sess octahedral symmetry (O_h), then the complex can gain optical activity to first order on a crystal field perturbation expansion only if the perturbing field transforms as a pseudoscalar function under the symmetry operations of the O_h point group (*i.e.*, the perturbation must transform as the A_{1u} irreducible representation of O_h). If the crystal field potential is expanded in spherical harmonic functions about the metal ion, the first term that transforms as A_{1u} is of degree nine ($l = 9$), and that part of the potential function which depends upon perturber positions is just the function F, as defined above (actually FR_p^{-19}, where R_p is the metal-perturber radial distance).

In most applications of the "octahedral sector rule," primary emphasis has been placed on the nonligating atoms of the ligand environment as perturber centers. However, in a recent study of chiral Co(III) complexes Bosnich[42] has also attempted to include distortions of the CoL_6 cluster in a structure-spectra analysis based on the octahedral sector rule. In this latter application the dissymmetrically disposed ligating atoms are treated as perturbers and each makes a contribution to the function F. The theoretical validity of the octahedral sector rule, as well as its reliability in making spectra-structure correlations, has been discussed recently by Richardson[41] and will not be further examined here. However, we did calculate F as a function of polar distortion angle σ for several values of the azimuthal distortion angle δ and found that the signs of F for $|\sigma| \leq 10°$, $|\delta| \leq 10°$ were identical with the signs of the net reduced rotatory strengths calculated for CoO_6. In Figure 5, F is plotted *vs.* σ for $\delta = 3°$. Note that although F and $[R]$ have the same signs in this plot for $|\sigma| \leq 4°$, the shapes of the $[R]$ and F curves are somewhat different.

V. Summary

Although there has been a great deal of spectra-structure rationalization based on Liehr's and Piper's molecular orbital models for d-d optical activity, virtually no model calculations have been reported in the literature. Our calculations support the contention that trigonal dihedral transition metal complexes gain substantial optical activity in the visible region by the dissymmetric positioning of the ligating atoms. However, we must conclude that the effect of the nonligating atoms need be included in some fashion if the relative intensities of the visible CD bands are to be accurately calculated and accounted for. These intensities are expected to be sensitive to the computational model for the molecular orbitals, but the signs of the bands appear insensitive to changes in the parameters of the MO model. It is this latter quality, the ability of Piper's model correctly to predict signs of the CD bands, that is its greatest strength.

The extension of Piper's model to include ligand p_π atomic orbitals leads to overestimates of the amount of π bonding. It is possible that this defect may be remedied by including nonligating atoms bonded to the ligator atoms. That is, some anisotropy must be introduced into the ligand-metal π system to reflect the presence of the chelate bridging atoms.

Registry No. Cobalt, 7440-48-4; chromium, 7440-47-3.

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Rates of Acid Hydrolysis and Stabilities of Ruthenium(II) Pentaammine Chloride and Bromide Complex Ions

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A cyclic voltammetric method has been used to study the acid hydrolysis reactions $Ru(NH_3)_5X^+ + H_2O \rightarrow Ru(NH_3)_5H_2O^{2+} + X^-$, where X^- is Cl^- and Br^-. First-order rate constants, k, were measured in *p*-toluenesulfonic acid media over a temperature range of 15–40°. For the Cl^- complex, $k = 6.3 \pm 0.3$ sec^{-1} at 25°, $\Delta H^{\ddagger} = 12 \pm 3$ kcal, $\Delta S^{\ddagger} = -16 \pm 6$ eu; for the Br^- complex, $k = 5.4 \pm 0.4$ sec^{-1} at 25°, $\Delta H^{\ddagger} = 14 \pm 3$ kcal, $\Delta S^{\ddagger} = -10 \pm 6$ eu. Equilibrium constants for the reactions are found to be 0.70 M for the Cl^- hydrolysis and 0.92 M for the Br^- hydrolysis.

Introduction

Ruthenium(II) pentaammine complexes containing a sixth ligand which is not a π acceptor are difficult to isolate in aqueous solution. Several workers[2-4] have reported that these complexes undergo hydrolysis reactions very quickly after being produced by the reduction of corresponding ruthenium(III) pentaammine complexes. We have been attempting fast electrochemical reductions of ruthenium(III) complexes of this type to produce and observe the reduced complexes before they react. The objectives of the work were to measure hydrolysis rates and stabilities of these labile complexes for comparison with those of previously studied d^6 metal-ammine complexes.

Experimental Section

Reagents. $[Ru(NH_3)_5Cl]Cl_2$ and $[Ru(NH_3)_5Br]Br_2$ were prepared from $RuCl_3$ (Fischer Scientific) as described in the literature.[5] Uv spectra of aqueous solutions containing known amounts of these

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salts were indistinguishable, within experimental error, from published spectra.[6-8]

$[Ru(NH_3)_5H_2O](SO_3C_7H_7)_3$ was prepared by dissolving approximately 0.1 g of $[Ru(NH_3)_5Cl]Cl_2$ in 2 ml of water, then adding 2 drops of concentrated NH_3, and heating to 72°. To the hot, wine red solution was added 5 *M* *p*-toluenesulfonic acid (Fischer Scientific) dropwise until the solution was acidic and no further precipitation of the pale pink solid was observed. After washing with 2 *M* *p*-toluenesulfonic acid and with ethanol, the solid was air dried. Due to the fact that the $Ru(NH_3)_5H_2O^{3+}$ ion and the *p*-toluenesulfonate anion absorb at the same wavelengths, it was not possible to obtain an accurate uv spectrum of the salt for characterization purposes. However, there was no evidence of $Ru(NH_3)_5Cl^{2+}$, the most likely impurity, in the spectrum that was obtained, and cyclic voltammetric experiments described below showed that the salt contained the $Ru(NH_3)_5H_2O^{3+}$ cation.

The electrochemical reactions performed during these studies were carried out at a mercury electrode. One of the limitations of this electrode is its relative ease of oxidation in solutions containing free halide ions.[9] The reduction potentials of the ruthenium complexes under study were found to be positive enough that mercury oxidation led to interferences during the electrochemical experiments. To minimize this interference the halopentaammineruthenium(III) dihalide salts were treated with stoichiometric amounts of silver *p*-toluenesulfonate solution to precipitate the uncomplexed halide ions, the silver halide being either separated by filtration or allowed to settle before experimentation proceeded. The silver *p*-toluenesulfonate solution was prepared by dissolving stoichiometric amounts of silver oxide and *p*-toluenesulfonic acid in distilled water.

All electrochemical experiments were performed in 0.171 *M* *p*-toluenesulfonic acid supporting electrolyte. All other chemicals used were reagent grade.

Apparatus. The instrumentation used in the cyclic voltammetric experiments was of the conventional three-electrode type and has been described previously.[10] Operational amplifiers on a McKee-Pederson MP-1001 console were used to construct the potentiostat and the current amplifier. A triangular-wave generator capable of supplying variable cyclic voltage scans of 1-sec to 1-msec duration was used as the voltage source.[11] Current-voltage curves were displayed on a Tektronix Type 564B storage oscilliscope. Potentials were measured with a Leeds and Northrup volt potentiometer.

The electrochemical cell contained three electrodes and provisions for bubbling helium through the test solutions between experiments to remove dissolved oxygen. The working electrode was a slowly dropping mercury electrode with a drop time of about 16 sec, the voltammetric experiments being performed during the last 600 msec of the drop life so that the electrode area was essentially constant. The reference electrode was a silver wire coated with silver chloride immersed in a 1 *M* NaCl-0.01 *M* HCl solution contained in a bent capillary probe and separated from the test solution by an agar plug. Placing the capillary probe close to the mercury electrode so that each fresh mercury drop grew against the tip of the probe reduced the effects of uncompensated resistance during the measurements.[12] The auxiliary electrode was a platinum wire. Water from a constant-temperature bath (Wilkens-Anderson Lo-Temp) was circulated through a water jacket surrounding the electrochemical cell to achieve temperature control to ±0.2°.

Spectra were recorded on a Cary recording spectrophotometer, Model 14. Stock solutions of acids were standardized with electrochemically generated hydroxide ion using a Sargent-Welch coulometric current source, Model IV.

Measurements of Rate Constants. First-order rate constants for the hydrolysis reactions were measured at several temperatures using a cyclic voltammetric method. Solutions containing about 1×10^{-3} *M* $Ru(NH_3)_5Cl^{2+}$ or $Ru(NH_3)_5Br^{2+}$ and 0.171 *M* *p*-toluenesulfonic acid were subjected to cyclic voltage scans between the limits −0.100 to −0.350 V *vs.* the silver–silver chloride reference electrode. Cycle times in the range 50–500 msec were employed. It was observed that under these conditions the experimental current-voltage curves followed the theoretical relationships derived by Nicholson and Shain[13] for a reversible electron-transfer reaction followed by an irreversible, first-order reaction in solution. The rate constants for the reactions in solution were derived from the experimental data using methods described by these workers;[10,14] all calculations and comparisons of data with theory being performed with the DePauw University Digital PDP 12 computer.

Measurements of Equilibrium Constants. Calculations of the equilibrium constants for the reactions under consideration required values for the dissociation constants of the corresponding ruthenium(III) complex ions. These constants have been determined previously,[2,7] but there is sufficient variation in the published values to warrant independent determinations.

A solution about 3×10^{-4} *M* in $[Ru(NH_3)_5Cl]Cl_2$, 0.020 *M* in KCl, and 0.10 *M* in $HClO_4$ was prepared and the uv spectrum was recorded from 450 to 250 nm. Ten grams of amalgamated zinc was added and the solution was agitated while maintaining the temperature of the mixture at 25°. Reducing agents are known to catalyze the hydrolysis of $Ru(NH_3)_5Cl^{2+}$.[2] Samples were withdrawn at 5-min intervals and the spectra were recorded until successive samples gave identical spectra, indicating that the dissociation reaction was at equilibrium (about 30 min was required). The difference in the absorbances of the equilibrium and initial solutions at the wavelength of maximum absorbance of $Ru(NH_3)_5Cl^{2+}$ (328 nm) was used with the excess chloride ion concentration to calculate the dissociation constant. In addition, the values of absorbance of the equilibrium solution at 328 nm and at 268 nm (the maximum wavelength for $Ru(NH_3)_5H_2O^{3+}$) were used with published values of molar absorptivities[8] to calculate directly the equilibrium concentrations and the constant.

This procedure was repeated with a solution containing about 3×10^{-4} *M* $[Ru(NH_3)_5Br]Br_2$ (λ_{max} 398), 0.020 *M* KBr, and 0.10 *M* $HClO_4$.

Results

Rate Constants for Ru(II) Hydrolysis Reactions. Traces of representative current-voltage curves obtained with solutions of $Ru(NH_3)_5Cl^{2+}$ are shown in Figure 1. During the cathodic portion of the cyclic scans, one wave is observed due to the reduction of the Ru(III) complex by a one-electron step to the corresponding Ru(II) complex. This electrode reaction is followed by a rapid reaction in solution in which the halide ligand in the reduced complex is replaced by a water molecule. During the subsequent anodic scan, two oxidation waves are observed—the first due to the reoxidation of unreacted ruthenium(II) halide complex and the second due to the oxidation of the product, $Ru(NH_3)_5H_2O^{2+}$. The potential corresponding to the reoxidation of the reaction product is found to be identical with that observed for the reoxidation of $Ru(NH_3)_5H_2O^{2+}$ produced by the reduction of $Ru(NH_3)_5H_2O^{3+}$ as shown in Figure 1. Similar results are observed with $Ru(NH_3)_5Br^{2+}$. Other workers have reported identical behavior of these ions.[4]

Experimental values of the ratio of the anodic to cathodic peak heights from the reduction and reoxidation of the unreacted complex, measured at known cycle times, were compared with theoretical relationships to obtain the rate constants for the hydrolysis reactions of the reduced complexes. The results of these calculations are shown in Table I.

A value of the rate constant for the hydrolysis of $Ru(NH_3)_5Cl^+$ has been measured using an electron pulse radiolysis technique.[3] The reported value is 4.7 sec^{-1} at 20° in close agreement with the corresponding result in Table I.

The experimental rate constants and temperatures were used to construct graphs of ln (k/T) *vs.* $1/T$. Values for the enthalpy and entropy of activation of the reactions were estimated from the slopes and intercepts of the graphs. For the chloropentaammine reaction, $\Delta H^{\ddagger}$ is 12 ± 3 kcal and

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Table I. Experimental Rate Constants

Complex ion	Temp, °C	k,[a] sec^{-1}
$Ru(NH_3)_5Cl^+$	20	4.4 ± 0.3
	25	6.3 ± 0.3
	35	11.9 ± 0.8
	43	20.2 ± 2.3
$Ru(NH_3)_5Br^+$	15	1.2 ± 0.3
	20	3.8 ± 0.5
	25	5.4 ± 0.4
	30	8.3 ± 0.5
	35	12.2 ± 1.0

[a] Each value reported is the average of between 4 and 16 individual results. The confidence intervals were calculated at the 90% probability level.

Table II. Equilibrium Data for Ruthenium Complexes

K_1,[a] M	$Ru(NH_3)_5Cl^{2+}$	0.0105 ± 0.0002 (0.014),[b] (0.007)[c]
	$Ru(NH_3)_5Br^{2+}$	0.0189 ± 0.0005 (0.038)[b]
$E°$,[d] V *vs.* nhe	$Ru(NH_3)_5Cl^{2+}$	−0.042
	$Ru(NH_3)_5Br^{2+}$	−0.034
	$Ru(NH_3)_5H_2O^{3+}$	+0.066
K_4, M	$Ru(NH_3)_5Cl^+$	0.70
	$Ru(NH_3)_5Br^+$	0.92

[a] Numbers in parentheses are previously reported values. [b] Reference 2. [c] Reference 7. [d] Values reported are formal potentials determined by cyclic voltammetry. See ref 4.

$\Delta S^\ddagger$ is −16 ± 6 eu; for the bromopentaammine reaction, $\Delta H^\ddagger$ is 14 ± 3 kcal and $\Delta S^\ddagger$ is −10 ± 6 eu.

A series of rate measurements were performed with $Ru(NH_3)_5Cl^+$ in which the hydronium ion concentration in the supporting electrolyte was varied from 0.54 to 0.03 M while keeping the ionic strength approximately constant with added sodium ion. The rate constant was found to increase by about 25% as the H_3O^+ concentration decreased over this range. This relatively small change was interpreted as an ionic strength effect and it is assumed that the hydrolysis reactions are essentially independent of acid concentration over this range.

Dissociation Constants. The reactions for the dissociation of the reduced complexes can be obtained by combining the reactions

$$Ru(NH_3)_5X^{2+} + H_2O \rightleftarrows Ru(NH_3)_5H_2O^{3+} + X^- \quad (1)$$

$$Ru(NH_3)_5X^+ \rightleftarrows Ru(NH_3)_5X^{2+} + e^- \quad (2)$$

$$Ru(NH_3)_5H_2O^{3+} + e^- \rightleftarrows Ru(NH_3)_5H_2O^{2+} \quad (3)$$

$$Ru(NH_3)_5X^+ + H_2O \rightleftarrows Ru(NH_3)_5H_2O^{2+} + X^- \quad (4)$$

Where X^- is Cl^- and Br^-. Thus, the dissociation constant for the reduced complex, K_4, is given by $K_1K_2K_3$. K_1 was determined in this study; K_2 and K_3 can be calculated from standard potential data. The results of this treatment are summarized in Table II.

Discussion

The kinetic results in Table I indicate that the rate constants for acid hydrolysis of $Ru(NH_3)_5Cl^+$ and $Ru(NH_3)_5Br^+$ are essentially the same. This is not the observed behavior of other metal-pentaammine-halide complexes[15]—in most cases the bromide complexes react faster than the chloride complexes.

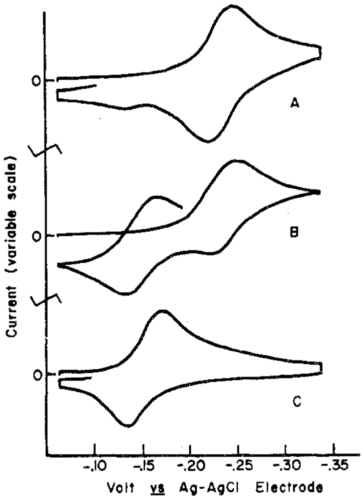

Figure 1. Typical cyclic voltammetric responses: (a) solution containing 10^{-3} M $Ru(NH_3)_5Cl^{2+}$, 100-msec cycle time; the formation of a small amount of the aquo complex is noted in the anodic scan; (b) same solution as in (a), 500-msec cycle time; the formation of a greater amount of the aquo complex is apparent in this slower experiment; (c) 10^{-3} M $Ru(NH_3)_5H_2O^{3+}$, 100-msec cycle time. The supporting electrolyte in each case is 0.171 M p-toluenesulfonic acid. The temperature is 25°.

In studies of families of metal-pentaammine complexes having leaving groups with little π-bonding character, it has been shown[16,17] that rate constants and equilibrium constants for acid hydrolysis reactions show linear free energy relationships with slopes close to unity. These observations are consistent with a general mechanism for these reactions in which bond breaking is more important than bond making in the activated complex. Thus, the larger rate constants for Br^- over Cl^- replacements are related to larger equilibrium constants for Br^- over Cl^- dissociations.

In the case of Ru(II), the dissociation constant for the bromide complex seems significantly larger than that of the chloride complex (Table II), while the hydrolysis rates are the same. It is tempting to conclude that bond making is more important in these reactions. However, the experimental uncertainties in both the kinetic and equilibrium data probably make such a conclusion very tenuous. In addition, the entropies of activation for the reactions studied here are not appreciably different from those for related d^6 and d^3 metal pentaammine halides[15] indicating similar transition states.

Registry No. $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; $[Ru(NH_3)_5Br]Br_2$, 16446-65-4; $[Ru(NH_3)_5H_2O](SO_3C_7H_7)_3$, 38673-79-9.

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