measured k values and calculated w values into (2) yields values of $m^2\lambda$ ranging from 4 to 6.8 kcal./mole. Thus, the reorganizational energies are small (*cf.* ref. 1), which is reasonable in view of the rapidity of the reactions. Since w is the same for this series of reactions in any one direction, the variations in rate constant are due to the contributions of the different free energies to the $m^2\lambda$ term.

Additional confirmation of the Marcus theory is possible when the rate constants for the exchange reactions of the two oxidation–reduction couples in each cross reaction are known.[9] In the cases of the $IrCl_6^{3-}$–$IrCl_6^{2-}$ and $Fe(DMP)_3^{2+}$–$Fe(DMP)_3^{3+}$ exchange reactions, for which some data exist, only lower limits on the rate constants have been reported. Thus, we calculate a value of about 2.5×10^4 M^{-1} sec.$^{-1}$ depending upon ionic radius for either exchange reaction, but the experimental values are $>3 \times 10^2$ and $>2 \times 10^3$ M^{-1} sec.$^{-1}$ for the iridium[10] and iron[11] systems, respectively. This comparison is, therefore, essentially in agreement with the Marcus theory.

Finally, it is to be noted that for the compounds studied, large changes in equilibrium quotient (and correspondingly in the E^0 values of the oxidation–reduction couples) result from the substitution of methyl groups on the chelating agent. To see if this substitution has a further steric effect on the rate, an experiment was carried out with hexabromoiridate and tris(bypyridine)iron(II). These ions are closer to being spherical than any of the others, and would therefore present the least steric hindrance. For a concentration as low as 10^{-5} M, however, it was not possible to observe a chemical relaxation, although a sizable "jump" was detected. The relaxation occurs at a time shorter than 5 μsec., which corresponds to a reverse rate constant around 10^{10} M^{-1} sec.$^{-1}$. Thus, even for these rapid electron-transfer reactions, there are severe spatial restrictions, the result of which is to cause the diffusion controlled rate constant to fall somewhat short of the theoretical limiting value.

Acknowledgment.—This investigation was supported by PHS research grant GM-08893-03 from the National Institute of General Medical Sciences, Public Health Service.

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[9] R. Campion, N. Purdie, and N. Sutin, *J. Am. Chem. Soc.*, **85**, 3528 (1963).

[10] E. N. Sloth and C. S. Garner, *ibid.*, **77**, 1440 (1955).

[11] L. Eimer and A. I. Medalis, *ibid.*, **74**, 1592 (1952).

Contribution from the Chemical Laboratories of
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Kinetics of the Acid and Base Hydrolyses of the Chloropentaammineruthenium(III) Ion[1]

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A study of the rates of hydrolysis of $[Ru(NH_3)_5Cl]^{2+}$ shows that base hydrolysis is very much faster than acid hydrolysis, the ratio of rate constants being more than 10^6. This result resembles that for cobalt(III) complexes, but is quite different from the behavior of rhodium(III) and chromium(III) complexes. The rates for the different metal ions can be explained satisfactorily by an SN1CB mechanism for base hydrolysis. The data for acid hydrolysis are not as well explained by a single mechanism. The equilibrium constant for the acid hydrolysis has been determined as a function of temperature. The aquopentaammineruthenium(III) ion is a relatively strong acid with a pK_a of 4.2 ± 0.1 at 25°.

Reactions of ruthenium complexes, in particular those possessing nonchelate ligands, are often complicated by disproportionation, olation, and precipitation phenomena. The formation of the well known ruthenium red cation is a pertinent example.[2] It is not surprising, therefore, that few mechanistic studies have been made on these systems. Details of the acid and base hydrolysis reactions for complexes of the type $[Ru(NH_3)_5X]^{2+}$ where X is a replaceable anionic ligand are a desirable prerequisite to the general investigation of substitution reactions of ruthenium(III). In this work acid and base hydrolysis studies of the chloropentaammineruthenium(III) complex are reported together with equilibrium data for acid hydrolysis. A recent report[3] of electron-transfer processes in ruthenium(II) and ruthenium(III) ammine complexes included an estimate of the equilibrium constant and half-life for the acid hydrolysis of the $[Ru(NH_3)_5Cl]^{2+}$ cation, but there have been no detailed studies reported.

In preliminary experiments it was found that substitution of the bromide ligand in $[Ru(NH_3)_5Br]^{2+}$ was faster than for the corresponding chloro complex. Attempts were made to follow the reaction rate by spectrophotometric and titrimetric methods in various phosphate and borate buffers but reproducibility was poor and depended upon the nature and concentration

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[1] Supported by the U. S. Atomic Energy Commission under Contract AT(11-1)-1087.

[2] J. M. Fletcher, *et al.*, *J. Chem. Soc.*, 2000 (1961).

[3] J. Endicott and H. Taube, *J. Am. Chem. Soc.*, **84**, 4984 (1962).

of the ions present. In addition faster rates were obtained if the bromopentaammine solution was not freshly prepared. More satisfactory results were obtained with the use of the chloropentaammine complex. Buffer systems were avoided and base hydrolysis was measured in sodium hydroxide solutions at various concentrations.

A variety of acids were tried in which to study the acid hydrolysis reaction. Perchloric or nitric acids (~10^{-3} *M*) were unsuitable, resulting in the formation of brown solutions accompanied by black precipitates. Spectrophotometric studies showed that although the aquo complex was formed initially, it rapidly gave brown products. Use of sulfuric acid did not lead to decomposition but instead gave the sulfato complex. No interference from the anion was apparent with *p*-toluenesulfonic or fluoroboric acids and most measurements have been carried out in the former at acid concentrations of at least 10^{-1} *M*. This was necessary to obviate the formation of the hydroxy complex $[Ru(NH_3)_5OH]^{2+}$ *via* acid dissociation of the acidic aquo species.

Experimental

Materials.—Hexaammineruthenium(III) chloride was obtained from Johnson Matthey Co., Ltd., London, and converted to chloro- or bromopentaammineruthenium(III) chloride or bromide by the method of Gleu.[4] The products were recrystallized from hot, dilute hydrochloric or hydrobromic acid and checked for purity by analysis, conductivity measurements, and comparison of their absorption spectra with published work.[5]

Anal. Calcd. for $[Ru(NH_3)_5Cl]Cl_2$: H, 5.16; N, 24.0; Cl, 36.27. Found: H, 4.84; N, 24.14; Cl, 36.8.

The conductivity of a freshly prepared 10^{-3} *M* solution was 240 ohm^{-1} cm.^{2} mole^{-1}.

Anal. Calcd. for $[Ru(NH_3)_5Br]Br_2 \cdot H_2O$: H, 3.88; N, 15.8; Br, 53.95. Found: H, 3.67; N, 15.85; Br, 53.5.

The conductivity of a 10^{-3} *M* solution was 255 ohm^{-1} cm.^{2} mole^{-1}.

The aquopentaammineruthenium(III) perchlorate was prepared as described previously[3,4] and its purity checked by examination of the absorption spectrum of a fresh preparation in 0.1 *M* perchloric acid. In aqueous solution alone the spectrum is that of a mixture of $[Ru(NH_3)_5H_2O]^{3+}$ and $[Ru(NH_3)_5OH]^{2+}$. The perchlorate is white when dry and pale yellow when wet. It is unstable in the solid state and gradually turns gray over a period of days. It was, therefore, always freshly prepared and used immediately.

All chemicals used were of reagent grade quality and solutions were made up with distilled water that had been boiled to remove dissolved oxygen and cooled in a nitrogen atmosphere. Fluoroboric acid was prepared with the aid of an Amberlite IR120 ion-exchange resin starting from sodium fluoroborate. The sodium hydroxide used was freshly prepared and standardized using potassium hydrogen phthalate plus phenolphthalein indicator.

Results

Absorption Spectra Studies.—The spectrum of the $[Ru(NH_3)_5OH]^{2+}$ complex was obtained by making just alkaline a fresh solution of $[Ru(NH_3)_5H_2O]^{3+}$, prepared as described above. The aquo complex had λ_{max} 268 mμ and ϵ_{max} 770 which immediately shifted in alkaline solution to λ_{max} 295 mμ with an extinction coefficient approximately twice as great. The spectrum of the hydroxy complex was not stable in the presence of alkali and continued to increase in intensity. This was accompanied by loss of ammonia and precipitation of a brown solid.

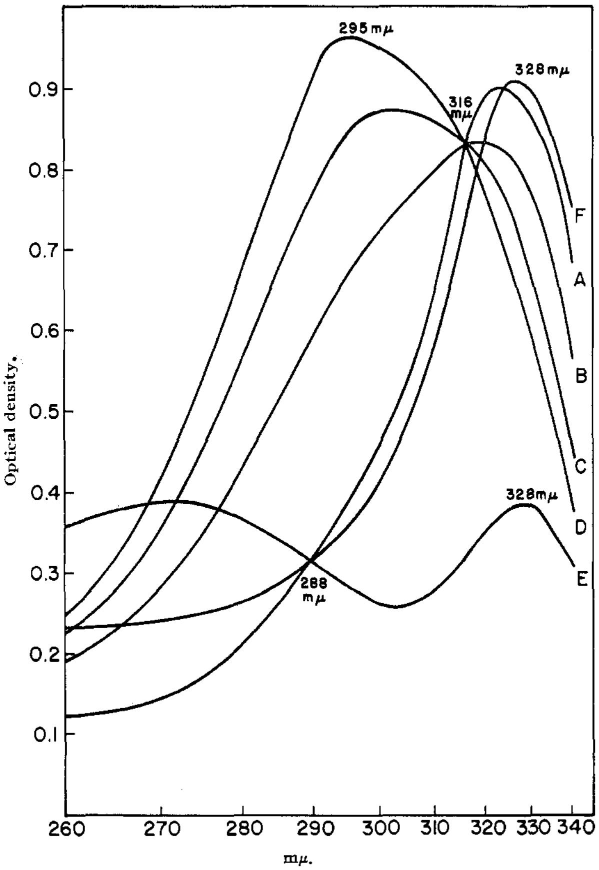

Fig. 1.—Spectral changes during base hydrolysis of $[Ru(NH_3)_5Cl]^{2+}$; [complex] = [base] = 5.0×10^{-4} *M:* A, initial; B, 180 sec.; C, 660 sec.; D, 960 sec; E, immediately after acidifying with 0.6 *M* HCl; F, acidified solution after 12 hr.

Figure 1 shows the changes in spectra that occur during base hydrolysis of $[Ru(NH_3)_5Cl]^{2+}$. The original peak in basic solution is at 324 mμ. This disappears during the course of reaction and a new peak at 295 mμ appears. There is a single isosbestic point at 316 mμ. More than one equivalent of hydrochloric acid is necessary to completely protonate the hydroxypentaammine complex. In the presence of excess acid the peak at 295 mμ is seen to shift immediately to give two bands at 270 and 328 mμ, respectively. The former is due to the aquopentaammine complex and the latter to the chloropentaammine. Overnight in the presence of excess hydrochloric acid, the equilibrium is driven almost entirely in the direction of the chloropentaammine species and there is an isosbestic point at 288 mμ.

It may be noted from Fig. 1 that the spectrum after standing overnight does not pass through the 316 mμ isosbestic, nor is it quite identical with that of the starting material. The maximum is now at 328 mμ instead of 324 mμ. The original complex also has its

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[4] K. Gleu and K. Rehm, *Z. anorg. allgem. Chem.*, **227**, 237 (1936).

[5] H. Hartman and C. Bushbeck, *Z. physik. Chem.* (Frankfurt), **11**, 120 (1957).

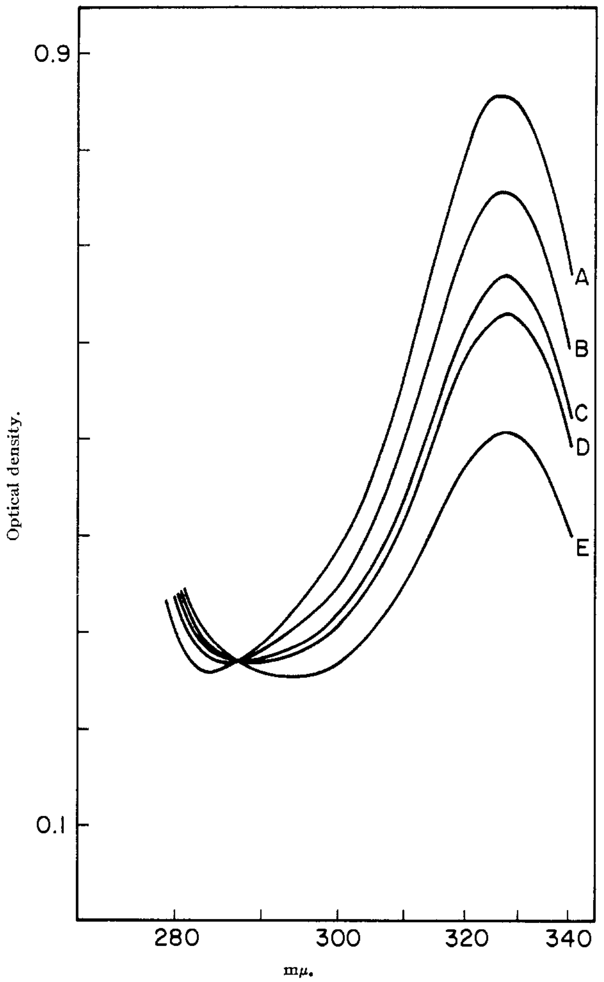

Fig. 2.—Spectral changes during acid hydrolysis of $[Ru(NH_3)_5Cl]^{2+}$; [complex] = 5.0×10^{-4} *M*: A, initial; B, 60 min.; C, 170 min.; D, 208 min.; E, 466 min.

maximum at 328 mμ in an acid medium.[5] Figure 2 shows the spectral changes during the acid hydrolysis (0.1 *M* *p*-toluenesulfonic acid) of $[Ru(NH_3)_5Cl]^{2+}$. The isosbestic point at 288 mμ is again observed. The intense absorption of the acid prevented measurements below 280 mμ.

pK_a Determination.—One hundred ml. of a 10^{-3} *M* solution of $[Ru(NH_3)_5H_2O](ClO_4)_3$ in carbon dioxide-free water was placed in a magnetically-stirred, thermostated beaker and titrated with a fresh solution of 10^{-2} *M* sodium hydroxide. The pH was measured with a Beckman glass electrode pH meter. The pK_a was obtained from the titration curve from points near the half-equivalence point. Duplicate determinations gave a pK_a of 4.2 ± 0.1 at 25.1°.

Kinetic Studies.—Both spectrophotometric and titration methods were used to follow the reactions investigated. The rates of base hydrolysis were followed by the increase in absorbance at 295 mμ using a Beckman Model DU spectrophotometer with a cell compartment thermostated at 24.6°. The desired concentration of sodium hydroxide in a volume of about 3 ml. of water was placed in a 1-cm. quartz cell and allowed to come to the compartment temperature. A freshly prepared solution of the chloropentaammine complex at the same temperature was pipetted into the cell so as to give a final concentration of 2.6×10^{-4} *M*. The reagents were mixed by quickly inverting the cell and readings were taken immediately. Reagent blanks were used in the reference at all times. It was important that the solution of the complex not be more than 3 hr. old, otherwise irreproducible, faster results were obtained.

Pseudo-first-order kinetics were obtained by using an excess of hydroxide ion and the rate constants were calculated from the usual first-order equation.

It was shown by the constancy of the isosbestic point at 316 mμ that use of excess base had not altered the course of the reaction, at least for a period of two half-lives. At longer times the isosbestic shifted to shorter wave lengths and ammonia was evolved with the eventual formation of a brown-black precipitate.

The values of k_{obsd} were independent of the complex concentration and dependent upon the hydroxide ion concentration. The results are given in Table I. Each value is the average of at least two experiments and has an accuracy of within 2%. The plot of k_{obsd} *vs.* hydroxide ion concentration is linear and fits the equation $k_{obsd} = k_{OH}[OH^-]$ where k_{OH} is the second-order rate constant for base hydrolysis. The slope gives a value of k_{OH} equal to 5.0 ± 0.1 M^{-1} sec.$^{-1}$. Less detailed study of $[Ru(NH_3)_5Br]^{2+}$ gave a preliminary value of k_{OH} equal to 18 M^{-1} sec.$^{-1}$ at 25°.

Table I

Pseudo-First-Order Rate Constants[a,b] for the Base Hydrolysis of $[Ru(NH_3)_5Cl]Cl_2$ in NaOH at 24.6 ± 0.1°

$10^4[OH]^-$, *M*	26.5	21.9	18.0	12.9	7.74	3.87
10^3k_{obsd}, sec.$^{-1}$	12.7	10.5	8.92	7.14	4.0[c]	1.3[d]

[a] Each value is the average of two or more measurements. [b] The complex concentration was usually 2.6×10^{-4} *M*. [c] Measured both spectrophotometrically and titrimetrically. [d] Calculated from the initial slope of the first-order plot. A direct calculation of the second-order rate constant gave the value 3.0 l. mole^{-1} sec.$^{-1}$.

Measurements of the rate of acid hydrolysis employed the following technique. One hundred ml. of a 10^{-1} *M* solution of *p*-toluenesulfonic acid was placed in a constant temperature bath and allowed to reach thermal equilibrium. A weighed sample of the chloropentaammine complex was added to the flask, which was shaken well to effect dissolution. The final concentration was usually 5×10^{-4} *M*. A 5-ml. aliquot was withdrawn at periodic intervals and pipetted into a dry test tube which was surrounded by an acetone–Dry Ice mixture in order to stop the reaction. The optical densities (*D*) of the samples were then measured at room temperature at 328 mμ. At this wave length the aquopentaammine species has nearly zero absorbance and the value for $[Ru(NH_3)_5Cl]^{2+}$ is known to be 1930.[5] Thus the concentration of aquo complex at any time, *x*, may be calculated from the expression $x = (1930a - D)/1930$, where *a* is the initial concentration of chloropentaammine complex.

In some of the experiments the reaction rate was followed by titration of the emergent chloride ion with mercuric nitrate solution and sodium nitroprusside as indicator.[6] For acid hydrolysis the experimental procedure was identical with that used in the spectrophotometric method. Each frozen sample was titrated rapidly as soon as it had become liquid again, and the rate constants were calculated by the method given below. For base hydrolysis separate solutions of chloropentaammine complex and sodium hydroxide were thermostated at 24.6° and then mixed. A 10-ml. sample was immediately withdrawn and pipetted into 4 ml. of 1 N sulfuric acid which was cooled thoroughly in ice and then titrated. Rate constants for base hydrolysis were calculated in the same manner as with the spectrophotometric method after substitution of titration volumes for absorbance readings.

Unlike base hydrolysis, which goes virtually to completion, acid hydrolysis was found to obey a rate law corresponding to an opposed first- and second-order reaction as illustrated by the equation

$$[Ru(NH_3)_5Cl]^{2+} + H_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Ru(NH_3)_5H_2O]^{3+} + Cl^- \quad (1)$$

Rate constants were calculated graphically by plotting $\log [ax_e + x(a - x_e)]/a(x_e - x)$ against time. The slopes of the straight lines obtained were then equal to $k_1(2a - x_e)/2.303x_e$, where a and x are as previously defined and x_e is the equilibrium concentration of aquo complex.[7] The rate constant k_1 refers to the forward process of reaction 1, that is, the aquation rate constant, and is usually called k_{H_2O} in the literature.

TABLE II

ACID HYDROLYSIS DATA FOR $[Ru(NH_3)_5Cl]Cl_2$ IN *p*-TOLUENESULFONIC ACID AT IONIC STRENGTH 0.1

Temp., °C.	Complex, M	k_1, sec.$^{-1}$	K_{eq}
35	5.0×10^{-4}	3.1×10^{-6}	151 ± 4
45	5.0×10^{-4}	8.45×10^{-6}	163 ± 4
	10.0×10^{-4}	7.11×10^{-6}	
53	5.0×10^{-4}	2.3×10^{-5}	...
64	2.5×10^{-4}	7.3×10^{-5}	187 ± 7
	5.0×10^{-4}	6.8×10^{-5}[a]	183 ± 50[a]
	5.0×10^{-4}	6.5×10^{-5}	187 ± 7
80	5.0×10^{-4}	3.28×10^{-4}	211 ± 5
90	5.0×10^{-4}	7.7×10^{-4}	237 ± 6

[a] In 10^{-3} M fluoroboric acid by titration.

The acid hydrolysis rate constants were independent of the initial concentration of chloropentaammine complex. Those obtained titrimetrically in 10^{-3} M fluoroboric acid agreed well with spectrophotometric data using 10^{-1} M *p*-toluenesulfonic acid. Table II summarizes the results. The temperature dependence of the rate constants was plotted in the usual way and from the slope an Arrhenius activation energy of 23.2 kcal. was calculated. The entropy of activation was −11 e.u.

Equilibrium Studies.—Measurements of the equilibrium concentration of $[Ru(NH_3)_5Cl]^{2+}$ enabled calculation of the equilibrium constant (K) for the anation reaction.

$$K = \frac{([Ru(NH_3)_5Cl]^{2+})}{([Ru(NH_3)_5H_2O]^{3+})(Cl^-)} \quad (2)$$

It was assumed that the equilibrium concentration of $[Ru(NH_3)_5H_2O]^{3+}$ was equal to the difference between the initial and equilibrium concentrations of $[Ru(NH_3)_5Cl]^{2+}$.

A plot of log K against the reciprocal of the absolute temperature gave a ΔH of 1.7 kcal. and a $\Delta S°$ of +15 e.u. The values of K quoted have an over-all accuracy of about 30%. Measurements of the reverse anation reaction have also been made as a check on the equilibrium. By adding an excess of Cl^- ions to the acidified reaction product from base hydrolysis the reappearance of the peak at 326 mμ could be followed. The same procedure was used starting from the aquopentaammine produced in acid hydrolysis. In each case the final solution was 0.1 M with respect to *p*-toluenesulfonic acid and of ionic strength 0.1. Good pseudo-first-order kinetics were found when base hydrolysis was used to generate the aquo species. Deviations occurred after reaction times of one to two half-lives when the aquo complex was made *via* acid hydrolysis. In this case satisfactory rate constants were obtained from the initial slopes of the first-order plots. At 90° the mean value of the pseudo-first-order constant was 1.4×10^{-3} sec.$^{-1}$ at a chloride ion concentration of 0.0105 M. Therefore, k_2, the second-order rate constant for anation, was calculated to be 0.13 M^{-1} sec.$^{-1}$, assuming $k_2 = k_{obsd}/[Cl^-]$. Combination of this value with the corresponding acid hydrolysis rate constant of 7.7×10^{-4} sec.$^{-1}$ gave an equilibrium constant of 171, in reasonable agreement with the spectrophotometric value of 237. The final spectrum after driving the reaction at 25° almost completely back to chloropentaammine complex is shown in Fig. 1. It is seen to agree fairly well with the original spectrum. At higher temperatures agreement was not as good. For example, at 90° only 85% of the theoretical amount of chloro complex was regenerated using excess HCl.

As a further check on the equilibrium constant, it was evaluated by titration of released chloride ion at 64°, using mercuric ion as a titrant. The solution contained 0.1 M *p*-toluenesulfonic acid, 5.00×10^{-4} M chloropentaammine, and 1.00×10^{-3} M chloride ion initially. At equilibrium $13.98 \pm 0.3 \times 10^{-4}$ M chloride ion was found. This gives $K = (1.02 \times 10^{-4})/(3.98 \times 10^{-4})(13.98 \times 10^{-4}) = 183$ which is in fortuitously good agreement with the value found spectrophotometrically.

Attempted Acid Hydrolysis of $[Ru(NH_3)_5Cl]Cl_2$ in H_2SO_4.—Acid hydrolysis of $[Ru(NH_3)_5Cl]Cl_2$ in 10^{-2} M H_2SO_4 at 80° was studied spectrophotometrically by the technique of periodically removing samples and quenching them in a freezing mixture. There was a

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(6) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1953, pp. 460, 547–549.

(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 173–174.

Table III

Rates of Acid Hydrolysis of $[Ru(NH_3)_5Cl]Cl_2$ in H_2SO_4 at 80°

H_2SO_4, *M*	Complex, *M*	$k \times 10^4$, sec.$^{-1}$
5.35×10^{-3}	5.0×10^{-4}	3.50[a]
5.35×10^{-3}	2.5×10^{-4}	3.40
5.35×10^{-2}	5.0×10^{-4}	2.70[b]
5.35×10^{-2}	5.0×10^{-4}	4.42

[a] Duplicate runs ±0.05. [b] By chloride titration.

shift in the absorption maximum from 328 mμ to a broad band at 308–310 mμ with an isosbestic at 312 mμ. This change was complete in about 5 hr. Overnight the band at 308 mμ disappeared to give a new peak at 260 mμ which was unidentified. The expected decrease in resistance of the solution during acid hydrolysis was not observed. Instead a 10^{-3} *M* H_2SO_4 reaction mixture increased in resistance, the over-all change being from 750 ohms initially to 1040 ohms at infinite time. It might also be mentioned that all attempts to affect a pH titration of the acid hydrolysis product gave only the curves expected for sulfuric acid itself. These observations are consistent with the reaction

$$[Ru(NH_3)_5Cl]^{2+} + SO_4^{2-} \longrightarrow [Ru(NH_3)_5SO_4]^+ + Cl^- \quad (3)$$

The rate of this anation was followed spectrophotometrically and also by titration. The results obtained at 80° are given in Table III.

Catalytic Effects.—It was noted that solutions of $[Ru(NH_3)_5Cl]^{2+}$ or $[Ru(NH_3)_5Br]^{2+}$ that had aged at room temperature for more than a few hours gave higher rates of base hydrolysis. Some study was made of the effect of added oxidizing agents. It was found that the pentachlorohydroxyruthenate(IV) ion[8] gave increased rates at 10^{-5} *M* concentrations. Ruthenium red[3] gave increased rates at 10^{-4} *M*. Added cerium(IV) sulfate (2×10^{-5} *M*) and dissolved oxygen had no effect. It appears that as well as the catalysis by ruthenium(II) reported earlier,[3] there is a ruthenium(IV) catalysis of some of the reactions of trivalent ruthenium.

Discussion

The fact that base hydrolysis is so much more effective than acid hydrolysis for ruthenium(III) puts it in the same category as cobalt(III), and in a different one from chromium(III) and rhodium(III) where base hydrolysis is relatively slow. This result is somewhat surprising since Ru(III), a d^5 system, might have been expected to show a similar relationship to Rh(III), a d^6 system, that d^3 Cr(III) shows to d^6 Co(III). Table IV shows a number of properties of the four elements for comparative purposes. It can be seen that the relative rate constants for base hydrolysis at 25° are Ru(III) > Co(III) > Cr(III) ~ Rh(III), at least for the chloropentaammines.[9] One also notes that the ratio of base hydrolysis to acid hydrolysis, k_{OH}/k_{H_2O}, is 2×10^2, 5×10^5, and 5×10^6 for Cr(III), Co(III), and Ru(III), respectively (at 25°), and 4×10^3 for Rh(III) (at 80°).

It turns out to be possible to explain the peculiar order of base hydrolyses in terms of the SN1CB mechanism proposed for cobalt(III) complexes.[12] There is no reason, of course, for a common mechanism to be followed. Particularly for Rh(III), where the predicted rate for the SN1CB mechanism is small, a change to an SN2 mechanism may occur.

The steps in the conjugate base mechanism are

$$[M(NH_3)_5Cl]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [M(NH_3)_4NH_2Cl]^+ + H_2O \quad (4)$$

$$[M(NH_3)_4NH_2Cl]^+ \xrightarrow{\text{slow}} [M(NH_3)_4NH_2]^{2+} + Cl^- \quad (5)$$

$$[M(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\text{fast}} [M(NH_3)_5OH]^{2+} \quad (6)$$

In the case of cobalt(III) it is postulated that the five-coordinated intermediate, $[M(NH_3)_4NH_2]^{2+}$, rearranges to a trigonal bipyramid. On the other hand, for rhodium(III), the evidence is strong that such rearrangement does not occur.[11]

If the equilibrium constant for (4) lies well to the left, the rate constant for base hydrolysis by this mechanism becomes the product of the equilibrium constant for (4) times the rate constant (5). Any factors which make the ammine complexes stronger acids and any factors which cause a high rate of dissociation of the amido complex will give a high rate of base hydrolysis. There are two kinds of evidence bearing on the acidities of the ammine complexes, which are all too small to be measured directly. One is the pK_a values of the related aquopentaammines and the other is the rate of base-catalyzed hydrogen–deuterium exchange in the ammines, *i.e.*, the forward rate constant for eq. 4. The relevant data are given in Table IV and it is seen Ru(III) is conspicuously more acid than the other metal ions with Cr(III) next. This is explicable in terms of the various factors which determine acid strengths, including the crystal field destabilization due to replacing an ammine group with an amide group.[13] The latter factor would be less for the partly filled t_{2g} subshells of Ru(III) and Cr(III) than for the $(t_{2g})^6$ subshell of Rh(III) and Co(III).

The tendency of the amido group to donate negative charge to the metal constitutes the driving force for the dissociation step of (5). This may occur through σ-bonding in part, but is much more effective if coupled to a rearrangement to a trigonal bipyramid so that strong ligand to metal π-bonding can occur.[14] In any case the extent of electron donation may be estimated from the electron affinity of the metal ion or ease of reduction. In the absence of reliable solution data for the second transition series, gas phase ionization potentials are used.

$$M^{3+}(g) + e \longrightarrow M^{2+}(g) \quad (7)$$

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[8] See P. Wehner and J. C. Hindman, *J. Phys. Chem.*, **56**, 10 (1952), for a discussion of the nature of this species in solution.

[9] For the dichlorobisethylenediamine complexes the differences between Cr, Co, and Rh are much greater.[10]

[10] See ref. 11 and R. G. Pearson, R. A. Munson, and F. Basolo, *J. Am. Chem. Soc.*, **80**, 504 (1958).

[11] S. A. Johnson, F. Basolo, and R. G. Pearson, *ibid.*, **85**, 1741 (1963).

[12] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 124 ff.

[13] Reference 12, pp. 387–394.

[14] R. G. Pearson and F. Basolo, *J. Am. Chem. Soc.*, **78**, 4878 (1956).

TABLE IV

SOME PROPERTIES OF SEVERAL METAL IONS

	Cr^{3+}	Co^{3+}	Ru^{3+}	Rh^{3+}
Electronic configuration	d^3	d^6	d^5	d^6
k_{OH} (25°), M^{-1} sec.$^{-1}$, $[M(NH_3)_5Cl]^{2+}$	1.65×10^{-3} [a]	8.5×10^{-1} [b]	4.9[c]	$\sim 2 \times 10^{-3}$ [d]
k_{H_2O}, sec.$^{-1}$, $[M(NH_3)_5Cl]^{2+}$	8.3×10^{-6} [e]	1.7×10^{-6} [e]	3.3×10^{-4} [c]	4.3×10^{-5} [f]
	25°	25°	80°	80°
E_a, acid hydrolysis, kcal.	22[e]	24[e]	23[c]	. . .[f]
pK_a, 25°, $[M(NH_3)_5H_2O]^{3+}$	5.2[g]	5.7[g]	4.2[c]	5.9[g]
$k_{exchange}$, 25°, M^{-1} sec.$^{-1}$, $[M(NH_3)_6]^{3+}$ [h]	2.6×10^6	1.6×10^6	6.0×10^8	2.1×10^5
Electron affinity,[i] e.v.	29.5	35.5	31	33
CFAE for trigonal[j] bipyramid	$5.74Dq$	$11.48Dq$	$8.90Dq'$	$1.48Dq'$
CFAE for coord. no. of 7[k]	$1.80Dq$	$3.63Dq$	$1.14Dq'$	$3.63Dq'$

[a] M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, **83**, 2453 (1961). [b] A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1262 (1955). [c] This work. [d] From ref. 11 and assumption that $E_a = 25$ kcal., which is the value for $[Rh(NH_3)_5Br]^{2+}$ and $[Rh(en)_2Cl_2]^+$. [e] Reference 12, p. 122. [f] References 11 and 24. Data insufficient to calculate E_a. [g] Reference 12, p. 387. [h] J. W. Palmer and F. Basolo, *J. Inorg. Nucl. Chem.*, **15**, 279 (1960). Rate constant is for hydroxide ion catalyzed deuterium exchange of $[M(NH_3)_6]^{3+}$ in heavy water. [i] Third ionization potential of metal correcting for spin pairing. [j] See ref. 12, p. 108 ff. Dq' is some 50% greater than Dq, which is about 5 kcal. [k] Five groups of octahedron unchanged; entering and leaving groups 25% further away. See ref. 18.

The usual third ionization potential is not suitable because it refers to high spin states for the ions. Following the procedure suggested by the work of Jørgensen[15] and Orgel,[16] we have made a rough correction for spin-pairing effects to calculate the low spin ionization potentials. The electron to be added is assumed to have zero spin and to go into that would be an e_g orbital in the complex. The correction is −1.5 e.v. for Cr(III), 2 e.v. for Co(III) and Rh(III), and 2.5 e.v. for Ru(III), with the ionization potential increased in the three latter cases. The correction was based on the change in the number of favorable spin exchange energy terms.[16] The ionization potentials of the high spin states are from the literature.[17] The corrected values are shown in Table IV and give Co(III) the greatest electron affinity and Cr(III) the least.

The third important property of the metal ion that must be considered is the loss of crystal field stabilization that occurs upon going from the octahedral ground state to the transition state. This may be called crystal field activation energy, CFAE, as suggested by Hush.[18] Table IV shows some approximate values of CFAE for two assumed structures of the transition state for strong field d^3, d^5, and d^6 ions. The ground state is considered as a regular octahedron and the activated complex as either a trigonal bipyramid or as a seven-coordinated structure with five groups left unchanged and the entering and leaving groups adjacent and somewhat further away.[19] Such a structure is energetically favorable in several respects and may be used as a model for both an SN2 mechanism and an SN1 mechanism in which the solvent traps the five-coordinate intermediate as soon as the leaving group bond is sufficiently lengthened.

Ligand–ligand repulsions and π-bonding favor the trigonal bipyramid structure, whereas crystal field effects oppose it, as Table IV shows. For the second transition series, ligand–ligand repulsions are less because of the greater ionic radius, and crystal field losses are larger. The parameter Dq is about 5 kcal. for the first transition series and Dq' is some 50% larger for the second. It may be concluded that the trigonal bipyramid is likely for cobalt and perhaps chromium but not for rhodium and perhaps not ruthenium.

Looking at all the information, the following conclusions can be drawn. As far as reaction 4 is concerned, formation of the amido complex, the order of reactivity is expected to be Ru > Cr > Co > Rh. Looking at electron affinity (tendency to π-bond), the order is Co > Rh > Ru > Cr. Looking at CFAE, for the same transition state, the order is Cr > Ru > Co > Rh. The high rate of base hydrolysis of ruthenium(III) can be rationalized best by a seven-coordinated intermediate with no rearrangement, since the tendency to π-bond is not great. The amido group is very easily formed, and the loss of crystal field stabilization is small. A *cis* amido group will cause substantial activation of the chloro group even if no rearrangement occurs. The relatively high rate of base hydrolysis of cobalt(III) is due to a large electron affinity (ease of reduction) and the lower rate of chromium(III) to a low electron affinity. The low rate for rhodium(III) is explained by a low acidity and large crystal field effects.

The rate constants for acid hydrolysis, k_{H_2O} in Table IV, show Ru > Rh and Cr > Co. Extrapolating the value for ruthenium to 25° by means of the activation energy gives $k_{H_2O} = 7 \times 10^{-7}$ sec.$^{-1}$. Thus, the over-all sequence is Cr > Co > Ru > Rh. The factors expected to influence these rate constants are crystal

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(15) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 1505 (1956).

(16) L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1960, pp. 47–50.

(17) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular 467, U. S. Government Printing Office, Washington, D. C., 1949 and 1952.

(18) N. S. Hush, *Australian J. Chem.*, **15**, 378 (1962).

(19) See ref. 11 and 18 for details. The activated complex has the composition $[M(NH_3)_5ClOH]^+$ but its structure may be $[M(NH_3)_4NH_2ClH_2O]^+$. That is, the entering group may be water.

field effects and the electron affinities. Assuming a seven-coordinated intermediate and allowing for $Dq' = 1.5Dq$, crystal field theory gives the theoretical order Ru > Cr > Co > Rh. The electron affinity term may be considered as causing a higher bond strength between the metal ion and the halide ion for a higher electron attraction. This produces the predicted rate sequence Cr > Ru > Rh > Co if bond breaking is more important than bond making as all other available evidence suggests.[20] The conclusion is that Co(III) is more reactive and Ru(III) less reactive than theory predicts. It is also noticeable that the activation energies of all four metal ions are always rather similar, though that for cobalt is usually some 2 kcal. higher than that for chromium[21] and that for rhodium some 2 kcal. higher than that for cobalt.[11] These changes are not nearly as large as those predicted from crystal field theory.[22] It is not clear whether the difference between theory and experiment is due to changes in the details of the mechanism or to the inadequacy of simple crystal field theory.[23]

The results of Table III clearly indicate that the mechanism for the sulfation reaction of $[Ru(NH_3)_5Cl]^{2+}$ is a slow aquation followed by a fast anation.

$$[Ru(NH_3)_5Cl]^{2+} + H_2O \xrightarrow{\text{slow}} [Ru(NH_3)_5H_2O]^{3+} + Cl^- \quad (8)$$

$$[Ru(NH_3)_5H_2O]^{3+} + SO_4{}^{2-} \xrightarrow{\text{fast}} [Ru(NH_3)_5SO_4]^+ + H_2O \quad (9)$$

The over-all rate is the same as that for acid hydrolysis. Sulfate ion is not a nucleophilic reagent for ruthenium(III) complexes, in agreement with the behavior found for many other nucleophiles and chloroammine complexes of cobalt(III), chromium(III), and rhodium(III).

The value of the equilibrium constant for acid hydrolysis at 25° extrapolated from the data of Table II is about 140. This is not in very good agreement with the preliminary figure of 43 at ionic strength 0.10 given by Endicott and Taube.[3] There is some error in our spectrophotometric data in that the equilibrium is reached slowly and it is known that some irreversible decomposition occurs. In the earlier work[3] equilibration was achieved rapidly by using ruthenium(II) catalysis. It should be noted, however, that we kave checked our results by using three independent methods.

An examination of Lamb's data[24] shows that the equilibrium constant for the formation of $[Rh(NH_3)_5Cl]^{2+}$ from $[Rh(NH_3)_5H_2O]^{3+}$ is nearly the same as for the ruthenium complex at the same ionic strength. For both metals this constant is very much larger than for $[Co(NH_3)_5Cl]^{2+}$ and $[Cr(NH_3)_5Cl]^{2+}$, where acid hydrolysis is essentially complete. Thus for the second transition series there is a preference for binding to chloride ion rather than water. The reason for this is not clear, but it may be due to a greater degree of covalent binding. Whatever the reason, it represents an additional factor which determines the rate of acid hydrolysis.

[20] See ref. 12. Also R. G. Wilkins, *Quart. Rev.* (London), **16**, 316 (1962); D. R. Stranks, "Modern Coordination Chemistry," R. G. Wilkins and J. Lewis, Ed., Interscience Publishers, New York, N. Y., 1960.

[21] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962).

[22] W. Plumb and G. M. Harris, private communication, report an activation energy of 33 kcal. for water exchange in $[Rh(H_2O)_6]^{3+}$ compared to 27.6 kcal. for $[Cr(H_2O)_6]^{3+}$.

[23] R. G. Pearson and R. D. Lanier, *J. Am. Chem. Soc.*, **86**, 765 (1964), have a discussion of this problem.

[24] A. B. Lamb, *ibid.*, **61**, 699 (1939).

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The Association between Chromium(VI) and Aquopentaamminecobalt(III) in Aqueous Perchlorate Media[1]

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From combined spectrophotometric and pH measurements we have obtained a value of $K = 9.82 \times 10^{-2}$ for the reaction $Co(NH_3)_5H_2O^{+3} + HCrO_4^- = C + H^+$ at 25° and $\mu = 0$. Here C represents the 1:1 complex between the cobalt(III) and CrO_4^{-2} ions. Kinetic evidence is presented which indicates it is a mixture of inner-sphere and outer-sphere species.

The reasons underlying this investigation are derived from the following observations: Taube and Posey[3] have demonstrated that the aquopentaamminecobalt(III) ion forms both inner- and outer-sphere complexes with sulfate ion; Tong and King[4] have shown that the Ce(IV)–Cr(VI) complex is more stable than the corresponding sulfate complex and have pointed out that in general Cr(VI) complexes should be more stable than the corresponding sulfate complexes; in a study of the interaction between Cr(III) and Cr(VI), King and Neptune[5] concluded that both inner- and outer-sphere complex ions might be present even though equilibrium was rapidly established.

[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Participant from Knox College in the Argonne Semester Program of the Associated Colleges of the Midwest.

[3] (a) H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, **75**, 1463 (1953); (b) F. A. Posey and H. Taube, *ibid.*, **78**, 15 (1956).

[4] J. Y.-P. Tong and E. L. King, *ibid.*, **76**, 2132 (1954).

[5] E. L. King and J. A. Neptune, *ibid.*, **77**, 3186 (1955).