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Acid Ionization Constant and Base-Catalyzed Hydrolysis of Ruthenium(III) Hexaammine Ion

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The optical spectrum of basic solutions of $Ru(NH_3)_6^{3+}$ was analyzed considering the presence of both the hydroxide ion-pair and the deprotonated species $Ru(NH_3)_5NH_2^{2+}$. The assumptions that the absorption peak at 402 nm is due to the deprotonated species and that its extinction coefficient is not temperature dependent enabled us to determine the formation constants of the two species separately. At an ionic strength of 0.1 M and a temperature of 25 °C, the formation constant of the ion pair is $K_1 = 5.4 \pm 0.8\ M^{-1}$ with $\Delta H_1° = 3.7 \pm 0.3$ kcal mol^{-1} and $\Delta S_1° = 18.6 \pm 0.9$ eu, while the formation constant of the deprotonated species from the ion pair is $K_2 = 1.8 \pm 0.2$ with $\Delta H_2° = 6.1 \pm 0.2$ kcal mol^{-1} and $\Delta S_1° = 21.6 \pm 0.8$ eu, and the $Ru(NH_3)_6^{3+}$ ion has an apparent acid dissociation constant with a pK of 13.1 ± 0.3. The base-catalyzed aquation reaction of $Ru(NH_3)_6^{3+}$ was found to proceed through two parallel reaction paths which could be described as a pH-independent and a base-catalyzed aquation reaction of the $Ru(NH_3)_5NH_2^{2+}$ ion. The spectrum of $Ru(NH_3)_5NH_2^{2+}$ was assigned to a ligand-to-metal charge-transfer transition and the optical electronegativity of the NH_2^- group was estimated as $\chi_{opt} = 2.8$.

Introduction

Alkaline aqueous solutions of $Ru(NH_3)_6^{3+}$ ion are known to have a deep yellow color.[2] Spectrophotometric studies of these solutions indicated a reversible pH-dependent absorption peak at 402 nm, which was assigned to a deprotonated ruthenium(III) hexaammine complex.[3] The deprotonated species has been implicated in several reactions of ruthenium hexaammine in alkaline solutions. Notable are its base-catalyzed proton-exchange reaction,[4] the reaction with NO to give the ruthenium pentaammine dinitrogen ion,[5a] and the aerial oxidation to give $Ru(NH_3)_5NO^{3+}$ complex.[5b] Since the formation of the deprotonated species occurs in highly basic solutions, a formation of an ion pair with the hydroxide ion should also be considered.[6,7] In the present work the estimation of the formation equilibrium constants of both the deprotonated species and the ion pair is undertaken, as well as the kinetics of the base-catalyzed aquation reaction.

Experimental Section

Materials. $Ru(NH_3)_6Cl_3$, supplied by Johnson Matthey Chemicals, was either used without further purification (batch no. 7) or recrystallized from 1 N HCl.[8] Identical results were obtained in both cases. Stock solutions of $NaCH_3SO_3$ were prepared by neutralizing methanesulfonic acid (Fluka, puriss) with an NaOH solution of known concentration.

Methods. The mixing of the solutions was performed by injecting a $Ru(NH_3)_6Cl_3$ solution into an NaOH solution which was contained in cylindrical cuvettes inside the spectrophotometer, using a Hamilton pushbutton-operated and volumetrically adjusted CR 700-200 syringe.[9-11] A double-wall cell compartment was designed for the Cary 14 spectrophotometer so that the spectrophotometric cell and the syringe were in contact with the internal walls of the thermostated compartment. The solutions in the spectrophotometric cell and the syringe were equilibrated with the thermostated compartment for about 15 min before the reaction was started by injecting the contents of the syringe into the cell. It was found, by immersing a copper–constantan thermocouple, that this period of time was sufficient for the temperature to reach its constant value.

Results

When solutions of $Ru(NH_3)_6^{3+}$ are brought to an alkaline pH, an immediate formation of the deprotonated species with an absorption peak at 402 nm is observed. The intensity of this peak gradually diminishes with time, and a concomitant increase of the absorption at 295 nm is noticed. Preliminary experiments indicated that the new absorption peak at 295 nm is due to the aquation product $Ru(NH_3)_5OH^{2+}$, as is apparent both from its known absorption spectrum and from its titration around pH 4 to give a spectrum identical with that of $Ru(NH_3)_5OH_2^{3+}$.[12]

Thus, we shall use as a working hypothesis for the explanation of our spectrophotometric data the scheme of eq 1–3.

$$Ru(NH_3)_6^{3+} + OH^- \overset{K_1}{\rightleftharpoons} Ru(NH_3)_6^{3+}\cdot OH^- \qquad (1)$$

$$Ru(NH_3)_6^{3+}\cdot OH^- \overset{K_2}{\rightleftharpoons} Ru(NH_3)_5NH_2^{2+}\cdot HOH \qquad (2)$$

$$Ru(NH_3)_5NH_2^{2+}\cdot HOH + H_2O \xrightarrow{k} Ru(NH_3)_5OH^{2+} + NH_3 + H_2O \qquad (3)$$

In this scheme the formation of both ion-pair and deprotonated species is assumed as fast preequilibria (eq 1 and 2) which is followed by a relatively slow hydrolysis reaction (eq 3).

The optical densities of alkaline solutions containing $Ru(NH_3)_6^{3+}$ ion, after some hydrolysis has occurred, can be written as eq 4, where R stands for the $Ru^{III}(NH_3)_5$ residue

$$A = \epsilon_0[RNH_3] + \epsilon_{IP}[RNH_3\cdot OH] + \epsilon_{NH_2}[RNH_2] + \epsilon_{OH}[ROH] \qquad (4)$$

and ϵ_i are the molar absorptivities of the various species in the solution. Equation 4 can be rearranged to eq 5, where C_0 is the total ruthenium concentration.

$$A = \frac{\epsilon_0 + \epsilon_{IP}K_1[OH^-] + \epsilon_{NH_2}K_1K_2[OH^-]}{1 + K_1[OH^-] + K_1K_2[OH^-]}(C_0 - [ROH]) + \epsilon_{OH}[ROH] \qquad (5)$$

Our results were obtained by following the absorption changes at 420 and 295 nm where the absorptions are mainly due to $Ru(NH_3)_5NH_2^{2+}$ and $Ru(NH_3)_5OH^{2+}$, respectively. These changes were linear within the first 20 s or more after the rapid mixing, depending on the temperatures and the concentrations of the hydroxide ions. While the initial slopes were utilized for the kinetic analysis of the hydrolysis reaction, the extrapolated values to time zero were utilized for the analysis of the equilibrium between various species present in the basic solutions of ruthenium(III) hexaammine, before any hydrolysis has taken place. We shall deal first with our equilibrium data and will give the kinetic results afterward.

Measurement of the Equilibrium Constants. In order to determine the equilibrium constants in our system, one has to vary the concentrations of the OH^- ion. This can be done by either keeping a constant ionic strength with an inert electrolyte or having the ionic strength varied through the experiment and taking the dependence of the equilibrium constant on the ionic strength into account. The first procedure has the drawback that ion pairs between the $Ru(NH_3)_6^{3+}$ ion

Table I. Thermodynamic Parameters of the Equilibrium Constants

	K_1		K_2		K_{ion}
$\Delta H°$, kcal mol^{-1}	3.6 ± 0.3^a	3.7 ± 0.3^b	6.1 ± 0.2^a	5.7 ± 0.3^b	23.0 ± 0.2^f
$\Delta S°$, cal mol^{-1} K^{-1}	15.0 ± 0.9^a	18.6 ± 0.9^b	21.6 ± 0.8^a	19.5 ± 1.0^b	17.0 ± 0.6^f
K at 25 °C	4.4 ± 0.4^a	$5.4 \pm 0.8^{b,c}$	1.8 ± 0.2^a	$1.3 \pm 0.2^{b,e}$	$(7.0 \pm 0.6) \times 10^{-14\,f}$
		$22 \pm 3^{b,d}$			

[a] Experiments at a constant ionic strength of 0.1 M. [b] Experiments at a variable ionic strength. [c] Value at an ionic strength of 0.1 M. [d] Value at a zero ionic strength. [e] The value of K_2 was assumed to be independent of the ionic strength. [f] Calculated from eq 11 with the values of K_1 and K_2 obtained at a constant ionic strength and using $\Delta H_w° = 13.4$ kcal mol^{-1} and $\Delta S_w° = -18.95$ cal mol^{-1} K^{-1} for the ionization constant of water at the temperature range of 0–60 °C.

and the anions of the electrolyte should be considered. This can be minimized by using an electrolyte that does not have a strong tendency to form ion pairs. Perchlorate salts are commonly considered as adequate for this purpose. However, in view of recent evidence of ion pairs of perchlorate with $Co(NH_3)_6^{3+}$ [13] and Am^{3+},[14] we have chosen to use CH_3SO_3Na as the inert electrolyte. Our preliminary difference spectrum measurements indicated less extensive ion-pair formation of $Ru(NH_3)_6^{3+}$ with the methanesulfonate ion as compared with the perchlorate ion. Still, in order to ascertain that ion pairs with $CH_3SO_3^-$ do not have a large effect on our results, we have run a separate series of experiments where no electrolyte has been added and have taken the variation of equilibrium constants with ionic strength into consideration. Since all of our measurements for the determination of equilibrium constants were obtained by extrapolating the optical densities of the solutions to the time of mixing the $Ru(NH_3)_6^{3+}$ and the NaOH solutions, the absorbance due to the hydrolysis product $Ru(NH_3)_5OH^{2+}$ can be neglected. Also, at the wavelength of 420 nm, it is possible to neglect the absorption of $Ru(NH_3)_6^{3+}$ which has its maximum absorption at 275 nm. Thus, eq 5 can be written in the form of eq 6, where A_0 is the absorbance at zero time.

$$C_0/A_0 = (1/(\epsilon_{NH_2}K_2 + \epsilon_{IP}))(1 + K_2 + 1/K_1[OH^-]) \qquad (6)$$

Experiments with a Constant Ionic Strength. Our experiments were done at an ionic strength of 0.1 M adjusted with CH_3SO_3Na. Plots of C_0/A_0 vs. $1/[OH^-]$ gave good straight lines, and their intercepts and slopes at various temperatures are given in Figures 1 and 2. According to eq 6, in case that either the deprotonated species or the ion pair were the only species present, the intercept would have equaled either $1/\epsilon_{NH_2}$ or $1/\epsilon_{IP}$ which are not expected to vary with temperature. For instance, our spectrophotometric measurements of solutions containing the $Ru(NH_3)_6^{3+}$ ion, which were dilute enough (10^{-3} M or less) so that contribution from ion-pair formation was negligible, indicated no temperature dependence of its molar absorbance.[6] The fact that the intercept varies as a function of temperature (see Figure 1) indicates the presence of both species in the solution.

On the basis of absorption spectra of ion pairs of $Ru(NH_3)_6^{3+}$ with halide ions, we have concluded in a previous work[6] that the ion pair $Ru(NH_3)_6^{3+}\cdot OH^-$ should have its maximum absorption around 305 nm. The molar absorbances of the ion pairs with Cl^-, Br^-, and I^- were in the range of 250–300 M^{-1} cm^{-1}, and we expect the molar absorbance of $Ru(NH_3)_6^{3+}\cdot OH^-$ to be of the same order of magnitude. Thus, at a wavelength of 420 nm at time zero we shall assume that the absorption is due solely to the $Ru(NH_3)_5NH_2^{2+}$ ions.

In that case the intercept and the slope are given by expressions 7 and 8.

$$\text{intercept} = (1/\epsilon_{NH_2})(1 + K_2^{-1}) \qquad (7)$$

$$\text{slope} = 1/\epsilon_{NH_2}K_1K_2 \qquad (8)$$

The fact that a semilogarithmic plot of the slope vs. inverse temperature gives a straight line is in agreement with our assumption that ϵ_{IP} can be neglected. The temperature variation of the intercepts was fitted to eq 7, where K_2 was expressed as

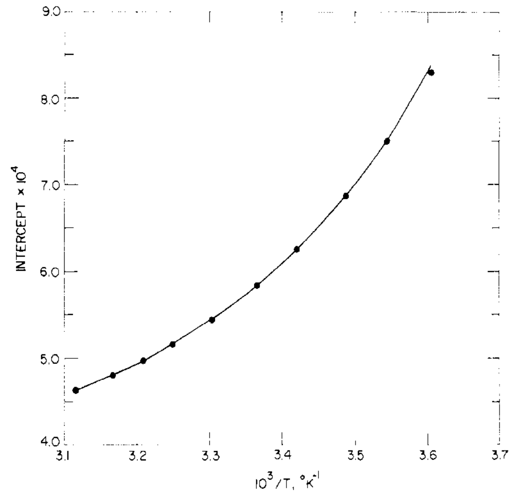

Figure 1. Intercepts of the linear plots of eq 6 obtained at a constant ionic strength of 0.1 M plotted against reciprocal temperature.

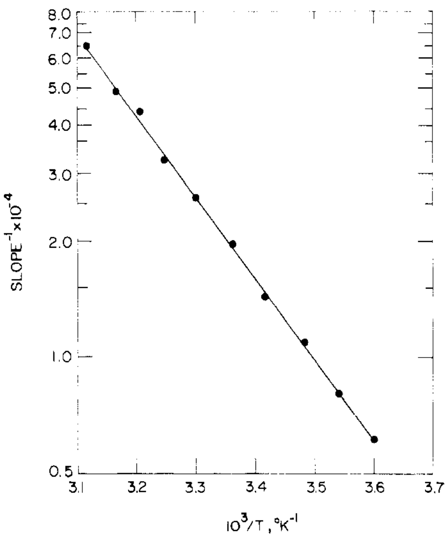

Figure 2. Slopes of the linear plots of eq 6 obtained at a constant ionic strength of 0.1 M plotted against reciprocal temperature.

$$K_2 = \exp(-\Delta H_2°/RT + \Delta S_2°/R) \qquad (9)$$

The fitted values of $\Delta H_2°$ and $\Delta S_2°$ are given in Table I while for ϵ_{NH_2} a value of $(2.8 \pm 0.1) \times 10^3$ M^{-1} cm^{-1} was obtained. Using the full absorption curve, the molar absorbance at 402 nm is $\epsilon_{max} = (3.1 \pm 0.1) \times 10^3$ M^{-1} cm^{-1}. The thermodynamic parameters of the ion-pair formation constant K_1, obtained from Figure 2, are also given in Table I.

Experiments with Variable Ionic Strength. In this set of experiments the OH^- concentrations were changed without compensating the ionic strength with added electrolyte. The

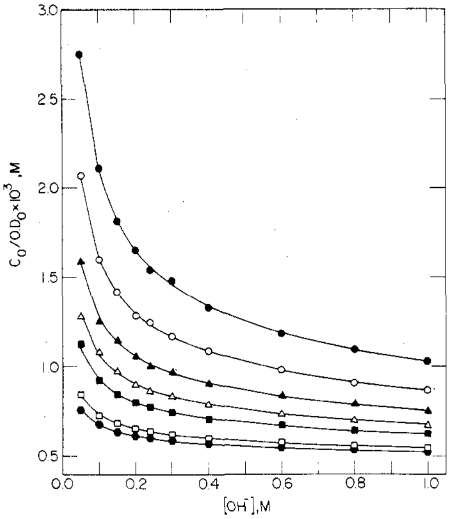

Figure 3. Plots of C_0/A_0 vs. [OH⁻] at various temperatures. No salt was added, in order to keep constant ionic strength. The lines were calculated using the fitted parameters according to eq 6 and 10. The temperatures were 8.3 °C (●), 14.8 °C (○), 21.5 °C (▲), 27.5 °C (△), 32.5 °C (■), 43 °C (□), and 47.5 °C (■).

variation of K_1 with ionic strength was assumed to follow the modified Debye-Hückel equation[15,16] (10), where $A' = 1.825$

$$\log K_1 = \log K_1^0 - \frac{6A'I^{1/2}}{1 + GaI^{1/2}} + BI \qquad (10)$$

$\times 10^6(DT)^{-3/2}$, $G = (8\pi Ne^2/(1000DkT))^{1/2}$, K_1^0 is the ion-pair formation constant at zero ionic strength, D is the dielectric constant of the solvent, and the distance of closest approach, a, was taken as $a = 4.4$ Å, a value similar to that estimated for $Ru(NH_3)_6^{3+}\cdot Cl^-$ ion pair.[6] The other symbols have their usual meaning.[16,17] K_2 is assumed not to vary with the ionic strength since there is no change in the net charge in eq 2.

The results of the absorbance measurements, A_0 were fitted to eq 6 and 10 using a nonlinear least-squares program. Since we expect ϵ_{NH_2} to be temperature independent, we have first fitted each series of experiments at a different temperature, with ϵ_{NH_2} fixed at the value of 2800 M^{-1} cm^{-1} obtained at ionic strength of 0.1 M, and let B be a free parameter. The values of B obtained by this procedure were randomly varied in the range 0.334–0.470 M^{-1}; yet the fitted K_1 and K_2 showed only a slight dependence on the exact value of B. Thus the fitting procedure was repeated with a value of $B = 0.399$ M^{-1}, which was the average of the values of B obtained in the first fit. In such a process, the values of K_1^0 and K_2 were obtained for each temperature. A comparison of the experimental data and the points calculated with the fitted parameters is shown in Figure 3. The values of K_1^0 and K_2 are plotted vs. reciprocal temperature in Figure 4. Their thermodynamic parameters are given in Table I. It may be noted that although the two series of experiments yielded somewhat different values of K_1 and K_2 at an ionic strength of 0.1 M, their product K_1K_2 is in better agreement. Since the number of parameters was greater in the second procedure, we consider the results of the first procedure of the constant ionic strength as more reliable.

The dissociation constant K_{ion} of the $Ru(NH_3)_6^{3+}$ ion is defined in eq 11. Its temperature dependence is described

$$K_{ion} = [Ru(NH_3)_5NH_2^{2+}][H^+]/[Ru(NH_3)_6^{3+}] = K_wK_1K_2 \qquad (11)$$

in Figure 5, and its thermodynamic parameters are given in Table I.

In a previous preliminary work,[3] pK_{ion} at 25 °C was estimated as $pK_{ion} = 12.4 \pm 0.5$, which deviates from the value $pK_{ion} = 13.1 \pm 0.3$ obtained in the present work. The reason for this discrepancy is that the dependence of the equilibrium constants on ionic strength was not taken into account in that work, although the ionic strength was varied through the experiment. Note that the values given for $\Delta H°$ and $\Delta S°$ in ref 3 are for reaction 12.

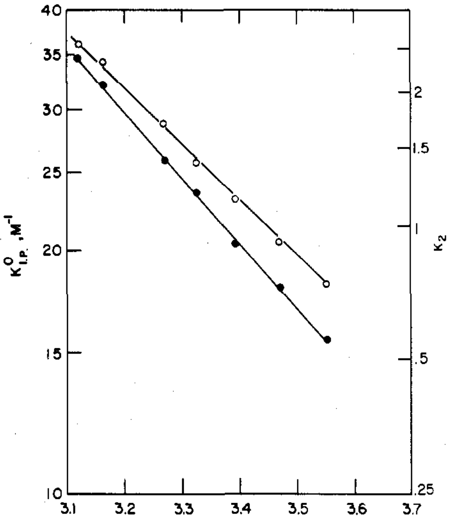

Figure 4. Semilogarithmic plots of K_1^0 (●) and K_2 (○) as a function of reciprocal temperature.

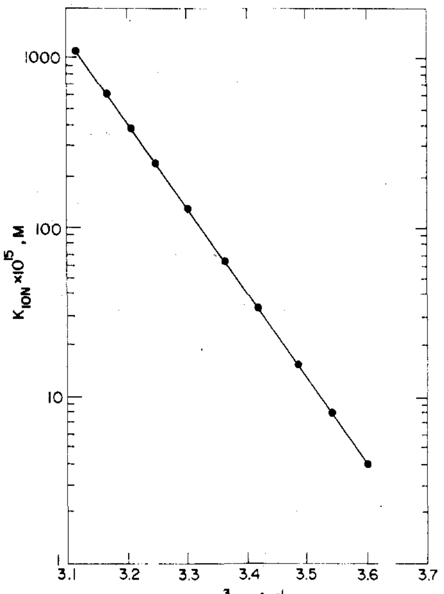

Figure 5. Semilogarithmic plot of the apparent acid dissociation constant of $Ru(NH_3)_6^{3+}$ ion as a function of reciprocal temperature.

$$Ru(NH_3)_6^{3+} + OH^- \rightleftarrows Ru(NH_3)_5NH_2^{2+} + H_2O \qquad (12)$$

Rate of Aquation of $Ru(NH_3)_6^{3+}$. The rate of the aquation reaction of $Ru(NH_3)_6^{3+}$ could be followed either by the decrease of the absorption of the $Ru(NH_3)_5NH_2^{2+}$ ion at 420 nm or by the increase of the absorption at 295 nm due to the formation of $Ru(NH_3)_5OH^{2+}$. According to eq 3, the rate of hydrolysis is proportional to the concentration of the deprotonated species:

$$d[ROH]/dt = k[RNH_2] \qquad (13)$$

Differentiation of eq 5 gives eq 14.

$$dA/dt = k(\epsilon_{OH} - A_0/C_0)[RNH_2] \qquad (14)$$

In the initial stage of the hydrolysis reaction, the concentration of the reaction product ROH can still be neglected

Table II. Activation Parameters of the Aquation Rate Constants

	k_1		k_2	
	295 nm	420 nm	295 nm	420 nm
$\Delta H^{\ddagger}$, kcal mol^{-1}	14.4 ± 0.5	16.6 ± 0.4	19.0 ± 0.7	17.4 ± 0.6
$\Delta S^{\ddagger}$, cal mol^{-1} K^{-1}	−21.8 ± 1.5	−14.3 ± 1.2	−1.5 ± 2.0	−6.4 ± 2.0
k at 25 °C	(2.9 ± 0.2) × 10^{-3}	(3.1 ± 0.4) × 10^{-3}	(3.3 ± 0.2) × 10^{-2}	(4.2 ± 0.5) × 10^{-2}

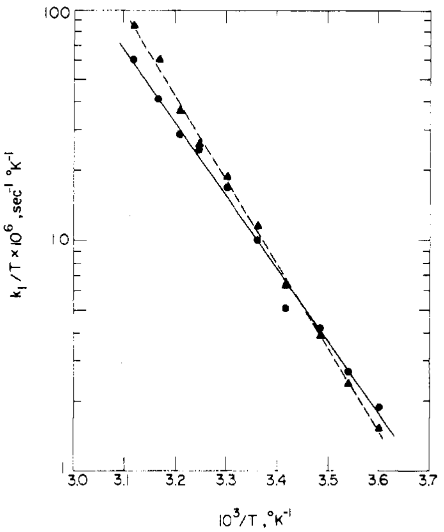

Figure 6. Eyring plot of the pH-independent rate constant for the aquation of the $Ru(NH_3)_5NH_2^{2+}$ ion: ●, measurements at 295 nm; ▲, measurements at 420 nm.

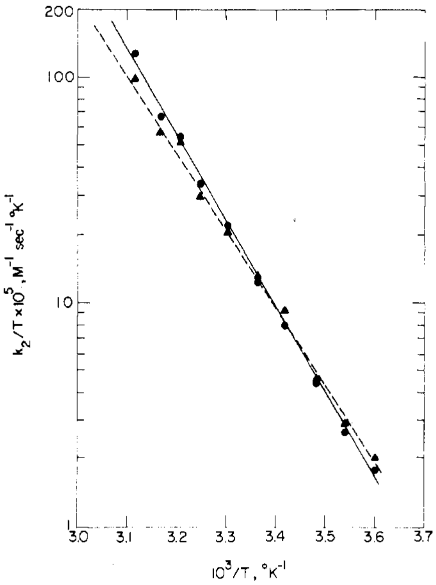

Figure 7. Eyring plot of the pH-dependent rate constant for the aquation of the $Ru(NH_3)_5NH_2^{2+}$ ion: ●, measurements at 295 nm; ▲, measurements at 420 nm.

relative to the other ruthenium species present in the solution. Thus the initial change of the absorbance is given by (15).

$$(dA/dT)_{init} = k(\epsilon_{OH}C_0 - A_0)/(1 + K_2^{-1} + (K_1K_2[OH])^{-1}) \qquad (15)$$

The initial slopes of the absorbance at 295 and 420 nm taken at a constant ionic strength of $I = 0.1$ M were fitted to eq 15 with K_1 and K_2 taken from the analysis of the initial absorbance (A_0) given above.

ϵ_{OH} in eq 15 is 2.1 × 10^3 M^{-1} cm^{-1} at 295 nm.[12] At 420 nm we estimated its value as 5 ± 1 M^{-1} cm^{-1}. More accurate measurement seems unnecessary, since its contribution in eq 15 is very small at this wavelength, at the high pH values used in our experiments.

The value of k was found to be pH dependent and a good fit was obtained when we assumed

$$k = k_1 + k_2[OH^-] \qquad (16)$$

Semilogarithmic plots of k_1/T and k_2/T vs. reciprocal temperature for the sets of measurements at 295 and 420 nm are given in Figures 6 and 7. The activation parameters are given in Table II. It is seen from Figures 6 and 7 and Table II that only a fair agreement was obtained between the results of the two wavelengths. The results of the measurements at 295 nm should be considered as more reliable, since they were more reproducible and less susceptible to systematic errors. The comparison with the results of the measurements at 420 nm was done only to find out whether the behavior of the absorbance at these two wavelengths conforms with the same reaction scheme.

Discussion

In the present work we estimated the relative concentrations of the ion pairs with hydroxide ions and the deprotonated species of $Ru(NH_3)_6^{3+}$ ions. Although it is possible that in other cases of deprotonation processes the formation of ion pairs with hydroxide ion is the first stage in the deprotonation reaction, in the case of the $Ru(NH_3)_6^{3+}$ the equilibrium constant of the deprotonation reaction is such that both species are present in the solution in comparable concentrations, and the determination of the two stages of the reaction is possible.

The ion-pair formation constant obtained in this work, K_1 = 22 M^{-1} at 25 °C and zero ionic strength (Table I), can be compared with ion-pair formation constants of the $Ru(NH_3)_6^{3+}$ and the halide ions, reported previously,[6] i.e., K_1 = 15, 11, and 9.8 M^{-1} for the chloride, bromide, and iodide, respectively. The slightly larger value of the ion-pair formation constant for the hydroxide ion is consistent with its smaller effective ionic radius.[18] The suggestion that the ion pair is the first stage in the formation of the yellow deprotonated species is consistent with the finding[7] that the formation of the yellow color is abolished in the presence of anions such as HPO_4^{2-} and SO_4^{2-} which are capable of ion pairing with the $Ru(NH_3)_6^{3+}$ ion and therefore competing with the hydroxide ion pairs. The presence of the deprotonated species in basic solutions of $(Ru(NH_3)_6^{3+}$ accounts for the reaction with NO to give[5a] $Ru(NH_3)_5N_2^{2+}$ and with oxygen to give[5b] $Ru(NH_3)_5NO^{3+}$. In both cases, the reactions can be understood if the presence of activated amide group is assumed. Again, the inhibition of the reaction with NO by PO_4^{3-} and borax is consistent with a competition with the OH^- ion pair and a concomitant decrease of the concentration of the deprotonated species.

The value of about 20 eu obtained for the $\Delta S°$ of reaction 2 may seem too high considering the fact that the overall charge of the ion pair is equal to that of the deprotonated species. However, assuming that the hydration entropy of the ion pair is the sum of the hydration entropies of $Ru(NH_3)_6^{3+}$ and OH^-, we expect it to be considerably more negative than that of the divalent deprotonated species. In fact, a value of about 20 eu is obtained for $\Delta S_2°$ when the Born equation[19a] is used as a rough measure of the hydration entropies of the above-mentioned ions.

A formation of a conjugate base has been commonly implicated in the mechanism of base hydrolysis of coordination complexes.[19-22] However, in most cases it was difficult to determine directly the concentration of the conjugate base and to correlate it with the reaction rate. In the case of the $Ru(NH_3)_6^{3+}$ complex, the formation of the conjugate base, i.e., $Ru(NH_3)_5NH_2^{2+}$, is observed in a straightforward manner.

The kinetics of the hydrolysis reaction could be explained on the basis of the participation of the deprotonated species. Our result indicates that there are two routes for the hydrolysis of $Ru(NH_3)_5NH_2^{2+}$, a pH-independent route and a pH-dependent route. The pH-independent route of the hydrolysis is analogous to the acid hydrolysis of cobalt(III) complexes, where electron-donating groups such as OH^- and Cl^- enhance the aquation rates, preferentially of a ligand in the cis position.[23] The amide group is expected[24] to have electron-donating properties exceeding that of Cl^- and thus it is not surprising that $Ru(NH_3)_5NH_2^{2+}$ is liable to hydrolysis at a much faster rate ($k_1 = 2 \times 10^{-3}$ s^{-1}) as compared to the hydrolysis of $Ru(NH_3)_5Cl^{2+}$ (7×10^{-7}).[19] The entropy of activation for k_1 is about −20 eu. A negative $\Delta S^{\ddagger}$ was also obtained for the acid hydrolysis of $Ru(NH_3)_5Cl^{2+}$: $\Delta S^{\ddagger} = -11$ eu. According to Edwards et al.,[25] these negative values indicate an S_N2 mechanism which is probably an interchange mechanism (either I_d or I_a).

The reaction path where the rate of hydrolysis is dependent on the hydroxyl ion concentration (k_2) can be envisaged to occur either through a doubly deprotonated species, $Ru(NH_3)_4(NH_2)_2^+$, or a nucleophilic attack of OH^- ion on the monodeprotonated species $Ru(NH_3)_5NH_2^{2+}$. The base hydrolysis of cobalt(III) complexes of the type $Co(NH_3)_5X^{2+}$ was considered to proceed by a conjugate-base mechanism since it was found to be much faster than the substitution by anions other than hydroxide.[19] This was particularly apparent for complexes containing an ionizable group such as H_2O or NH_3. Thus it seems likely that the conjugate-base mechanism, i.e., the formation of the doubly deprotonated species, is operative in the base hydrolysis of the $Ru(NH_3)_5NH_2^{2+}$ as well. The actual concentration of this species is, however, expected to be very small at pH values below 13. According to eq 14 and Table II, at pH 13 the two reaction paths proceed at the same rates. Since the hydrolysis of the $Ru(NH_3)_4(NH_2)_2^+$ complex is expected to be much faster than that of the $Ru(NH_3)_5NH_2^{2+}$ complex, it follows that its concentration is much smaller. This consideration gave us justification to neglect the doubly deprotonated species in our spectrophotometric work.

Table III. Spectroscopic Parameters of Some Ruthenium Pentaamine Complexes

ion	λ, nm	ε, M^{-1} cm^{-1}	χ_{opt}
$Ru(NH_3)_5Cl^{2+}$ [a]	328	2.0×10^3	(3.0)
$Ru(NH_3)_5Br^{2+}$ [a]	398	1.95×10^3	2.8
$Ru(NH_3)_5NH_2^{2+}$ [b]	402	2.8×10^3	2.8
$Ru(NH_3)_5OH^{2+}$ [c]	295	2.1×10^3	3.1

[a] Reference 26. [b] Present work. [c] Reference 12.

The position of the absorption maximum and the extinction coefficient obtained for the complex $Ru(NH_3)_5NH_2^{2+}$ indicates a ligand-to-metal charge-transfer transition similar to that in $Ru(NH_3)_5Cl^{2+}$ and $Ru(NH_3)_5Br^{2+}$ complexes.[26] A comparison of the spectra of these complexes and that of $Ru(NH_3)_5OH^{2+}$ is given in Table III. The extinction coefficients of all four complexes are of the same order of magnitude. Furthermore, from the position of the absorption maxima it is possible to estimate the optical electronegativities[27,28] of the ligands NH_2^- and OH^-. Since the complexes are not octahedral, it may not be justified to base our calculation on the optical electronegativity of the ruthenium(III) metal ion. It is possible, however, to take the electronegativity of the chloride ion ($\chi_{opt}(Cl^-) = 3.0$) as a reference using expression (17). The

$$\bar{\nu}(X^-) - \bar{\nu}(Cl^-) = 30(\chi_{opt}(X^-) - \chi_{opt}(Cl^-)) \times 10^3 \text{ cm}^{-1} \quad (17)$$

application of eq 17 also eliminates the necessity to consider the value of the spin-pairing energy.[28] Values of the optical electronegativities for the Br^-, NH_2^-, and OH^- calculated on the basis of eq 17 are given in Table III. The value obtained for the Br^- agrees with that obtained for octahedral complexes. There seems to be no other data on the optical electronegativities of NH_2^- and OH^-, except for a remark by Jörgensen[28] who concluded on the basis of the spectrum of $Pt(NH_3)_5NH_2^{3+}$ that the optical electronegativity of the NH_2^- group is lower than that of the NH_3 group.

Registry No. $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_5NH_2^{2+}$, 35273-31-5.

References and Notes

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