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The Rate of Hydrolysis of $(NH_4)_2RuNOCl_5$ and $(NH_4)_2RuNOCl_4OH$

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The rates of hydrolysis of $(NH_4)_2RuNOCl_5$ and $(NH_4)_2RuNOCl_4OH$ have been measured at an ionic strenght of 0.50 *over a wide range of temperatures and pH. All reactions studied were first order in complex. The rate of hydrolysis of $(NH_4)_2RuNOCl_5$ was more rapid in basic solution than in acid solution by 25-50%. Values for these rate constants at 55° are $k_{acid} = 5.20\times10^{-5}$ sec^{-1}, $\Delta H^* = 29.2$ kcal/mole, $\Delta S^* = 10.6$ e.u.; $k_{base} = 7.13\times10^{-5}$ sec^{-1}, $\Delta H^* = 27.5$ kcal/mole, $\Delta S^* = 6.2$ e.u. The rate of hydrolysis of $(NH_4)_2RuNOCl_4OH$ proceeded at a rate independent of the hydrogen ion concentration below pH = 2.5 and in the range $7.5 < pH < 9.5$. The acid base limiting rates differ by approximately 800. Values of the rate constants at 55° and the activation parameters are: $k_{acid} = 8.90\times10^{-6}$ sec^{-1}, $\Delta H^* = 26.0$ kcal/mole, $\Delta S^* = -2.5$ e.u.: $k_{base} = 7.14\times10^{-3}$ sec^{-1}, $\Delta H^* = 24.4$ kcal/mole, $\Delta S^* = 5.7$ e.u. In addition the equilibrium quotient for the reaction*

$$RuNOCl_3(H_2O)_2 + Cl^- \rightarrow RuNOCl_4H_2O^-$$

has been evaluated and the rate of anation of the trichloro complex evaluated.

Introduction

As part of continuing study of the chemistry of nitrosylruthenium we have investigated the hydrolysis of some chloro complexes of this ion. The entire series of complexes having the formula $RuNOCl_x(H_2O)_{5-x}{}^{(3-x)+}$ have been characterized in earlier work[1] for values of x from 1 to 5. In none of these ions was there evidence that different geometric isomers were present.

More recently, the infrared spectrum of nitrosylruthenium complexes have been investigated[2,3] in our laboratories. These results showed that the Ru–X bonds *trans-* to the NO is considerably weaker than the other ligands coordinated to the metal. By analogy to the Pt^{II} complexes[4] it might be expected that this bond weakening may result in an unusually large kinetic lability of the *trans-* ligand. Since very little evidence of a kinetic *trans-* effect in octahedral complexes is available at the present time[5] a kinetic study of the nitrosylruthenium complexes would add to the limited knowledge currently available. Only one previous report has dealt with ligand substitution kinetics of nitrosylruthenium in a quantitative manner.[6]

Experimental Section

Compounds. The ammonium and potassium salts of pentachloronitrosylruthenate were prepared form ruthenium chloride (Englehard Industries). The metal chloride was dissolved in concentrated hydrochloric acid and heated near boiling while a stream of NO gas was slowly bubbled through the solution. After 48 hours of this treatment the solution was cooled and a stoichiometric amount of either potassium or ammonium chloride was added. The solution was evaporated to a small volume and the resulting dark crystal were separated. The compound was recrystallized from 6 *M* hydrochloric acid, washed with a small volume of water and dried in a vacuum desiccator over $CaCl_2$.

Attempts to prepare $(NH_4)_2RuNOCl_4OH$ by the method of Papiev and Poria-Koshits[7] were unsuccessful. This compound was made as follows. $Ag_2RuNOCl_4OH$ was made using the method described previously.[1] An excess of this slightly soluble salt was stirred for a short time with 10 ml of an ammonium chloride solution. The mixture of solid AgCl and $Ag_2RuNOCl_4OH$ was separated by filtration and the solution was evaporated to dryness under vacuum.

Analysis for $(NH_4)_2RuNOCl_4OH$. Calcd: Ru, 31.01; Cl, 43.51; N, 12.90; H, 2.76. Found: Ru, 31.05; Cl, 43.28; N, 12.73; H, 2.75.

$RuNOCl_3(H_2O)_2 \cdot 3H_2O$ was made by evaporating $(NH_4)_2RuNOCl_5$ solution to drynes and heating the resulting residue for several hours to expel ammonium chloride. The resulting brick red powder was convertd to $RuNOCl_3(H_2O)_2 \cdot 3H_2O$ as previously described.[1]

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[1] E.E. Mercer, W.M. Campbell, and R.M. Wallace, *Inorg Chem.*, 3, 1081 (1964).

[2] J.R. Durig, W.A. McAllister, J.N. Willis, and E.E. Mercer, *Spectrochim. Acta, 22,* 1091 (1966).

[3] E.E. Mercer, W.A. McAllister, and J.R. Durig, *Inorg. Chem.*, 5, 1881 (1965).

[4] F. Basolo and R.G. Pearson, « Mechanisms of Inorganic Reactions », John Wiley and Sons, Inc., New York, 1967, p. 351 ff.

[5] Reference 4, p. 176.

[6] I.L. Jenkins and A.G. Wain, *J. Inorg. Chem.*, 3, 28 (1956).

[7] I.A. Papierev and M.A. Poral-Koshites, *Kristallografiya, 4,* 30 (1950).

A wide variety of buffering systems were used in the pH studies. These included borate, phosphate, acetate, tartrate, and citrate systems. Over most pH ranges that required buffering two or more systems were used. All other chemicals used were reagent grade.

Kinetic Studies. All kinetic runs were made in solutions of ionic strength equal to 0.5 which was maintained with $NaClO_4$.

The reactions were all followed spectrophotometrically using the Cary Model 14 spectrophotometer and 1 cm quartz cells. In addition some experiments on the rate of reaction of the pentachloronitrosylruthenate were performed using an ion exchange method.

Ion Exchange Method. A 50 ml sample of the reaction solution was thermostated in a polyethylene bottle at the desired temperature (~50°). The samples were protected from light by black paint on the outside of the reaction container. 1 ml aliquots were periodically removed from the reaction vessel and were added directly to an 0.8×8 cm anion exchange column of Dowex 1×2, 100-200 mesh, in the perchlorate form. Water at 0° was circulated through an outer jacket on the ion exchange column throughout the entire separation procedure. The column was eluted successively with 0.01 M, $HClO_4$, 0.1 M $HClO_4$ and finally a solution that was 0.1 M $HClO_4$ and 2.9 M $NaClO_4$. The first eluent removed cationic and neutral species, and the second and third eluting solutions removed the tetrachloro and pentachloronitrosylruthenate complexes respectively. Each of these fractions were collected separately in 10 or 25 ml volumetric flasks. Sufficient concentrated sodium hydroxide solution was added to each flask to make the final concentration of base approximately 1 M. The solutions were heated at 80° for 1-2 hours to hydrolyze the complexes. Bromine water was added drowpise to oxidize the ruthenium to a mixture of RuO_4^- and RuO_4^{2-}. The solutions were cooled to room temperature and the ruthenium was determined spectrophotometrically using the method reported previously.[8] In all experiments 98-100% of the ruthenium present was recovered in the eluted samples. This method was used on solutions of $(NH_4)_2RuNOCl_5$ in 0.01-0.1 M H^+ and .01-0.2 M-OH^-.

This method was used in only a few experiments because it was very time consuming and ruthenium concentrations lower than about 10^{-2} M could not be used.

Spectrophotometric Method. The visible spectra of $(NH_4)_2RuNOCl_5$, $(NH_4)_2RuNOCl_4OH$, and $RuNOCl_3(H_2O)_2 \cdot 3H_2O$ in acid solution have been reported previously.[1] In the present work the molar extinction coefficients of freshly prepared solutions of each of these compounds have been determined from 2300 Å to 4000 Å. On the basis of these spectra a wavelength of 2600 Å was chosen to follow the rate of disappearance of $(NH_4)_2RuNOCl_4OH$. Since in basic solution the rate of disappearance of $RuNOCl_4OH^{2-}$ is much more rapid than that of $RuNOCl_5^{2-}$ this same wavelength was used to follow the rate of hydrolysis of $RuNOCl_5^{2-}$ in basic medium. In acid solution a wavelength of 3000 Å was used to study the hydrolysis of $(NH_4)_2RuNOCl_5$. Since the tetra- and trichloro complexes of nitrosylruthenium have nearly the same molar extinction coefficient at this wavelength, hydrolysis of the tetrachloro complex has almost no effect on the absorbance of the solution. The molar extinction coefficients of the important complex at 2600 Å and 3000 Å are given in Table I.

Table I. Molar Extinction Coefficients of Nitrosylruthenium Compounds in 0.10 M $HClO_4$, $\mu = 0.50$

Compound	$\varepsilon_{2600} M^{-1}$ cm^{-1}	$\varepsilon_{3000} M^{-1}$cm^{-1}
$(NH_4)_2RuNOCl_5$	10,670	1980
$(NH_4)_2RuNOCl_4OH$	8,550	745
$RuNOCl_3(H_2O)_2 \cdot 3H_2O$	3,200	790

In a kinetic run 100 ml of the reaction medium was thermostated in painted polythylene bottles for at least 1 hour before adding the ruthenium compound. Zero time was assumed to be the time when the solid ruthenium compound was added to the solution. Aliquot samples of about 5 ml were removed periodically and quenched by cooling rapidly in an ice bath. The sample was transferred to a 1 cm quartz spectrophotometer cell and the absorbance was measured immediately at the desired wavelength. Plots of log $(A_t - A_\infty)$ vs. time were used to evaluate the first order rate constant for each run. A_∞ was determined experimentally for each individual run by measuring the absorbance after 10 half-lives or greater. In basic medium the solutions became turbid at very long times (about 10 half-lives) which caused the apparent absorbance to increase. For this reason A_∞ readings were made at the minimum time possible. The concentration of the complexes used in these spectrophotometric runs was between 1×10^{-3} and 1×10^{-4} M. In all cases the first order plots were linear over the time period followed (75 to 90% completion).

Buffers were used to control the pH of the reaction medium in all runs made between a pH of 2 and 12. In the solutions which were more acidic or basic than these limits buffering was unnecessary. The pH of each solution was determined at the reaction temperature at the beginning and end of each run. It did not change more than 0.01 units in any run. The pH was measured with a Beckman research model pH meter with Beckman glass and calomel electrodes. The meter was standardized using standard pH 4, 7, and 10 buffers at the reaction temperature. Temperature corrections of the standard buffers were made in accord with the manufacturers specifications.

Equilibrium quotient determination. In acid solution ($[H^+] = 0.1$ M) at an ionic strength of 0.5 the hydrolysis of $(NH_4)_2RuNOCl_4OH$ did not go to completion when the concentration of Cl^- was greater than 0.1 M. The equilibrium constant for

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[8] E.E. Mercer and R.R. Buckley, *Inorg. Chem.*, *4*, 1692 (1965).

$$RuNOCl_3(H_2O)_2 + Cl^- \underset{k_{34}}{\overset{k_{43}}{\rightleftharpoons}} RuNOCl_4(H_2O)^- \qquad (1)$$

reaction (1) was determined by ion exchange separation of equilibrium mixtures and the absorbance of solutions that had reached equilibrium. The two methods allowed a range ruthenium concentrations from 1 x 10^{-4} to 1 x 10^{-2} *M* to be used.

In the ion exchange method solutions were made approximately 10^{-2} *M* in $(NH_4)_2RuNOCl_5$, 0.1 *M* $HClO_4$ and sufficient sodium chloride and sodium perchlorate were added to give an ionic strength of 0.5. The solution was thermostated at 55° until the absorbance of the solution was constant (about 1 week). A 6 ml sample was absorbed on an exchange column of Dowex 1×2, 100-200 mesh, in the chloride ion form, which was thermostated at 0°. Cationic complexes were removed with 1 x 10^{-3} *M* $HClO_4$, the neutral trichloride was eluted with 0.01 *M* $HClO_4$, the tetrachloronitrosylruthenate was removed with 0.1 *M* $HClO_4$, and finally $RuNOCl_5^{2-}$ was eluted with a solution 0.1 *M* $HClO_4$ and 3.0 *M* $NaClO_4$. Each fraction was collected and analyzed for ruthenium as described above for the kinetic runs. It was necessary to use a chloride column to achieve a separation of the cations from $RuNOCl_3(H_2O)$. Between chloride concentrations of 0.1 and 0.5 *M* only the tri– and tetrachloro complexes were found to be present at equilibrium. Recovery of ruthenium was 98% or greater in all these separations.

The hydrolysis of $(NH_4)_2RuNOCl_4OH$ in acid solution with chloride ion initially present was followed spectrophotmetrically with time at 2600Å. The absorbance at zero time was used to calculated the concentration of ruthenium present (1 x 10^{-4} to 1 x 10^{-3} *M*). The infinite time absorbance combined with the molar extinctions for both the tri– and tetrachloro complexes enables one to calculate the ratio of $[RuNOCl_3(H_2O)_2]/[RuNOCl_4H_2O^-]$. This ratio combined with the total chloride ion concentration yields the equilibrium quotient desired. In addition, from the rate of reaction in these runs, the apparent first order rate constant is given by the expression:

$$k = k_{43} + k_{34}[Cl^-].$$

The equilibrium constant may then be derived from microscopy reversibility.

The temperature of the thermostat was regulated to ±0.01° in all studies made.

Results

All of the hydrolysis reactions studied were found to obey first order rate laws, independent of the method used in following them. All of the equilibrium runs and kinetic studies reported here were made at an ionic strength of 0.50.

The Rate of Hydrolysis of $(NH_4)_2RuNOCl_5$. The rate of hydrolysis of this compound was studied at 50.49° by both methods described above (see experimental). This duplication of method allowed us to cover a concentration of ruthenium of 1×10^{-4} to 1.2×10^{-2} *M*. The rate constants determined in both acidic and basic solutions were essentially the same for both methods. Comparison of the two methods is shown in the data given in Table II. Because the spectrophotometric method was much more convenient all of the remaning data reported come from this source. The rate of hydrolysis of $(NH_4)_2RuNOCl_5$ was followed at several temperatures between 45 and 65° and at pH's between that of 0.5 *M* $HClO_4$ and 0.5 *M* NaOH. This data is summarized in Table III. At all temperatures below pH = 2.50 and above pH = 6.60 the rate constants were independent of pH. The rates, however, were more rapid in basic solution than in acid by 25 to 50%, depending upon the temperature.

In the experiments in acid solution in which sodium chloride replaced some or all of the sodium perchlorate, the reactions showed an apparent induction period. Linear first order plots were obtained beyond about 25% reaction. The rate constants given for these experiments are derived from these linear regions. No change was observed when chloride was added to the reaction mixture in basic solution.

The activation enthalpy and entropy for these reactions in the pH independent regions are given in Table IV. These were evaluated from all rate data in the base and acid limiting regions using a least

Table II. Comparison of the Rates of Hydrolysis of $(NH_4)_2RuNOCl_5$ Determined by Ion Exchange with Those Determined Spectrophotometrically. T = 50.49°C μ = 0.50

Source of Ru	$[RuNOCl_5^{2-}]$	$[H^+]$	$[OH^-]$	Method	$k_1 sec.^{-1} \times 10^5$
$K_2RuNOCl_5$	1.0×10^{-2}	0.10		I[a]	2.78
$(NH_4)_2RuNOCl_5$	0.8×10^{-2}	0.10		I	2.77
»	1.2×10^{-2}	0.10		I	2.75
»	1.0×10^{-2}	0.01		I	2.63
»	1.2×10^{-2}	0.01		I	2.97
»	1.0×10^{-3}	0.01		Spec.[b]	2.75
»	5.0×10^{-4}	0.10		Spec.	2.78
»	1.0×10^{-2}		0.01	I	4.13
»	1.2×10^{-2}		0.01	Spec.	3.99
»	1.0×10^{-3}		0.10	I	3.98
»	1.0×10^{-4}		0.10	Spec.	4.00
»	1.0×10^{-2}		0.2	Spec.	4.05
»	1.0×10^{-4}		0.2	I	4.13

[a] I - Ion Exchange Method; [b] Spec. = Spectral Method.

squares computer program. The uncertainties given in the table are estimated.

The Rate of Hydrolysis of $(NH_4)_2RuNOCl_4OH$. A complete study of the hydrolysis of this compound over a wide range of temperature and pH has been made. Experiments were performed at temperatures between 25 and 65° and in the pH range 1 < pH < 10. The reactions were all first order in complex over the range of concentrations studied. The intermediate pH region was studied using buffered solutions. At most pH values two different buffer systems were used to check for any specific interactions of the buffering agents with the complex. In all cases the rates of hydrolysis were independent of the specific buffer systems and the concentration of the buffer.

Table III. Rates of Hydrolysis of $(NH_4)_2RuNOCl_5$ [a], $\mu = 0.50$

T°C	$-\log[H^+]$ [b]	Initial[Cl^-]	$k \times 10^5 sec^{-1}$ [c]
45.00	1	0	1.24
45.00	12.6		1.86
50.49	1		2.76
	2		2.76
	2.47		2.78
	3.27		3.40
	4.58		3.79
	6.60		3.99
	11.25		4.07
	12.55		4.09
	12.95		6.70
55.00	0.7		5.20
	1.0		5.20
	2.70		5.45
	3.71		5.50
	4.42		6.64
	5.88		7.00
	6.56		7.13
	11.1		7.13
	12.1		7.13
	12.1	0.40	7.13
	1	0.10	4.96
	1	0.30	4.62
	1	0.40	4.28
	1	0.50	4.11
65.00	1		20.1
	11.9		26.2

[a] The concentration of $(NH_4)_2RuNOCl_5$ was between 1×10^{-3} and 1×10^{-4} *M* in all experiments reported in this table. [b] The figures in this column which lie between 2.47 and 6.60 are the experimentaly determined pH. For more acidic solution $-\log[HClO_4]$ is used, while in the basic region this number was calculated assuming $-\log[H^+] = pK_w + \log[NaOH]$. K_w at each temperature was taken from data in Harned and Owen « The Physical Chemistry of Electrolyte Solutions », Second Edition, Reinhold (1950). [c] Each rate constant reported represents the average of two or more separate runs. In all cases the average deviation of the rate constants was less than ± 1.5%.

Table V. The Rates of Hydrolysis of $(NH_4)_2RuNOCl_4OH$ at $\mu = 0.5$ [a]

T°C	pH [b]	$k \times 10^5 sec^{-1}$ [c]
45.00	1	0.29
	2.70	0.91
	3.88	7.50
	4.49	22.5
	5.09	65.1
	6.45	186
	9.62	236
50.49	1	0.53
	1.97	0.67
	2.47	1.18
	2.85	2.16
	3.27	3.78
	3.31	4.36
	3.80	10.6
	4.00	16.4
	4.58	49.8
	5.10	13.3
	6.00	28.0
	6.51	32.0
	6.53	35.6
	7.74	37.5
	8.32	403
	8.68	413
	9.56	448
	9.58	458
	9.88	455
	9.96	462
	10.14	442
	10.83	925
	10.92	950
55.00	1	0.89
	2.70	3.24
	3.32	9.55
	3.71	21.4
	3.98	36.0
	4.41	81.8
	4.48	93.4
	5.05	150
	6.56	609
	7.57	715
	9.36	816
	9.92	937
65.00	1	3.33

[a] The concentration of $(NH_4)_2RuNOCl_4OH$ was between 1×10^{-3} and 1×10^{-4} *M* in all experiments reported in this table. [b] For the experiments in 0.1 *M* $HClO_4$ the pH was not measured. These experiments are listed in the table as pH = 1. [c] Each rate constant reported represents the average of two or more experiments. In all cases the average deviation of the rate constant is less than ± 1.5%.

Table IV. Enthalpies and Entropies of Activation for the Hydrolysis of Nitrosylruthenium Complexes.

Compound	Medium	ΔH^*	ΔS^*
$(NH_4)_2RuNOCl_5$	acid base	29.2±0.5 27.5±0.5	10.6±2 6.2±2
$(NH_4)_2RuNOCl_4OH$	acid base	26.0±0.5 24.4±0.5	—2.5±2 5.7±2

The data on the rate of hydrolysis of the tetrachloronitrosylruthenate is summarized in Table V. The rate in acid solution below a pH of 2.5, and in the pH range from 7.5 to 9.5 were found to be independent of hydrogen ion. The rate of reaction in the intermediate range of pH is approximately –1 order in hydrogen ion. The activation enthalpy and entropy for both limiting rates were calculated from the temperature dependence of the rate constants and are given in Table IV.

In basic solution the rate of hydrolysis of $(NH_4)_2$-$RuNOCl_4OH$ was independent of chloride ion up to concentrations of 0.5 *M*. In the acid limiting region however, chloride ion addition resulted in incomplete hydrolysis, approaching an equilibrium mixture of the tri- and tetrachloro complexes. The value of the equilibrium quotient for this reaction was determined both by ion exchange separations and spectrophotometric analysis of equilibrium mixtures at several chloride ion concentrations. The results of these experimets are summarized in Table VI.

Assuming microscopic reversibility the rate constant for the anation of trichloronitrosylruthenium was calculated to be 4.1×10^{-5} M^{-1} sec^{-1}. This value is in reasonable agreement with the value of 4.6×10^{-5} M^{-1} sec^{-1} obtained from the rate of approach to equilibrium in the hydrolysis of $(NH_4)_4RuNOCl_2OH$ when chloride ion was initially present. The rate constant obtained from the equilibrium data is the more reliable value.

Table VI. The Equilibrium Quotient at 55° for the reaction $RuNOCl_3(H_2O)_2+Cl^-$ $RuNOCl_4(H_2O)^-$.

Method	$\frac{[RuNOCl_4(H_2O)^-]}{[RuNOCl_3(H_2O)_2]}$	$[Cl^-]$	K
Ion Exchange	0.517	0.117	4.4
	1.21	0.315	3.9
	1.65	0.414	4.0
	2.00	0.513	3.9
		average	4.0±0.2
Spectral	0.344	0.10	3.4
	0.438	0.10	4.4
	1.25	0.30	4.2
	1.42	0.30	4.7
	1.49	0.40	3.7
	1.93	0.40	4.8
	1.92	0.50	3.9
	1.87	0.50	3.7
		average	4.1±0.4

Discussion

The difference in the rates of hydrolysis of the pentachloronitrosylruthenate in acid and base was unexpected. The rather abrupt change over a narrow range of hydrogen ion concentration suggests a conjugate base mechanism. However, this explanation is unacceptable in the absence of protons in the complex. The possibility of a medium effect causing the change in rate seems unlikely since this would be expected to produce a more gradual, continuous change in the rate.

The possibility of protonation of the complex in acidic solution on the oxygen of the nitrosyl group was considered as an explanation of the pH dependence. However, this would require that K_a for ionization of this proton be approximately 10^{-4}. Since no evidence for a weakly acidic proton is observed in the potentiometric titration of $H_2RuNOCl_5$ this explanation must be rejected.

A possible mechanistic explanation for the observed rate behavior involves the formation of an intermediate, in which a chloride ion has dissociated but remains in the same solvent cage. This intermediate undergoes nucleophilic attack or re-entry of the chloride. While this mechanism can explain the data, it suffers from several weaknesses. Two anions sharing the same solvent cage seem rather improbable. Furthermore, the nucleophilicity of hydroxide relative to water would have to abnormally large.[9,10] It should be possible to test this mechanism by study of competition reactions with other nucleophiles.

The observed behavior of the rate of hydrolysis of $(NH_4)_2RuNOCl_4OH$ as a function of hydrogen ion is very well interpreted in terms of the conjugate base mechanism which is widely accepted to explain the base catalysis observed in cobalt(III) ammine complexes. Application of this model to the present system result in the following mechanism:

$$RuNOCl_4(H_2O)^- \overset{K}{\rightleftharpoons} RuNOCl_4OH^{2-} + H^+ \qquad (2)$$

$$RuNoCl_4(H_2O)^- + H_2O \overset{k_3}{\rightleftharpoons} RuNOCl_3(H_2O)_2 + Cl^- \qquad (3)$$

$$RuNOCl_4OH^{2-} + \overset{k_4}{\rightleftharpoons} RuNOCl_3OH^- + Cl^- \qquad (4)$$

$$RuNOCl_3OH^- + H_2O \overset{fast}{\rightleftharpoons} RuNOCl_3(H_2O)(OH)^- \qquad (5)$$

The observed rate constant asusming this mechanism is:

$$k=\frac{k_3[H^+]+k_4K}{K+[H^+]} \qquad (6)$$

A comparison of the rates calculated from equation (6) to the experimental points is shown in Figure 1 for the experiments at 50.49°. The best value of the acid ionization constant to fit the data was determined by trial and error. k_3 and k_4 were set equal to the acid and base limiting rates in all cases. The equilibrium constant for equation (2) has been repor-

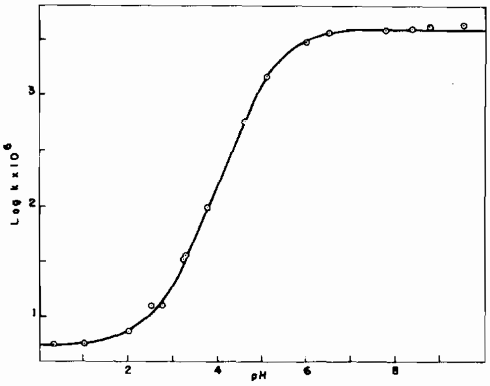

Figure 1. The rate of hydrolysis of $(NH_4)_2RuNOCl_4OH$ at 50.49°, μ = 0.50 the line was calculated equation (11); the points are the experimentally measured rates.

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(9) A. Haim and W.K. Wilmarth, *Inorg. Chem.*, *1*, 573 (1962).
(10) J. Halpern, R.A. Palmer, and L.M. Blakly, *J. Amer. Chem. Soc.*, *88*, 1877 (1966).

ted previously from potentiometric data as 9.5×10^{-7} at 5°C.[1] At 50.49° we calculate from the kinetic data a value of 4.5×10^{-6} *M*. Since the rate of hydrolysis in the region of pH from 7.5 to 9.5 was not exactly constant, some adjustment of this rate constant was made to obtain the best fit. In most cases this best fit was obtained using the rate constant observed at about the middle of this range. The very small pH dependence in the range is possibly due to a medium effect or the rapid reaction that occurs above a pH of 10.

In this nitrosylruthenium complex the rate of reaction of the basic form ($RuNOCl_4OH^{2-}$) is about 800 times that of the acid form. This is much less than is normally observed in the ammonia complexes of cobalt(III) and to a lesser extent chromium(III). It is usually postulated the the π donation of electrons from the ligand stabilizes a five coordinate transition state, thus enhancing the rate of substitution of the conjugate base. In ammine complexes this π donation can only occur when the complex is in the form of the conjugate base. On the other hand, both water and hydroxide ion may provide electrons through π bonding. Thus the somewhat lower ratio of the base hydrolysis rate to that in acid may indicate that water is also stabilizing the transition state by π donation.

In both the pentachloro and tetrachloro complexes the rate increased further at higher hydroxide ion concentration. In the case of the pentachloro salt, a concentration of hydroxide ion of 0.5 *M* was necessary to observe this rate enhancement. It was observed at pH = 10.5 when the reactant was $(NH_4)_2$-$RuNOCl_4OH$. This could not be followed spectrophotometrically because the reaction was accompanied by the formation of a precipitate. In very qualitative experiments it appeared the the hydroxide ion dependence was not 1. This increased rate probably results from a nucleophilic attack by hydroxide ion on the nitrogen of the nitrosyl producing a nitro group. The change in charge of the complex as well as the change in the metal nitrogen bonding, would increase the lability of the coordinate chlorides. Several authors have noted reactions in which such nucleophilic attack on nitrosylruthenium complexes take place. Meyer *et al.*[11] for example have shown that $RuNO(bipy)_2Cl^{2+}$ can be reversibly converted into the corresponding nitro complex by addition of base.

While earlier infrared studies[2] indicated that the NO group was weakening the bond of the ligand *trans* to it, there is no kinetic evidence that this results in a greater lability of this group. The rate of hydrolysis of $RuNOCl_5^{2-}$, in which the *trans* chloride is presumably the leaving group, is only 4 to 6 times more rapid than the hydrolysis of $RuNOCl_4(H_2O)^-$. This is a smaller change in rate than would normally be expected from the difference in the ionic charges of the two complexes. This may lend some support to the π stabilization of the transition state by water, which was postulated above. Such an effect would tend to diminish the expected difference in rates between the two complexes studied here.

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