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The Preparation and Kinetics of Hydrolysis of Pentaammineperrhenatocobalt(III) Ion

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A well-defined compound containing coordinated ReO_4^- has been isolated by the dehydration of $[Co(NH_3)_5OH_2](ReO_4)_3 \cdot 2H_2O$ under vacuum at 95–130°. In aqueous solution, $[Co(NH_3)_5ReO_4]X_2$ aquates at a measurable rate and follows the rate law: rate $= (k_0 + k[H^+] + k_{OH}[OH^-])[Co(NH_3)_5ReO_4^{2+}]$. The values $k_0 = (3.12 \pm 0.44) \times 10^{-4}$ sec^{-1}, $k_H = 1.22 \pm 0.03$ M^{-1} sec^{-1}, and $k_{OH} = (2.89 \pm 0.11) \times 10^4$ M^{-1} sec^{-1} were obtained at 25° and $\mu = 0.004$–0.12. Using O^{18} as a tracer, the formation in the solid state was found to occur by fission of the Co–O bond while hydrolysis in dilute H^+ or OH^- occurred by Re–O bond breaking. In the neutral region (pH 4–7) more complex oxygen-transfer behavior was observed. Hydrolysis was strongly catalyzed by HOAc, OAc^-, and H(phthalate)$^-$.

Introduction

In the light of the recent demonstrations[2,3] of ClO_4^- coordination to Co(II) and Ni(II) in the solid state and in nonaqueous solution, a revival of interest in the preparation of a nonlabile ClO_4^- complex such as was attempted by Duval[4] has occurred. A careful study by Jones and Swaddle[5] showed no evidence of formation of $Co(NH_3)_5ClO_4^{2+}$ by thermal dehydration of $[Co(NH_3)_5OH_2](ClO_4)_3$ or by Duval's approach. Our experiments, similar to those of Jones and Swaddle,[5] yielded the same conclusions.

Since ReO_4^- is closely related to ClO_4^- but is much more labile to oxygen substitution[6] and presumably more easily coordinated, a study was undertaken to prepare substances with coordinated ReO_4^- in the hope that the principles developed might lead to the ultimate preparation of $Co(NH_3)_5ClO_4^{2+}$.

In its own right $Co(NH_3)_5OReO_3^{2+}$ is of interest since its hydrolysis is likely to involve both Co–O and Re–O fission: the former in the neutral solution and the latter in acidic and basic media.[7] Furthermore it was of interest to learn what effect $(NH_3)_5Co$– attachment to ReO_4^- has on its oxygen-exchange properties.

Thus this paper reports the preparation of $Co(NH_3)_5OReO_3^{2+}$,[8] some kinetic studies on its hydrolysis, and O^{18}-transfer measurements on the preparative reaction and on the hydrolysis in aqueous solution.

Experimental Section

The starting material, $[Co(NH_3)_5OH_2](ClO_4)_3$, was prepared from $[Co(NH_3)_5CO_3]NO_3$[9] by a standard method, recrystallized from dilute acid three times, and dried under vacuum. Perrhenic acid, normal and O^{18} enriched, was converted to anhydrous $NaReO_4$ as previously outlined.[6] All other substances used were reagent grade, recrystallized where critical. The solvent water was distilled from $KMnO_4$ followed by two slow distillations.

$[Co(NH_3)_5OH_2](ReO_4)_3 \cdot 2H_2O$.—To 6.0 g of $[Co(NH_3)_5OH_2](ClO_4)_3$ dissolved in 100 ml of water was added 6.0 ml of 5.4 M $HReO_4$ solution. After about 30 min the solid product was collected on a filter, washed with methanol and acetone, and dried over $Mg(ClO_4)_2$ at room temperature and pressure; yield 95+% of theoretical.

Dehydration of $[Co(NH_3)_5OH_2](ReO_4)_3 \cdot 2H_2O$.—At about 50–60° the lattice water was lost completely under vacuum (10^{-3} mm) in about 3 hr. The time required depended on the sample size and on the extent of contact with the glass vessel. In six experiments the average per cent of water lost was 3.81% with an average deviation of 0.05% (theoretical for $2H_2O$, 3.80%). This confirmed the formula as the dihydrate. No color change was observed in this dehydration.

Dehydration of $[Co(NH_3)_5OH_2](ReO_4)_3$.—Between 95 and 130° ($10^{-3}$ mm) the coordinated water was lost quantitatively over a period of 2–5 hr. No NH_3 loss was detectable in the condensed H_2O. During this time the solid changed from pink to purple. The vacuum rose to its initial value when the dehydration was complete and the product was pure $[Co(NH_3)_5OReO_3](ReO_4)_2$.

In six trials the amount of coordinated water (determined gravimetrically) released in this step was 1.91% with an average deviation of 0.04% (theoretical, 1.90% based on $[Co(NH_3)_5OH_2](ReO_4)_3 \cdot 2H_2O$). Thus both steps showed 5.72% water loss to be compared with a theoretical value of 5.70% for $3H_2O$.

The perrhenate salt of the perrhenato complex is quite insoluble in water. In order to prepare useful, more soluble salts (*i.e.*, NO_3^-, Cl^-, ClO_4^-), an ion-exchange technique was used.

Dowex 1-X4 was converted to the NO_3^-, Cl^-, or ClO_4^- form and washed with 10^{-3} M 2,6-lutidine solution.[10] At 10–15° in the presence of H_2O, $[Co(NH_3)_5OReO_3](ReO_4)_2$ was ground with the resin and the solution was separated. Addition of saturated, neutral LiCl, $LiNO_3$, or $LiClO_4$ solution at 0° gave crystals of $[Co(NH_3)_5OReO_3]X_2$ in 60–80% yield.[11] They were washed with methanol and acetone and dried at room temperature under vacuum. The NO_3^- and ClO_4^- salts showed no change in properties over a period of 6 months. However, in the solid state, internal replacement took place with the chloride salt giving some $Co(NH_3)_5Cl^{2+}$.

The formula weights of the salts were determined by allowing them to aquate in water giving $Co(NH_3)_5OH_2^{3+}$ and ReO_4^-,

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[1] Undergraduate Research Associate, NSF, 1967.

[2] F. A. Cotton and D. L. Weaver, *J. Am. Chem. Soc.*, **87**, 4189 (1965).

[3] S. F. Pavkovic and D. W. Meek, *Inorg. Chem.*, **4**, 1091 (1965); A. E. Wickenden and R. A. Krause, *ibid.*, **4**, 404 (1965); B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3091 (1961).

[4] R. Duval, *Ann. Chim.* (Paris), **18**, 241 (1932).

[5] W. E. Jones and T. W. Swaddle, *Can. J. Chem.*, **45**, 2647 (1967).

[6] R. K. Murmann, *J. Phys. Chem.*, **71**, 974 (1967).

[7] The rate law for H_2O exchange with ReO_4^- is $R = k[ReO_4^-] + k_1[ReO_4^-][H^+]^2 + k_2[ReO_4^-][OH^-]$, where k is extremely small compared to k_1 and k_2.[6]

[8] It is assumed that ReO_4^- is attached to cobalt through an oxygen. The ir spectra are in agreement with but do not prove this assumption.

[9] F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

[10] The complex ion hydrolyzes rapidly in acid or base. Dilute solutions of this sterically hindered base retard hydrolysis.

[11] This preparation is described in more detail in work submitted for publication in *Inorg. Syn.*

TABLE I

Salt[b]	Formula wt	
	Exptl	Theoret
$[ROH_2](ClO_4)_3$	458.2 ± 0.5[a]	460.5
$[ROH_2](ReO_4)_3 \cdot 2H_2O$	948 ± 2	948.7
$[ROReO_3](ReO_4)_2$	893 ± 5	894.1
$[ROReO_3](ClO_4)_2$	591 ± 1	593.2
$[ROReO_3](Cl)_2$	469 ± 2	465.2
$[ROReO_3](NO_3)_2 \cdot H_2O$	535 ± 1	536.3

[a] Average deviation from mean, two to three determinations. [b] R = $(NH_3)_5Co$.

absorbing the roseo ion on neutral Dowex 50W-X2 resin (H^+ form), and titrating the released H^+ with standard NaOH solution conductometrically. It was assumed that the formula weight is three times the equivalent weight. See Table I for an analysis of formula weights. Elemental analyses were made[11] and were in satisfactory agreement with these formulas.

Products of Hydrolysis.—Samples of $[Co(NH_3)_5OReO_3]X_2$ were allowed to aquate at the appropriate pH and absorbed on a Dowex 50W-X2 column in the Na^+ form. ReO_4^- was found in the eluate and after concentration it was precipitated with excess solid CsCl. The cobalt complex was eluted with 3 M HCl and the resulting solution analyzed spectrophotometrically at 492 mμ (ϵ 47.7).[12] When the hydrolysis was carried out in the presence of OAc^-–HOAc mixtures or H(phthalate)$^-$, the resin was first eluted with 1 M KCl at pH 3 to remove +2 ions[12] (if present) and then with 3 M solution to elute the roseo ion.

Rates of Hydrolysis.—Solid powdered $[Co(NH_3)_5OReO_3]X_2$ dissolves slowly in water especially in the presence of alkali metal salts. Thus the solid was ground with water and an aliquot was injected into a spectrophotometric cell (1, 2, 5, or 10 cm) containing the appropriate salts at the proper pH and constant temperature. Measurements of absorbance were made at 530 and 580 mμ as a function of time using either a Beckman DU or a Beckman B spectrophotometer with constant-temperature cell compartments. The latter was connected to a Bausch and Lomb 505 recorder and was used primarily for the faster reactions. The perrhenate complex has a maximum at 530 mμ, and the difference in molar absorbance between $Co(NH_3)_5ReO_4^{2+}$ and $Co(NH_3)_5OH_2^{3+}$ is greatest at 580 mμ. Where it was possible to measure A_0 accurately, the A_0/A_∞ ratio agreed to ±2% with the extinction coefficients separately measured on the pure compounds taking into account the acid ionization of the roseo complex. In the neutral region, however, some variation of this ratio was observed.

The initial rate measurements were analyzed by a linear least-squares program on a 7040 computer utilizing the first-order equation $\ln [(A_0 - A_\infty)/(A_0 - A)] = k_{obsd}t$ and gave standard deviations of about 2% in the slope. k_{obsd} is very sensitive to pH, and since one of the products is acidic (roseo salt), buffered media had to be used where possible. Initial experiments showed marked catalysis by acetate and phthalate buffers which led us to the use of redistilled 2,6-lutidine and its acid salt as the buffer system. This amine has been shown[13] to have little or no catalytic activity in other systems. In the weakly acidic and basic regions using this buffer, k_{obsd} was reproducible to ±5% with all new reagents. In the highly basic and acidic regions where $t_{1/2}$ is short, k_{obsd} was reproducible to ±8%. Also in the neutral region, where A_∞ was not completely reproducible and where pH control was not adequate, precision was not high. In all regions the pH was measured before and after reaction by means of a Beckman GS or a Heath pH meter using lithium-glass electrodes standardized at a pH of 4, 7, and 9 with commercial buffers.

In order to evaluate the separate catalytic effects of HOAc and OAc^-, standardized acetic acid solutions were neutralized with appropriate amounts of standard NaOH solution to give OAc^-:HOAc ratios of 2:1, 1:1, and 1:2. These solutions were then diluted to appropriate concentrations for use. With the hydrogen phthalate ion catalysis studies, solutions of KH(phthalate) were used directly.

The visible spectrum of $[Co(NH_3)_5OReO_3](ClO_4)_2$ was determined by measuring the absorbance of standard solutions over a small wavelength range as a function of time and extrapolating to the time of solution. The infrared spectra were obtained on Nujol mulls on a Perkin-Elmer 237B spectrometer.

Oxygen-Transfer Experiments. A. Solid-State Formation of $[Co(NH_3)_5OReO_3](ReO_4)_2$.—This reaction was carried out with $[Co(NH_3)_5OH_2](ReO^*_4)_3 \cdot 2H_2O$[14] which was prepared by the action of a $[Co(NH_3)_5OH_2](ClO_4)_3$ solution in normal water with the stoichiometric amount of $NaReO^*_4$ of known enrichment in normal water at 0° at a pH of 3.8–4.2. The solid was collected, washed with methanol and acetone, and dried over $Mg(ClO_4)_2$ for 2 days at room temperature and pressure. It is known that, under the reaction conditions given, essentially no oxygen exchange occurs with either reactant.[6,15]

A portion of this salt was evacuated (10^{-5} mm) and warmed to 50°, and the released water was collected at Dry Ice temperature (lattice water). After all water was removed at this temperature, the temperature was raised to 110–120° and the water was collected quantitatively (coordinated water). After this water was completely removed, the dry salt was retained for O^{18} analysis. The three samples and the solvent water were converted to CO_2 by the Anbar[16] method, purified by vapor-phase chromatography using silicone oil on Firebrick, and analyzed on a Nuclide RMS-16 mass spectrometer. The 46/(44 + 45) ratio, R_N, was measured. All values were compared to a standard normal CO_2 sample which was given a value of 4.00×10^{-3} for R_N.

B. Oxygen Transfer in Hydrolysis.—With rapid reactions, *i.e.*, 0.1 M H^+ and 0.1 M OH^-, the solid complex, $[Co(NH_3)_5O^*ReO^*_3](NO_3)_2$, was ground with an excess of Dowex 1-X4 in the Cl^- form at 0°. The solution was separated and treated with excess HBr and NaBr to precipitate $[Co(NH_3)_5OH_2]Br_3$. This was collected, washed with HBr (5 M), methanol, and acetone, and dried under vacuum. The coordinated water was converted to CO_2 by the Anbar method[16] either on the complex directly or on the water collected by heating the salt at 110° under vacuum. The CO_2 obtained was purified and analyzed for O^{18} content using the mass spectrometer.

Since ReO_4^- exchanges its oxygens with water very rapidly in 0.1 M H^+ or OH^- no information could be obtained about transfer to this ion.

In the neutral region (pH 4–7) and for reactions catalyzed by $OAc^- + HOAc$, $[Co(NH_3)_5O^*ReO^*_3](NO_3)_2$ was dissolved in water at the appropriate pH and buffered with 2,6-lutidine and HNO_3; the reaction was then allowed to proceed to 90–95% completion. During this time the solution pH was monitored and 2,6-lutidine was added to maintain the selected pH. The solution was then brought to a pH of 8 with the same base (this rapidly completed the reaction) and passed over a column of neutral Dowex 50W-X2 in the Na^+ form. The ReO_4^- which passed through was collected and precipitated at 0° with excess Cs^+. $Co(NH_3)_5OH_2^{3+}$ was eluted from the column with 3 or 6 M HCl and precipitated with HBr–NaBr. During the time required for this separation and precipitation, less than 1% oxygen exchange occurs on the reaction products when separately treated. Both $CsReO_4$ and $[Co(NH_3)_5OH_2]Br_3$ and in some cases the water from the latter were treated by the Anbar method, and the CO_2 obtained was purified and analyzed for O^{18} content.

Several variants of this procedure were used in the neutral region. (a) Separate aliquots of the reaction mixture were treated with HBr or Cs^+ which precipitated $[Co(NH_3)_5OH_2]Br_3$ or $CsReO_4$ directly without previous separation. (b) Separate

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[12] D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967).

[13] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967, p 437.

[14] O* refers to the oxygen(s) containing an excess of O^{18} over normal abundance. Usually it was four to eight times the normal amount.

[15] H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).

[16] M. Anbar and S. Guttman, *Intern. J. Appl. Radiation Isotopes*, **4**, 233 (1959).

aliquots of the reaction mixture were treated with either Dowex 1-X4 or Dowex 50W-X2 resin to remove one ion and the other precipitated as in (a). (c) The hydrolysis was conducted in the presence of either Dowex 1-X4 or Dowex 50W-X2 resin and the ion not absorbed was precipitated in the usual fashion. Analysis for O^{18} content was conducted as described above.

Results

The analytical data and properties given in the Experimental Section are in agreement with the formulation $Co(NH_3)_5OReO_3^{2+}$. The ir spectra, Figure 1, of two compounds with and without coordinated ReO_4^- show the ReO_4^- band split due to the asymmetry introduced by coordination. Also the water band at about 3500 cm^{-1} is missing with $[Co(NH_3)_5OReO_3]Cl_2$. The visible spectrum given in Figure 1 has a maximum at 530 mμ (ε 63.5), is closely related to those of other $Co(NH_3)_5X^{2+}$ ions, and suggests that ReO_4^- belongs close to Cl^- (ϵ_{max} at 532) in the spectrochemical scale.

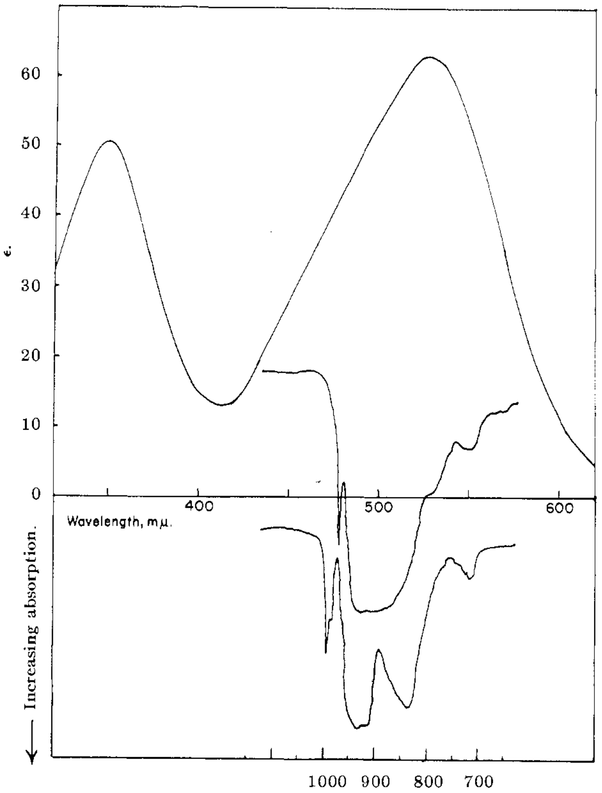

Figure 1.—Upper curve: visible spectrum of $Co(NH_3)_5$-$OReO_3^{2+}$ extrapolated to time of mixing. Lower curves: infrared spectra of $[Co(NH_3)_5OH_2](ReO_4)_2\cdot 2H_2O$ (top) and $[Co(NH_3)_5OReO_4]Cl_2$ (bottom). Nujol mulls.

Hydrolysis of $Co(NH_3)_5OReO_3^{2+}$ in dilute acid or base or in the neutral region gives ReO_4^- and $Co(NH_3)_5$-OH_2^{3+} (or the hydroxo complex) as the only observable products. The experimental yields were >95 and 98 ± 2% of theory, respectively.

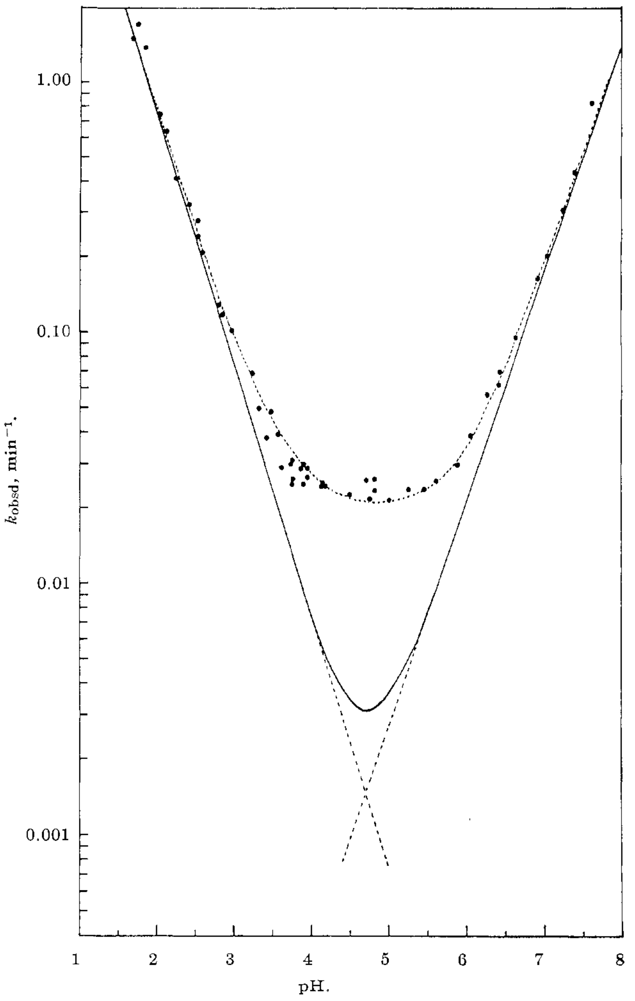

Figure 2.—Observed rate constants of hydrolysis of $Co(NH_3)_5$-$OReO_3^{2+}$ at 25.0° and μ = 0.02–0.15: - - - -, calculated curve from given rate constants; ——, sum of H^+ and OH^- paths without k_0 path; ●, experimental points.

The first-order rate constants of hydrolysis observed are plotted as a function of pH in Figure 2. These data include about an equal number of approximately equally spaced runs in an unbuffered media at μ = 0.02–0.15 (LiCl) and in 0.10 M 2,6-lutidine. Within the experimental error no difference could be discerned using the complex in the Cl^-, NO_3^-, or ClO_4^- form, and using 580- or 530-mμ wavelengths for observations gave identical results. In the slower region, runs were made with no added buffer and gave the same results as with 0.01 M 2,6-lutidine (Table II). The behavior shown in Figure 2 was interpreted in terms of the rate law: $-d[Co(NH_3)_5OReO_3^{2+}]/dt = (k_0 + k_H[H^+] + k_{OH}[OH^-])[Co(NH_3)_5OReO_3^{2+}]$. The values of the rate constants were evaluated graphically by successive approximation assuming first-order behavior in both H^+ and OH^- as suggested by the graph. The constants were also evaluated by a least-squares treatment of the equation $k_{obsd} = k_0 + k_H[H^+] + k_{OH}k_w/[H^+]$, solved on a 7040 computer which gave values similar to those obtained graphically. However, owing to the low value of H^+ in the neutral and basic regions, the k_H term was emphasized in the computer calculation. Thus the graphical method gives constants which more accurately reproduce the data: $k_0 = (3.12 \pm 0.44) \times 10^{-4}$ sec^{-1}, $k_H = 1.22 \pm 0.03$ M^{-1} sec^{-1}, and $k_{OH} = (2.89 \pm 0.11) \times 10^4$ M^{-1} sec^{-1} at 25° and μ = 0.004–0.12. The ± values represent two standard deviations.[17] The slow rate of solu-

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[17] R. B. Bean and W. J. Dixon, *Anal. Chem.*, **23**, 636 (1951).

TABLE II
RATE OF HYDROLYSIS OF $Co(NH_3)_5OReO_3^{2+}$.
2,6-LUTIDINE EFFECT AT 25° AND $\mu = 0.01$ (NaCl)

[Buffer],[a] M	$t_{1/2}$, min	[Buffer],[a] M	$t_{1/2}$, min
0.000	28.1[b]	0.004	27.0
0.001	28.4	0.008	28.1
0.002	28.2	0.010	28.3

[a] 2,6-Lutidine–hydrochloric acid buffer, pH 3.88–3.72. [b] With no buffer the pH changed during reaction from 3.90 to 3.62.

tion and the faster than usual rate of hydrolysis prevented more precise measurements.

Temperature dependence studies were made at 0, 25, 35, and 50° at pH 6.39, 4.79, and 2.58 (only the three lower temperatures were used in the latter case) at $\mu = 0.10$ (2,6-lutidine–nitric acid). The apparent E_a values were 14.5, 15.9, and 8.2 kcal/mol, respectively. The fractions of reaction carried by the k_0, k_H, and k_{OH} terms at 25° were estimated for each pH: pH 6.39 (0.26, 0, 0.74); pH 4.79 (0.87, 0.08, 0.05); pH 2.58 (0.08, 0.92, 0). In obtaining these values the assumption is made that, at constant pH but at varying temperatures, the relative contribution from each path is constant. Obviously this cannot be the case and so the E_a's can only be given qualitative significance but may be used to calculate the rate at conditions differing from those measured.

The effect of HOAc–OAc^- and H(phthalate)$^-$ is shown in Figure 3. From the pH dependence at constant $[HOAc]_T$, after correction for the rate in the absence of catalyst, the rate constants for the catalytic paths were calculated assuming first-order behavior of both HOAc and OAc^-. Thus for the expression

$$-\frac{d}{dt}[Co(NH_3)_5OReO_3^{2+}] = (k_{HOAc}[HOAc] + k_{OAc^-}[OAc^-])[Co(NH_3)_5OReO_3^{2+}]$$

$k_{HOAc} = 1.53 \times 10^{-1}$ and $k_{OAc^-} = 6.41 \times 10^{-2}\ M^{-1}\ sec^{-1}$ at 25° and $\mu = 0.10$ (LiCl).

The H(phthalate)$^-$ ion is a much more effective catalyst than the acetate system and the rate increases linearly with its concentration. However, at catalyst concentrations approaching zero, curvature is noted and extrapolation of the linear portion to zero concentration gives a value considerably higher than that observed in the absence of catalyst at the same pH. At pH 3.9, 4.1, and 4.6, the observed rate coefficient was constant within experimental error (±5%). For comparison purposes, rate = k_{HPH}[H(phthalate)$^-$][$Co(NH_3)_5OReO_3^{2+}$] may be defined and at pH 4.10, [H(phthalate)$^-$] = 0.01 M, and $k_{HPH} = 2.0\ M^{-1}\ sec^{-1}$. Deviations at low catalyst concentrations may be due to more extensive ionization of the catalyst ion.

In some early runs, measuring the catalytic activity of the above buffers, using the rhenium complex in the chloride form, the A_∞'s deviated from the expected values. This prompted ion-exchange studies on the product ions to discern the presence of acetato- or phthalatocobalt(III) complexes. The problem resolved itself when it was found that $[Co(NH_3)_5OReO_3]Cl_2$ changes in the solid state to $[Co(NH_3)_5Cl](ReO_4)Cl$ and that the starting material contained traces of $(NH_3)_5CoCl^{2+}$. Further ion-exchange studies with the complex ion nitrate showed no (±1%) $(NH_3)_5CoOAc^{2+}$ or the analogous phthalato complex in the reaction products when hydrolysis was carried out at pH 4–5 in 0.1 M acetate or phthalate ion solutions.

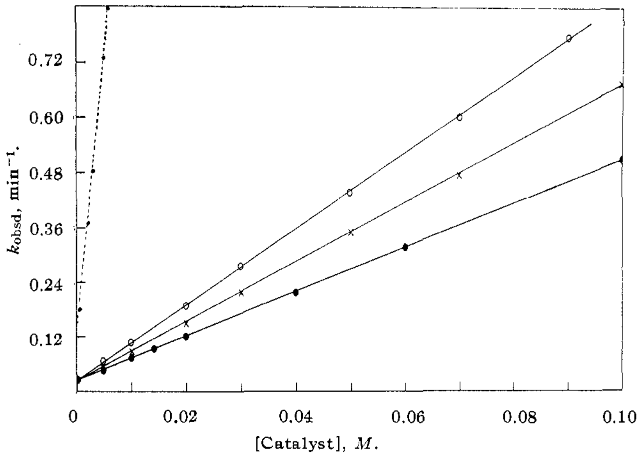

Figure 3.—Observed rate constants of hydrolysis of $Co(NH_3)_5OReO_3^{2+}$ as a function of [catalyst] at 25.0° and $\mu = 0.10$ (LiCl): ——, HOAc + OAc^-; – – – –, H(phthalate)$^-$, pH 4.10. Ratio HOAc:OAc^-: ●, 0.33; ×, 1.0; ○, 3.0.

O^{18}-Transfer Experiments. A. Formation.—Table III gives a representative experiment to discern which oxygens are given off as water when $[Co(NH_3)_5OH_2](ReO^*_4)_3 \cdot 2H_2O$ is warmed under vacuum. The ± values are average deviations of four separate experiments. It is clear from these results that the lattice water does not exchange with ReO_4^- upon dehydration and that at least 98% of the water liberated during ReO_4^- coordination comes from $Co(NH_3)_5OH_2^{3+}$.

TABLE III
O^{18} EXPERIMENTS ON SOLID-STATE CONVERSION OF
$[Co(NH_3)_5OH_2](ReO_4)_3 \cdot 2H_2O$ TO $[Co(NH_3)_5OReO_3](ReO_4)_2$

Material	10^3R_N[a]	% oxygen from ReO_4^-[b]
Std H_2O	4.000	
$NaReO_4$	16.280	
Lattice H_2O	3.927	0.11 ± 0.32
Coord H_2O	4.169	1.4 ± 0.8
$Co(NH_3)_5OReO_3^{2+}$	16.107[c]	

[a] $R_N = 46/(44 + 45)$ for CO_2 normalized to 4.00×10^{-3} for standard CO_2. [b] Average of four determinations; ± values indicate average deviation of the mean. [c] This value when compared with that for $NaReO_4$ suggests that some exchange occurred in the preparation of $[R_5CoOReO_3](ReO_4)_2$.

B. Hydrolysis.—Table IV gives the results of studies designed to determine whether Co–O or Re–O rupture occurs during acid and base hydrolysis of $(NH_3)_5Co–O^*–ReO^*{}_3^{2+}$. A representative run in $10^{-3}\ M\ H^+$ and 0.1 $M\ OH^-$ is given with the ± values representing the average deviation for three separate experiments. Under these pH conditions, ReO_4^- exchanges its oxygens with the solvent too rapidly to permit measurements on it. The results show that Re–O cleavage occurs a minimum of 98% of the time in dilute H^+ or OH^-.

Table V shows the results of experiments conducted in the neutral region (pH 4–7). In this pH range the

TABLE IV

OXYGEN ATOM TRANSFER IN THE HYDROLYSIS OF $[Co(NH_3)_5OReO_3](NO_3)_2$

Species	10^3R_N	% transfer to roseo
Acid Region,[a,b] at 5–10°, $[HClO_4] = 2 \times 10^{-3}$ *M*, [Complex] $= 6 \times 10^{-3}$ *M*		
$Co(NH_3)_5O^*ReO^*{}_3{}^{2+}$	15.681	
$Co(NH_3)_5OH_2{}^{3+}$	15.640	99.6 ± 0.6[c]
Basic Region,[a] at 5–10°, [NaOH] = 0.10 *M*, [Complex] $= 8 \times 10^{-3}$ *M*		
$Co(NH_3)_5O^*ReO^*{}_3{}^{2+}$	16.107	
$Co(NH_3)_5OH_2{}^{3+}$	16.201	100.7 ± 0.8[c]

[a] Conducted in the presence of excess Dowex 1-X4 in the ClO_4^- form to remove ReO_4^-. [b] Solvent water; $R_N = 4.00 \times 10^{-3}$. [c] Average of three determinations; ± values indicate average deviation from the mean.

$t_{1/2}$ for O^{18} exchange of both ReO_4^- and $Co(NH_3)_5OH_2{}^{3+}$ is long, and less than 1% exchange would occur during the time periods involved. Columns six and seven refer to the observed number of oxygens in ReO_4^- or $Co(NH_3)_5OH_2{}^{3+}$ originating from $Co(NH_3)_5ReO_4{}^{2+}$. If complete Re–O fission occurs, the values should be 3 and 1, respectively. The final column is the sum and should have a value of 4 if no perrhenate-complex oxygen is lost to the solvent. Both ReO_4^- and $Co(NH_3)_5OH_2{}^{3+}$ contain appreciable solvent oxygen with the maximum occurring at a pH of about 5. Since this cannot come about *via* water exchange of the products,[6] it must reflect either some Co–O bond breaking or oxygen exchange of the three ReO_4^- oxygens not associated with cobalt, with solvent in $Co(NH_3)_5OReO_3{}^{2+}$, or with both.

TABLE V

OXYGEN TRANSFER IN THE HYDROLYSIS OF $Co(NH_3)_5OReO_3{}^{2+}$ AT 25°, [COMPLEX] = *ca.* 0.01 *M*, AND R_N(SOLVENT) $= 4.0 \times 10^{-3}$

10^3R_N (R_5CoReO_4)	pH	[Buffer],[a] *M*	10^3R_N ($CsReO_4$)	10^3R_N (R_5CoOH_2)	No. of $O^*(ReO_4^-)$[d]	No. of O^*(roseo)[e]	Total[f]
18.84	4.2	0.005	13.52	8.46	2.57	0.57	3.14
18.84	5.5	0.005	12.22	9.70	2.22	0.38	2.60
18.84	5.5	0.005	. . .	10.04	. . .	0.41	. . .
18.84	6.4	0.005	13.98	10.07	2.69	0.41	3.10
18.84	6.9	0.005	14.76	12.24	2.90	0.56	3.46
18.84	4.53	0.1 (OAc^-)	15.74	14.47	3.16	0.71	3.87
15.19[c]	6.9	0.10 (HNO_3)	10.05	. . .	2.16		
18.84[c]	6.5–5	None	11.52	8.13 (7.66)[b]	2.01	0.28	2.29
15.71	5.1	0.05	10.74	7.31	2.30	0.28	2.58

[a] 2,6-Lutidine–hydrochloric acid unless otherwise indicated. [b] Same reaction conducted in the presence of Dowex 1-X4 to remove ReO_4^-. [c] Both ions precipitated directly without chromatographic separation. [d] Number of oxygens of $R_5CoOReO_3{}^{2-}$ retained by ReO_4^-. [e] Number of oxygens retained by $R_5CoOH_2{}^{3+}$. [f] Column six plus column seven. Maximum value 4.0; minimum value 0.

Discussion

All of the experiments described in this paper are in agreement with ReO_4^- coordinated through an oxygen in $(NH_3)_5CoOReO_3{}^{2+}$. The O^{18} results conclusively show that heating $[Co(NH_3)_5OH_2](ReO_4)_3 \cdot 2H_2O$ under vacuum yields H_2O which comes almost exclusively from the roseo ion. It is somewhat perplexing to note that although the Br^-, Cl^-, $SO_4{}^{2-}$, and ReO_4^- salts are dehydrated in this fashion (at about the same conditions), the ClO_4^- salt is not. It seems unlikely that differences in the crystal structure can account for this. If the process were predominantly controlled by water dissociation, the nature of the negative ion should have little effect. Thus we are led to the conclusion that in the solid state the replacement takes place by a concerted action in which the entering group exerts considerable influence. It would seem desirable to do some quantitative studies on the relative ability of negative ions to replace the coordinated water in the solid state.

The rate law for hydrolysis of $Co(NH_3)_5OReO_3{}^{2+}$ is to be expected on the basis of a mechanism involving Re–O fission by comparison with studies on the ReO_4^-–H_2O exchange. The rhenium–oxygen fission is shown to be the primary process in acid and base by the O^{18}-transfer experiments. A comparison of rate constants of aquation for some similar complexes which must involve Co–X fission (Table VI[18]) shows that the ReO_4^- complex behaves differently reflecting this change in mechanism. The acetato complex is constituted similarly to that under consideration; however, it has been shown[19] that dissociation (pH 4–5) occurs predominantly by Co–O fission. The radically different kinetic behavior of these two complexes again suggests a different mechanism.

TABLE VI

RATE CONSTANTS OF HYDROLYSIS IN BASIC AND ACIDIC MEDIA AT 25°[18]

	k_{OH}, M^{-1} sec^{-1}	k_0, sec^{-1}
$(NH_3)_5CoI^{2+}$	23	8×10^{-6}
$(NH_3)_5CoBr^{2+}$	7.5	6×10^{-6}
$(NH_3)_5CoCl^{2+}$	0.85	2×10^{-6}
$(NH_3)_5CoOAc^{2+}$	7×10^{-4}	1×10^{-7}
$(NH_3)_5CoOReO_3{}^{2+}$ [a]	2.9×10^4	3.1×10^{-4}

[a] $k_H = 1.22\ M^{-1}$ sec^{-1}.

The first-order H^+ dependence was anticipated from the ReO_4^-–H_2O exchange rate law which has an $[H^+]^2$ term. For the $[H^+]^2$ term, the $(NH_3)_5Co^{3+}$ entity takes the place of an H^+ and thus for the complex an $[H^+]$ term suffices. Since the acid association constants of ReO_4^- are not known, a direct comparison of $HReO_4$ with $Co(NH_3)_5OReO_3{}^{2+}$ is not possible, but it does appear necessary for two positive-charged ions

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(18) See ref 13, p 164.

(19) C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 1692 (1953).

(2 H^+ or $Co(NH_3)_5^{3+}$ + H^+) to associate before the hydrogen ion path can take place. The rate of acid hydrolysis of $Co(NH_3)_5OReO_3^{2+}$ is greater than the rate of water exchange of ReO_4^- below about 5 M H^+. Thus the $(NH_3)_5Co$– group does weaken the Re–O bond to which it is attached at least kinetically.

Likewise a comparison of the OH^- term for ReO_4^-–H_2O exchange with the hydrolysis constant, values which in this case are both of the same form (k_{OH}(exch) = 2.15×10^{-3} M^{-1} sec^{-1}; k_{OH}(hyd) = 2.89×10^4 M^{-1} sec^{-1} at 25° and $\mu = 0.1$), shows marked enhancement of the rate of Re–O fission due to association with the cobalt ion. Since the O^{18} content of ReO_4^- could not be determined owing to rapid exchange with solvent in basic media, no information as to the coordination number of Re in the transition state is obtained. However, it appears that the hydrolysis is general acid–base catalyzed, and if OAc^- functions similarly to OH^-, then the fact that at pH 4.0 little solvent water is found in the ReO_4^- produced suggests that the coordination number of Re does not rise above 4 during the aquation.

The conclusions reached in the acid and base regions are of significance in the matter of the mechanism of H_2O–ReO_4^- exchange, but this discussion will be made in a paper on ReO_4^-–H_2O exchange in methanol.[20]

The rate constant for the neutral region, k_0, must be taken as an upper limit for the solvent-assisted path. Since the aquation has been shown to be catalyzed by H^+, HOAc, $HPhth^-$, OAc^-, and OH^-, and qualitative measurements suggest most other acids or bases behave in a like manner, it is not unreasonable to expect $(NH_3)_5CoOH_2^{3+}$ and $(NH_3)_5CoOH^{2+}$, which are reaction products, to raise the apparent rate. This may account for the low precision in the neutral region where this catalysis would be most easily seen. Since only a small portion of the reaction appears to be carried by this path, deviations from first-order behavior would be small and would be within the error limits of the optical measurements.

A comparison of the catalytic effectiveness of various ions and molecules on the hydrolysis rate can be made from the following second-order constants for the species given: OH_2, 5.7×10^{-6}; H^+, 1.2; HOAc, 0.15; OH^-, 2.9×10^4; OAc^-, 0.064; $H(phthalate)^-$, 2.0. The values for the most part parallel those obtained for the $Cr_2O_7^{2-}$ hydrolysis,[21] showing, however, a higher sensitivity to reagent basicity.

Interpretation of the O^{18}-transfer measurements in the neutral region is complicated by the fact that of necessity the time of contact between $Co(NH_3)_5OReO_3^{2+}$ and water varies with the rate of reaction. This is dependent on the pH which is related to the fraction of reaction carried by the k_0, k_H, and k_{OH} terms. The results suggest that (a) the k_H and k_{OH} rate terms occur predominantly with Re–O bond breaking and little ReO_3–H_2O exchange and (b) extensive complex oxygen exchange occurs with the solvent when the k_0 path predominates. The latter may occur by an expansion of the coordination number of Re during the solvent-assisted aquation or by H_2O-oxygen exchange with the three Re oxygens not associated with Co. Further studies in the neutral region are contemplated.

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[20] R. K. Murmann, to be submitted for publication.

[21] Summarized in ref 13.