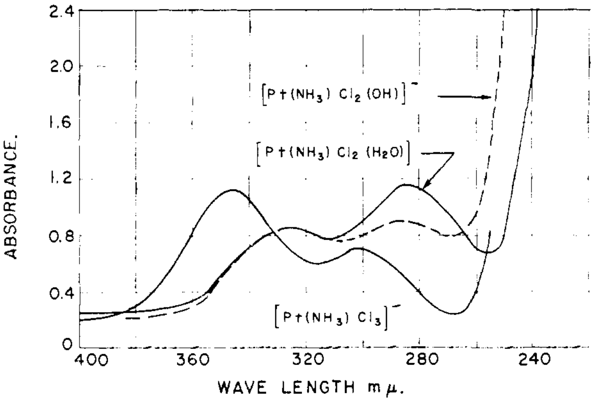

Fig. 2.—Ultraviolet spectra of solutions: $[Pt(NH_3)Cl_3]^-$, spectrum for 0.001 *M* solution of $K[Pt(NH_3)Cl_3]$ in 10.00 cm. cell with excess KCl to suppress aquation; $[Pt(NH_3)Cl_2(H_2O)]$, spectrum for 0.001 *M* solution in 10.00 cm. cell. This solution is an aged effluent from the Dowex-1 anion-exchange columns in which $[Pt(NH_3)Cl_2(H_2O)]$ is the dominant species, *p*H 4.0; $[Pt(NH_3)Cl_2(OH)]^-$, spectrum obtained when the *p*H of the solution for the $[Pt(NH_3)Cl_2(H_2O)]$ spectrum was raised to 9.0 by the addition of NaOH.

The titration curve of Fig. 1 indicates that $[Pt(NH_3)Cl_2(H_2O)]$ is an acid with a *pK* of about 7. Neutralization of the free acid by base gave immediately the third spectrum shown in Fig. 2, labelled $[Pt(NH_3)Cl_2(OH)]^-$ since this anion must be the predominant platinum species. Although there were distinct differences, the spectrum of $[Pt(NH_3)Cl_2(OH)]^-$ was not greatly different from that of its conjugate acid. After the neutralization, however, slow changes in the spectrum indicated that a further substitution reaction occurred.

After they had aged for several days, the effluent solutions from the anion-exchange columns were chemically analyzed for platinum content, total equivalents of acid and total chloride. Results of the analyses are in Table I.

TABLE I

ANALYSES OF SOLUTION SEPARATED BY ANION EXCHANGE FROM AGED $K[Pt(NH_3)Cl_3]$ SOLUTIONS

Effluent at room temperature, 24 ±1°

Constituent	Concn., mmoles./ml.
Total Pt	2.40×10^{-3}
Total Cl	4.73×10^{-3}
Equiv. acid	2.74×10^{-3}

Base Hydrolysis of $[Pt(NH_3)Cl_2OH]^-$.—Since *cis*-$[Pt(NH_3)_2Cl_2]$ is prepared by the action of ammonium acetate on $[PtCl_4]^=$, stoichiometric amounts of ammonium acetate were added to dilute solutions of the anion-column separated $[Pt(NH_3)Cl_2(H_2O)]$. To other solutions were also added NH_3, KOH and $K(C_2H_3O_2)$ in amounts equivalent to the platinum complex. A dark-green precipitate usually was observed after about 1 hr. with 0.01 *M* platinum concentrations. No precipitation was discerned over a period of several hours with 0.001 *M* concentration, and changes in the ultraviolet spectrum could be followed readily for each of the bases. All of the reagents appeared to produce eventually very similar spectra. In Fig. 3 is given an example of the observed spectral changes when NH_3 was added. Furthermore, analysis of the solution showed that uncomplexed NH_3 had not changed significantly. These results were interpreted to indicate that a second hydrolysis had occurred, giving the complex $[Pt(NH_3)Cl(OH)_2]^-$. The spectral changes, shown in Fig. 4, followed after the ammoniacal hydrolysis solution had been treated with H_2SO_4 and KCl. It can be seen that the reaction had been reversed, and it appears from the spectra that $[Pt(NH_3)Cl_2(H_2O)]$ re-forms. In other cases for which much higher concentrations of chloride were added, the final spectrum changes indicated first the formation of $[Pt(NH_3)Cl_2(H_2O)]$ followed by nearly complete conversion to $[Pt(NH_3)Cl_3]^-$.

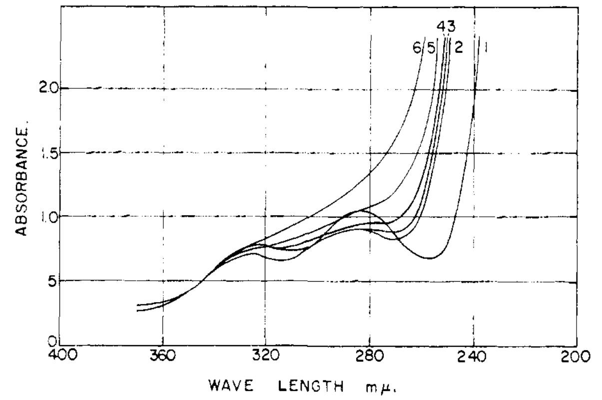

Fig. 3.—Effect of the addition of NH_3 on the ultraviolet spectrum of aged $[Pt(NH_3)Cl_2(H_2O)]$ solution to give 0.001 *M* total Pt and 0.0015 *M* NH_3; temp., 24 ± 1°, 10.00 cm. cells: (1) Initial $[Pt(NH_3)Cl_2(H_2O)]$ soln.; (2) 2 min. (NH_3 added at $t = 0$); (3) 17 min.; (4) 53 min.; (5) 85 min.; (6) 154 min.

Results and Discussion

Acid Hydrolysis Equilibria.—The system was considered in which $K[Pt(NH_3)Cl_3]$ and KCl were dissolved in H_2O and allowed to approach a steady state with regard to the reactions 1 and 2. If K_2 is very small, the equivalents of acid indicated by the potentiometric titration end-point, such as shown in Fig. 1, give the value of x_∞. The complete titration curves indicate that $[Pt(NH_3)$-

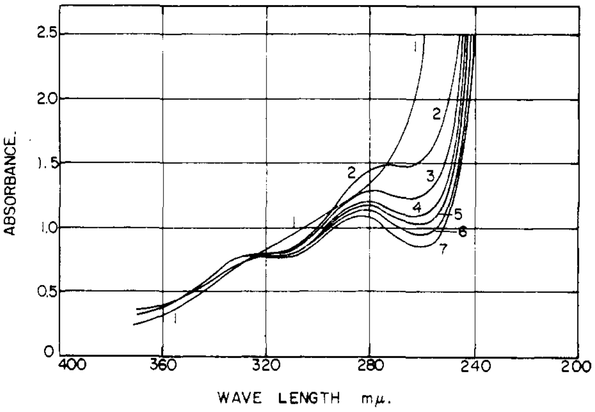

Fig. 4.—Changes in the ultraviolet spectrum of $[Pt(NH_3)Cl(OH)_2]^-$ solution following the addition of H_2SO_4 to give *p*H 4 and KCl to give 0.01 *M* KCl; temp., 24 ± 1°, 10 cm. cells: total platinum = 0.001 *M* (1) same as curve 6 in Fig. 3; (2) $t = 3$ min. (H_2SO_4 added at $t = 0$); (3) $t = 10$ min. (KCl added at $t = 6$ min.); (4) $t = 13$ min.; (5) $t = 18$ min.; (6) $t = 31$ min.; (7) $t = 56$ min.

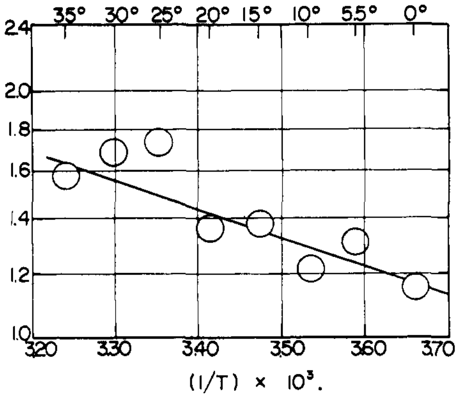

Fig. 5.—Equilibrium constant for the first acid hydrolysis reaction: log K_1 *vs.* $1/T$.

$Cl_2(H_2O)]$ is an acid with a *pK* of approximately 7. The titration curves were obtained rapidly over 10–15 min. intervals to indicate clearly the location of the end-points. However, as the acid is removed by neutralization, it is continually regenerated by reaction 1. Also, the second hydrolysis removes additional base. Therefore, values of x_∞ were taken from one point titrations, in which the estimated base to reach the end-point was added, and the *p*H of the solution was determined immediately. A small correction to the end-point *p*H could be made from the titration curve to give the equilibrium equivalents of acid, or x_∞. Values of K_1, determined at various temperatures, are included in Fig. 5. Consistency in the values of K_1 over a fourfold platinum concentration ($a = 0.00415 - 0.0166$ and $b = 0$) supported the assumption that K_2 is very small.

a = original concn. of $[Pt(NH_3)Cl_3]^-$ (before aging)
b = original concn. of Cl^- (before aging)
x = concn. of $[Pt(NH_3)Cl_2(H_2O)]$ at time t
x_∞ = concn. of $[Pt(NH_3)Cl_2(H_2O)]$ at the steady state
y = concn. of $[Pt(NH_3)Cl(H_2O)_2]^+$ at time t
y_∞ = concn. of $[Pt(NH_3)Cl(H_2O)_2]^+$ at the steady state
$K_1 = x_\infty(b + x_\infty + 2y_\infty)/(a - x_\infty - y_\infty)$ = equilibrium constant of reaction 1
$K_2 = y_\infty(b + x_\infty + 2y_\infty)/x_\infty$

For reaction 1 ΔF^0 at 25° is 2.5 kcal. The temperature dependence of K_1 is small and ΔH^0 is only +2.1 kcal. These values give an entropy of aquation of −1 e.u. for $[Pt(NH_3)Cl_3]^-$, reaction 1, a value in excellent agreement with the value of +1 e.u., predicted by the treatment of Latimer and Jolly.[7]

In the aged solutions which were passed through the ion-exchange column, the high dilution (*ca.* 2 l. at 2.40×10^{-3} *M* total Pt) provided the optimum chance for observing the second aquation equilibrium. The exchange resin removed Cl^- and $[Pt(NH_3)Cl_3]^-$ from the solution, substituting sulfate. Immediately after passage through the resin, the $[Pt(NH_3)Cl_2(H_2O)]$ concentration was x_∞ and the $[Pt(NH_3)Cl(H_2O)_2]^+$ concentration was y_∞. Upon further standing, additional aquation followed so that

$$[Pt(NH_3)Cl(H_2O)_2]^+ = y_\infty + \Delta y_\infty$$
$$[Pt(NH_3)Cl_2(H_2O)] = (x_\infty - \Delta y_\infty)$$
$$(Cl^-) = \Delta y_\infty$$

A potentiometric titration curve with sodium hydroxide showed only a single break corresponding to an acid with *pK* between 7 and 8. The same end-point, *p*H 9.35, which was taken for the aged $K[Pt(NH_3)Cl_3]$ solutions, served for these titrations. It did not appear feasible to add the large amounts of Na_2SO_4 to adjust the ionic strength in these experiments, so they were carried out at the very low ionic strength provided by the electrolytes under study. The equivalents of acid determined were greater than the moles of platinum in these solutions. For the interpretation, it was assumed that whereas $[Pt(NH_3)Cl_2(H_2O)]$ provides one replaceable hydrogen in the aqueous system, two hydrogens can be replaced in $[Pt(NH_3)Cl(H_2O)_2]^+$ to give $[Pt(NH_3)Cl(OH)_2]^-$. This should then be the same species produced by the treatment of NH_3, $NH_4(C_2H_3O_2)$, etc. From the excess acid equivalents the concentration of $[Pt(NH_3)Cl(H_2O)_2]^+$ was estimated by the use of the equations

$$[Pt]_{tot} = x_\infty + y_\infty \qquad (3)$$
$$[H^+] = x_\infty + 2y_\infty + \Delta y_\infty \qquad (4)$$

Since the equilibrium 2 was established both before the solution was passed through the ion-exchange resin and after the second aging

$$K_2 = \frac{y_\infty(x_\infty + 2y_\infty)}{x_\infty} = \frac{(y_\infty + \Delta y_\infty)\,\Delta y_\infty}{(x_\infty - \Delta y_\infty)} \qquad (5)$$

With the use of the analytical data in Table I, these three equations can be solved to give: $x_\infty = 2.36 \times 10^{-3}$ *M*, $y_\infty = 0.04 \times 10^{-3}$ *M*, $\Delta y_\infty = 0.30 \times 10^{-3}$ *M*. The total chloride analyses are satisfactorily consistent with the predicted quantity, $(2x_\infty + y_\infty)$. The indicated value of K_2 is 4×10^{-5} for room temperature, 27 ± 1°. With the uncertainties in the determinations of K_2 it appeared pointless to attempt an evaluation of the temperature dependence of this constant. The small magnitude of the constant, K_2, served to justify the assumption that the acid equivalents of the aged $K[Pt(NH_3)Cl_3]$ solutions gave accurately the concentration of $[Pt(NH_3)Cl_2(H_2O)]$ for the determination of the values of K_1, shown in Fig. 5.

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[7] W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 1548 (1953).

Kinetics of the Acid Hydrolysis of $[Pt(NH_3)Cl_3]^-$.—It is expected that in case the amount of $[Pt(NH_3)Cl(H_2O)_2]^+$ can be neglected, the approach to equilibrium with respect to reaction 1 will be given by the differential equation

$$dx/dt = k_1(a - x) - k_{-1}(x)(b + x) \qquad (6)$$

The solution of equation 6 is

$$\ln(x - x_\infty)[x_0 - x_\infty + \sqrt{(b + K)^2 + 4Ka}]/(x_0 - x_\infty)[x - x_\infty + \sqrt{(b + K)^2 + 4Ka}] = -k_{-1}t\sqrt{(b + K)^2 + 4Ka} \qquad (7)$$

where x_0 is the value of x at $t = 0$. A typical experimental plot of this function from a solution followed by the spectrophotometric method is given in Fig. 6. The description of the system by equation 7 appears satisfactory. From the equilibrium constants, given by the smooth line of Fig. 5 and from the slopes of the lines such as the one in Fig. 6, values of k_1 and k_{-1} have been calculated and are included in Table II. Also included are the indicated values of $\Delta H\ddagger$ and $\Delta S\ddagger$, based on the assumption that transmission coefficients are unity.

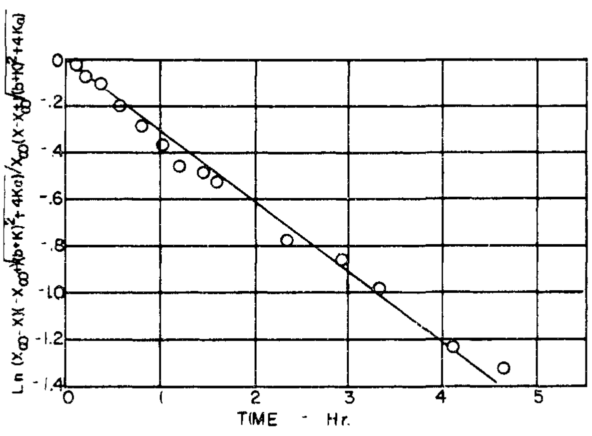

Fig. 6.—Kinetics of approach to steady state for reaction 1 followed spectrophotometrically (343 mμ): for 25°, a = 0.0166, b = 0.

TABLE II

RATE CONSTANTS FOR THE FIRST AQUATION OF $[Pt(NH_3)Cl_3]^-$ (REACTION 1)

Temp., °C.	k_1, sec.$^{-1}$ × 10^5	k_{-1}, l. mole^{-1} sec.$^{-1}$ × 10^3
0.0	0.21	0.19
5.5	0.37	.30
15.0	1.31	.98
20.0	2.35	1.65
25.0	3.6	2.5
30.0	5.8	3.7
$\Delta H^\ddagger$, kcal.	18.9	16.8
$\Delta S^\ddagger$, e.u.	−15	−14

The numerical values of k_1 and k_{-1} at 25° are close to the values of 3.9×10^{-5} and 2.1×10^{-3} found for the corresponding rate constants in the $[PtCl_4]^=$: $[PtCl_3(H_2O)]^-$ system, despite the differences in charge.[1] Banerjea, Basolo and Pearson[2] have noted that for a large number of substitution reactions in which chloride is replaced by the other groups in *cis*- and *trans*-$[Pt(NH_3)_2Cl_2]$, in $[Pt(NH_3)_3Cl]^+$, in $[Pt(en)Cl_2]$ and in $[PtCl_4]^=$, the rate is independent of the substituting group. The first-order rate constants are all very close to the value of k_1. They propose that acid hydrolysis may therefore be a common step in such reactions which involve the substitution of ligands which are weakly *trans*-directing.

It was noted that the rate of the acid hydrolysis was independent of pH if the pH were less than *ca.* 4.5, so the predominant species of the first hydrolysis was the acid rather than its conjugate base. A solution of aged $K[Pt(NH_3)Cl_3]$ in water normally attains a pH of 4.5–5.0.

In solutions for which the pH has been raised to values of 6 to 10 by the addition OH^-, NH_3, ammonium acetate or sodium acetate, the spectral changes indicated the stepwise base hydrolysis to give, first, $[Pt(NH_3)Cl_2(OH)]^-$ and then, $[Pt(NH_3)Cl(OH)_2]^-$.

Kinetics of Second Hydrolysis Reaction.—The small equilibrium constant, K_2, precluded the possibility of obtaining directly an accurate value of the rate constant for the forward reaction, k_2. The effluent solutions from the ion-exchange column were observed to be stable for long periods of time and frequently were stored at a pH of about 4 without observable changes for several weeks in an ice-bath. However, the spectral changes upon the addition of limited amounts of base indicated the formation of $[Pt(NH_3)Cl(OH)_2]^-$, for which Fig. 3 is a typical example. If acid is added to the resulting solution of $[Pt(NH_3)Cl(OH)_2]^-$ to convert it into the form $[Pt(NH_3)Cl(H_2O)_2]^+$, the rate of reverse reaction of equation 2 can be followed after the addition of chloride. From the results of such an experiment, Fig. 4, it can be seen that the spectrum changed rapidly when H_2SO_4 was added to give the initial neutralization of the OH^- groups. Addition of a large excess of chloride gave further rapid changes in which the valley at 260 mμ and the shoulder at 325 mμ, characteristic of $[Pt(NH_3)Cl_2(H_2O)]$, reappeared. That the final spectrum of Fig. 4 did not return exactly to the initial spectrum of Fig. 3 may be due to the formation of limited amounts of *cis*-$[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)Cl_3]^-$ or possibly a polymer in the system. The largest measurable absorbance changes occurred at the 260 mμ valley of the $[Pt(NH_3)Cl_2(H_2O)]$ spectrum. Therefore, for a very rough estimate of the rate constant, $k_{-2}[Cl]$ was set equal to the initial slope of the curve, $\ln(A - A_0)$ *vs.* t, where

A = absorbance at 260 mμ as a function of time, t, after the addition of chloride, Fig. 4

A_0 = absorbance at 260 mμ of curve 1, Fig. 3, with $[Pt(NH_3)Cl_2(H_2O)]$ the predominant species

The value found was k_{-2} = 0.2 l. mole^{-1} sec.$^{-1}$ for 24 ± 1°. With the value for K_2 given above, a value of 1×10^{-5} sec.$^{-1}$ is indicated for k_2. This value is therefore in line with the k_1 and the other first-order constants for the substitution reactions studied by Banerjea, Basolo and Pearson.

Although information about the equilibrium and kinetics for the acid hydrolysis has been obtained, the interesting question of the stereochemistry remains unanswered. Since the hydrolysis is enhanced by dilution, it does not appear likely that pure hydrolysis products will be obtained by crystallization procedures in view of the complexity of the system.

It is to be noted that these acid hydrolysis reactions provide a means for the isotopic exchange of chloride ligands with chloride ion in the solution. The use of radioactive chlorine-36 therefore may possibly give information which will clarify some of the stereochemical features of the reaction. There is also the question whether isotopic exchange may take place by alternative mechanisms. The authors are conducting exchange experiments with Cl^{36} which will be reported at a later date.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Thermal Decomposition of Methyl Cyclobutyl Ketone[1,2]

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The vapor-phase thermal decomposition of methyl cyclobutyl ketone has been investigated over the temperature range 360–410°. During the initial stages of the reaction ethylene and methyl vinyl ketone, which are the only important products, were found to be present in essentially equivalent amounts. On the basis of experiments at pressures from 10 to 65 mm. and from data taken during the course of the decomposition the reaction is first order. No appreciable inhibition of the decomposition by propylene, toluene or nitric oxide was observed. Experiments with initial pressures near 50 mm. gave an activation energy of 54.5 kcal./mole. The first-order rate expression is $k = 3.4 \times 10^{14}\, e^{-54500/RT}$ sec.$^{-1}$.

The thermal decompositions of methyl alkyl ketones have been observed to proceed by free radical chain processes.[3] On the other hand cyclobutane[4] and several other four-membered ring compounds[5,6] appear to undergo simple ring cleavage reactions which are not inhibited by propylene, toluene or nitric oxide. Therefore, the investigation of the thermal decomposition of methyl cyclobutyl ketone was of interest, particularly for comparison with the behaviors of these related compounds. Moreover, the photochemical decomposition of methyl cyclobutyl ketone has been investigated at 2654 Å. with temperatures from 60 to 250°.[7] Carbon monoxide, ethylene, methane and cyclobutane are the principal products, but at the lower temperatures methylcyclobutane, ethane and cyclobutene are present also. Free radical processes were used to explain the formation of the products.

Experimental

Materials and Apparatus.—The methyl cyclobutyl ketone was prepared by passing a mixture of cyclobutanecarboxylic acid and acetic acid (1:2.5 mole ratio) over a manganous oxide catalyst at 380–390° and collecting the products in a receiver cooled to −78°.[8] A number of samples were prepared and purified. In the first two preparations the sample was separated into fractions by distillation in a Claisen flask. Rate measurements were made with the fourth fraction of the first preparation (A-4) and a small fraction (B) taken after the distillation of 60% of the second sample. In the third preparation the fourth fraction from the first distillation was fractionated in a small column equipped with Podbielniak Heligrid packing. Sample C-4c was the third fraction. The D samples were from the fourth preparation after distillation in a Claisen flask and fractionation in a nitrogen atmosphere at a reflux ratio greater than six to one in a column with 85 cm. of Lecky-Ewell packing. Sample D-2 was one which was purified by conversion to the semicarbazone, recrystallization, and regeneration of the ketone. The melting point of the semicarbazone was 148.0–148.5°; literature value, 148–149°.[9] Sample D-5 was a portion of the fifth fraction placed directly on the vacuum line and used for rate studies. Sample D-5a was a portion placed in storage at about −15°; after seven months' storage plus some contact with air this sample gave a peroxide test with the sensitive ferrous ion–thiocyanate reagent. Before this sample was used in a few experiments the peroxides were reduced to a hardly detectable level by long shaking with mercury. The infrared absorption spectra of samples B, D-2 and D-5 were obtained in a one-meter gas cell with Perkin–Elmer models 12AB and 21 infrared spectrometers. Since the spectra from the three samples were in agreement, no indication of the presence of an impurity was obtained. None of the fractions used for kinetic measurements had a boiling range in excess of 0.2° and in most cases the boiling point was constant (within 0.1°) during the collection of the sample. The indices of refraction ($n^{20}D$) for the various samples were: B, 1.4322; C-4c, 1.4317; D-2, 1.4321; D-5, 1.4322. The index of refraction has been reported as 1.4322 at 19.3[9a] and 1.4315 at 20°.[10]

Propylene (99.5%) was obtained from the Ohio Chemical and Surgical Equipment Co. Toluene (Mallinckrodt analytical reagent) was dried over anhydrous calcium sulfate. In general all compounds were degassed immediately prior to use. Nitric oxide (Matheson) was distilled under vacuum two times. Before each use the nitric oxide was degassed at −196° and then distilled from a storage bulb (placed in a bath at −78°) into a small tube at −196°.

The furnace, temperature control, and vacuum system were similar in design to those described earlier.[11] For the study of surface effects the cylindrical Pyrex reaction vessel (310 ml.) was replaced by one packed with thin-walled Pyrex tubing which increased the surface-to-volume ratio 28-fold. The temperature at the center of the reaction bulb was

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[2] Abstracted from the Ph.D. thesis submitted by Louis G. Daignault.

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