Table II. Positional Functions of Perturbing Methyls in Δ-*cis*-Co(*cis,cis*-Metach)$_2$$^{3+}$ Ion

Function	$CH_3(1)$	$CH_3(2)$
XY	+6.6	+6.6
$X(X^2 - Y^2)$	−9.4	−9.4
XZ	+6.6	+8.4
$X(Z^2 - X^2)$	+9.4	0
YZ	+8.4	+6.6
$X(Y^2 - Z^2)$	0	+9.4

groups outside of the octahedral [ML_6] chromophore. This is exactly the case that *cis*-Co(Metach)$_2$$^{3+}$ ion represents; the ion has a plane of symmetry except for the skew position of the methyl groups.

Convenient use of Richardson's sector rules requires approximate values for the cartesian positional coordinates of the perturber sites. The estimated coordinates[19] of $CH_3(1)$ on the right-coordinate system defined in Figure 3 are (2.27, 2.90, 2.90). $CH_3(2)$ has coordinates (−2.90, −2.27, −2.90), for the Δ isomer. The signs and approximate magnitudes of the various necessary positional functions are given in Table II.

The sign of the sum of the applicable pair combinations (XY with $Z(X^2 - Y^2)$, XZ with $Y(Z^2 - X^2)$, and YZ with $X(Y^2 - Z^2)$) is positive. This predicts positive net rotatory power in the $^1A_{1g} \rightarrow {}^1T_{1g}$ region for the Δ enantiomer's CD spectrum and, of course, implies that the enantiomer isolated in this study is the Λ-*cis*-Co(*cis,cis*-Metach)$_2$$^{3+}$ ion.

Along another line, Hawkins'[20,21] octant rule is not really intended for a case of this type and naturally gives a zero octant sign for the sum of the contributions of all atoms except the two methyl groups. However, considering the methyl groups, the octant sign for the Δ enantiomer is negative and the octant sign for the Λ enantiomer is positive. This again predicts positive rotational strength for the Δ enantiomer and negative rotational strength for the Λ enantiomer in the $A_1 \rightarrow A_2$ transition.

Acknowledgment. The help of Steve S. Breitweiser in recording the PMR spectra is gratefully acknowledged.

Registry No. 2,4,6-Trinitrotoluene, 118-96-7; 2,4,6-triacetaminotoluene, 55470-90-1; *cis*-1(e)-methyl-2(e),4(e),6(e)-triacetaminocyclohexane, 55470-91-2; *cis*-1(e)-methyl-2(e),4(e),6(e)-triaminocyclohexane trichloride, 55470-92-3; bis(1(a)-methyl-2(a),4(a),6(a)-triaminocyclohexane)cobalt(III) chloride, 55493-48-6; (−)$_{589}$-*cis*-Co(Metach)$_2$Cl$_3$, 55528-70-6.

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(19) These coordinates are estimated by bond vector calculations using the following typical values of bond distances and angles: Co–N, 1.95 Å; C–N, 1.47 Å; C–C, 1.54 Å; N–Co–N, 90.0°; Co–N–C, 109.5°; N–C–N, 109.5°; C–C–C, 109.5°.
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Kinetic Isotope Effects in Reductions of Cobalt(III)–Pentaammine Complexes

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Deuterium isotope effects arising in the rates of reduction of Co^{III}(NH$_3$)$_5$L complexes have been studied. Only the ammine ligands of the cobalt(III) were deuterated. Ratios of k_H/k_D have been determined for L = OH$^-$, CN$^-$, SCN$^-$, N$_3$$^-$, pyridine, nicotinamide, isonicotinamide, 4-pyridinecarboxylic acid, acetate ion, and fumarate ion. Reductions by Cr^{2+} and V^{2+} have been included. Ratios of k_H/k_D near unity are consistent with a chemical mechanism for the Cr^{2+} reductions of the isonicotinamide, 4-pyridinecarboxylic acid, and fumarate complexes. Ratios of k_H/k_D near unity are consistent with substitution-limited reductions for V^{2+} reductions of the azido and isonicotinamide complexes.

Comparisons of the rate of reduction of a pentaamminecobalt(III) complex and the corresponding ammine-deuterated pentaamminecobalt(III) complex are made in this study. Cr^{2+} and V^{2+} are used as reducing agents. It was expected that the k_H/k_D ($k_{Co^{III}(NH_3)_5X}/k_{Co^{III}(ND_3)_5X}$) ratios would be valuable criteria in distinguishing certain types of mechanisms. The mechanisms of several of the present systems were known from previous studies. The results of these can be used to calibrate the k_H/k_D ratios.

It is a well-known consequence of the Franck–Condon principle that the inner coordination shells of both metal centers must undergo a reorganization prior to electron transfer, such that the energy of the system is unchanged in the actual electron-transfer step. For most electron-transfer reactions this adjustment of bond lengths about the metal centers and the accompanying polarization of solvent molecules is the rate-determining process.[2] In such cases, an isotopic change in the inner coordination shell of either reactant would change the energy requirements of activation and thereby give rise to a kinetic isotope effect. Such an isotope effect has been observed in nitrogen[3] and oxygen[4] isotopic fractionation experiments, which make use of the natural isotopic abundances of either nitrogen or oxygen. A comparison of the reduction rates of the ammine-deuterated and undeuterated pentaamminecobalt(III) complexes is a convenient technique because the deuterated complexes are readily prepared from their corresponding undeuterated complexes. A k_H/k_D ratio is expected to be greater than one when reorganization about cobalt(III) is part of the activation process.

Zwickel and Taube[5] have previously examined this k_H/k_D

type of isotope effect for the outer-sphere reduction of hexaamminecobalt(III) and aquopentaamminecobalt(III) by $Cr(bipy)_3^{2+}$. They observed an isotope effect for the former system, but none for the latter. Zwickel and Taube[6a] also studied the inner-sphere chromium(II) reduction of the aquopentaamminecobalt(III) complex in D_2O and found no k_H/k_D isotope effect.[6b]

In electron-transfer reactions where reorganization about the cobalt(III) center is not the rate-determining process, a ratio near 1 is expected. As a consequence, the k_H/k_D ratio obtained for a particular system can give valuable information, and the results obtained here are discussed in terms of reaction mechanisms.

Experimental Section

Reagents. Water redistilled from alkaline permanganate was used for all solutions. $LiClO_4 \cdot 3H_2O$ (G. F. Smith Co.) was recrystallized before use. Stock solutions of $Cr(ClO_4)_3$ were prepared by reducing primary standard grade $K_2Cr_2O_7$ with H_2O_2 in aqueous perchloric acid. Vanadyl perchlorate was prepared by treating $VOSO_4$ with ammonium carbonate and redissolving the precipitate in perchloric acid as described by Rossotti and Rossotti.[7] $Cr(ClO_4)_2$ and $V(ClO_4)_2$ solutions were prepared by reducing acidic $Cr(ClO_4)_3$ and $VO(ClO_4)_2$ solutions over amalgamated zinc in an atmosphere of nitrogen.

Preparation of Pentaamminecobalt(III) Complexes. Perchlorate salts of the following complexes were prepared by methods previously described: nicotinamidepentaamminecobalt(III),[8] isonicotinamidepentaamminecobalt(III),[8] acetatopentaamminecobalt(III),[9] fumaratopentaamminecobalt(III),[10] 4-pyridinecarboxylatopentaamminecobalt(III),[11] and cyanopentaamminecobalt(III) perchlorate.[12] For reasons that we do not understand, the first step of the latter preparation was not always successful.

Aquopentaamminecobalt(III) perchlorate was prepared by treating the carbonatopentaammine nitrate[13] with a large excess of perchloric acid and recrystallizing from perchloric acid several times. Isothiocyanatopentaamminecobalt(III) perchlorate was prepared by Werner's method[14] except that the perchlorate salt of aquopentaammine was used in place of the sulfate. Azidopentaamminecobalt(III) perchlorate was prepared from the corresponding chloride salt[15] by treatment with silver perchlorate solution, filtration, and crystallization from a reduced volume.

Pyridinepentaamminecobalt(III) perchlorate was prepared by a modification of the method described by Nordmeyer and Taube.[8] To 26 ml of *N,N*-dimethylformamide and 40 ml of pyridine was added 6 g of $[Co(NH_3)_5OH_2](ClO_4)_3$. The solution was maintained at 100° for about 30 min. It was then cooled and maintained at room temperature as 80 ml of water and then 80 g of NaI were added. After cooling of the solution in ice, the yellow crystals were collected and washed with anhydrous ethyl ether. The crude iodide salt was recrystallized from an acidic solution by adding a few drops of perchloric acid followed by about 80 g of NaI. The iodide salt of pyridinepentaamminecobalt(III) is light sensitive, and solutions or wet crystals of the salt were kept in the dark when possible. The recrystallized iodide salt was converted to the perchlorate salt by successive crystallizations from perchloric acid solutions.

Preparation of Ammine-Deuterated Pentaamminecobalt(III) Complexes. Cobalt ammines are known to undergo hydrogen exchange which is first order in hydroxide ion.[16] It was therefore convenient to prepare the deuterated forms of the above pentaamminecobalt(III) complexes directly from the hydrogen form.

The hydrogen form of the complex was dissolved in D_2O (Bio-Rad Laboratories with enrichment of 99.89% or higher) and the pH of the solution was adjusted to about 8 (universal pH paper) with anhydrous sodium carbonate. Exposure of the solution to the air was avoided in order to minimize the incorporation of H_2O from atmospheric water vapor. After allowing more than sufficient time for the exchange (usually about 1.5 hr), the salts were recovered by adding the D_2O solution to about 1–3 times its volume of 70% perchloric acid with mixing. The collected crystals were washed with either absolute methanol or ethanol, sometimes followed by anhydrous ethyl ether, then air-dried, and finally dried in the vacuum desiccator.

The deuterated nicotinamide-, isonicotinamide-, aquo-, fumarato-, and 4-pyridinecarboxylatopentaamminecobalt(III) complexes were each recrystallized from a perchloric acid solution in normal water to convert the labile hydrogen(s) on the sixth ligand to light hydrogen(s). In the above deuteration procedure, crystals usually formed immediately upon contact of the D_2O solution with perchloric acid solution. Therefore, the percent deuteration of the labile hydrogens was not known. The number of ammine deuterium atoms could most easily be determined from microanalytical results when the labile hydrogens were known to be undeuterated. This recrystallization was also done for the deuterated cyano complex where it was thought that the crystal contained half a water of hydration per cobalt.

Preparation of *trans*-$[Co(NH_3)_4(ND_3)O_2CCH_3](ClO_4)_2$. It is known that for the fumaratopentaamminecobalt(III) complex the rate constant for the hydrogen exchange is about 2 orders of magnitude greater for the trans ammine than for the cis ammines.[17] By proper buffering and timing it was possible to deuterate the trans-ammine hydrogens of the acetato complex and leave the cis-ammine hydrogens predominantly in the light form.

A buffer was prepared by dissolving anhydrous sodium acetate in D_2O and adding the required amount of glacial acetic acid (anion:acid = 4.2:1; acetate concentration 0.4 *M*). The hydrogen form of acetatopentaamminecobalt(III) perchlorate was dissolved in a minimum of the buffered D_2O solution, and the solution was kept at 21°. After 95 min the trans-deuterated acetate salt was recovered by adding the D_2O solution to 70% perchloric acid. The above time was determined by trial and error using NMR spectra to determine the extent of cis and trans deuteration.

Analyses. Elemental analyses for carbon, nitrogen, cobalt, total hydrogen, and atom percent of excess deuterium were done on the deuterated complexes by Josef Nemeth of Urbana, Ill. From the results of these analyses the number of D atoms per molecule for each deuterated oxidant was calculated. For all compounds the theoretical value for the number of D atoms per molecule was 15.

Perchlorate concentration was determined by the method of Gould and Taube[18] as modified by Deutsch and Taube.[19]

The concentration of vanadium in the stock vanadyl perchlorate solutions was determined by first oxidizing the vanadium(IV) to vanadium(V) with $KMnO_4$ solution and then titrating the vanadium(V) with standard Fe(II) solution using diphenylaminesulfonic acid as indicator.

Apparatus. Spectrophotometric measurements were made on a Cary 14 recording spectrophotometer. Cells containing kinetic runs were immersed in a constant-temperature water bath within the Cary cell compartment.

NMR spectra were taken on a JOELCO C-60HL.

Preparation of Reaction Mixtures. Solutions with oxygen-sensitive reductants ($Cr(ClO_4)_2$ or $V(ClO_4)_2$) were prepared, stored, transferred, and used in a nitrogen atmosphere. In most cases this was accomplished by using a syringe and serum-stoppered vessels. Slower reactions were studied by transferring and isolating solutions with glass fixtures only.

The ionic strength of reaction mixtures was adjusted to 1.00 *M* with $LiClO_4$ solution.

All reactions were done in H_2O. In each case the solid oxidant was added to an acidic solution to dissolve. This was done to prevent the exchange of the ammine hydrogens in the deuterated complexes. For uniformity, this procedure was followed for the undeuterated complexes as well. Reaction mixtures for the deuterated and undeuterated oxidants were prepared from the same stock solutions and from the same diluted stock reductant. Deuterated and undeuterated runs were done alternately.

Treatment of Data. The reactions studied were all known to be second-order reactions which are first order in oxidant and first order in reductant. All of these reactions were followed spectrophotometrically at the wavelength maximum of the cobalt(III) complex. The spectrophotometric data from the first- and second-order runs were handled in the usual way.[8]

Most of the second-order data as well as plots of rate constants vs. a function of acid concentration were treated with the Wang 700 linear regression analysis program and plotter (program no. 1010GC/ST3).

The ratio of rate constants was evaluated for each redox system. This ratio is naturally dependent on the deuterium enrichment of the deuterated complex and therefore all of the calculated ratios were corrected to represent the ratio where the deuterated complex has 15 ammine deuteriums. In order to make this correction it was necessary to know the number of D atoms per molecule for each deuterated oxidant. It was assumed for this correction that the isotope effect was additive and that each deuterium atom contributed an equal

Table I. Summary of k_H/k_D Ratios for the Chromium(II) Reductions of Pentaamminecobalt(III) Complexes[a]

Ligand[b]	D atoms/ molecule	k_{lit},[c] M^{-1} sec^{-1}	k_H,[c] M^{-1} sec^{-1}	k_D,[c] M^{-1} sec^{-1}	k_H/k_D[c]
Pyridine	14.23	4.0×10^{-3} [h]	$(3.79 \pm 0.03) \times 10^{-3}$	$(2.61 \pm 0.04) \times 10^{-3}$	1.48 ± 0.03
Pyridine	12.01		$(3.80 \pm 0.02) \times 10^{-3}$	$(2.73 \pm 0.02) \times 10^{-3}$	1.51 ± 0.01
Nicotinamide	13.02	4.9×10^{-2} [h]	$(4.76 \pm 0.02) \times 10^{-2}$	$(3.45 \pm 0.07) \times 10^{-2}$	1.45 ± 0.03
Isonicotinamide	12.59	17.4[h]	16.4 ± 1.3	15.5 ± 1.9	1.07 ± 0.16
Isonicotinamide	12.5		18.8 ± 1.4	17.1 ± 0.6	1.12 ± 0.09
4-Pyridinecarboxylato	14.02				
Acid-independent path (k_0)		1.3[i]	0.999 ± 0.008	0.907 ± 0.011	1.11 ± 0.02
Inverse-acid path (k_{-1})		2.5×10^{-2} [d, i]	$(1.06 \pm 0.25) \times 10^{-2}$ [d]	$(1.01 \pm 0.34) \times 10^{-2}$ [d]	1.05 ± 0.43
Fumarato	13.82				
Acid-independent path (k_0)		1.6[j]	1.69 ± 0.04	1.37 ± 0.04	1.26 ± 0.05
Acid path (k_1)		4.0[e,j]	3.40 ± 0.08[e]	3.34 ± 0.08[e]	1.02 ± 0.03
Hydroxo	13.58[f]	3.1[f,k]	2.48 ± 0.09[d,f]	2.06 ± 0.10[d,f]	1.58 ± 0.10
Cyano	12.54	35.8[l]	71.3 ± 1.2	53.4 ± 4.2	1.41 ± 0.11
Isothiocyanato	13.96	19[m]	15.0 ± 0.3	11.4 ± 0.5	1.34 ± 0.07
Acetato	13.28	0.28[n]	0.293 ± 0.006	0.207 ± 0.002	1.48 ± 0.03
Acetato	3.564[g]		0.302 ± 0.002	0.270 ± 0.012	1.60 ± 0.07

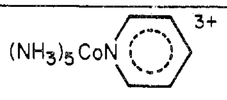
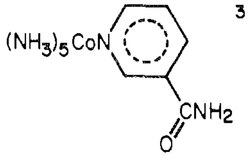
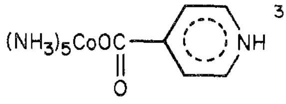
[a] All reactions were done at 25°; ionic strength was 1.00 *M* unless otherwise noted. The k_H/k_D ratios have been corrected to represent an isotope effect where the enrichment of the deuterated complex is 15 D atoms/molecule. [b] The oxidant is the pentaamminecobalt(III) complex of this ligand. [c] Error limit is the standard deviation. [d] Units sec^{-1}. [e] Units M^{-2} sec^{-1}. [f] Kinetics done on the aquopentaamminecobalt(III) complex. The enrichment is that reported for the aquo complex. The rate constants are those for the inverse acid path. [g] D atoms predominantly on the ammine trans to the acetate. [h] Reference 8; R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966); E. S. Gould, *J. Am. Chem. Soc.*, **87**, 4730 (1965). [i] Reference 20. [j] J. K. Hurst and H. Taube, *J. Am. Chem. Soc.*, **90**, 1178 (1968). An earlier value is reported in ref 9. [k] Reference 21. An earlier value is reported in ref 6a. [l] Reference 22. Ionic strength was 0.150 *M*. The difference in ionic strength accounts for the difference between k_{lit} and k_H. [m] Reference 23. [n] M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971). Rate constant evaluated at $(H^+) = 0.65$ *M*.

share (a multiplicative factor) to the isotope effect. For a deuterated complex with *n* D atoms/molecule, the expression below was used to calculate the k_H/k_D ratio for 15 ammine D atoms

$$(k_H/k_D)_{\text{for 15 D atoms}} = (k_H/k_D)^{15/n}{}_{\text{for } n \text{ D atoms}}$$

All k_H/k_D ratios reported in the following sections are isotope effects for 15 D atoms. The error limit with each of these ratios is the standard deviation.

Table II. Structural Formulas of Selected Oxidants

Ligand	Pentaamminecobalt(III) complex
Pyridine	
Nicotinamide	
Isonicotinamide	
4-Pyridinecarboxylato	

Results

For each system studied at least two or three kinetic runs were done on both the deuterated and undeuterated complexes, and sometimes as many as nine or ten runs on each were done. When reactions were followed at several different acid concentrations, then at least two runs were done at each acid concentration.

Reductions of isothiocyanatopentaamminecobalt(III) were carried out using stock solutions of the isothiocyanato complex made in dilute acid. Aliquots of the stock solutions were used for the kinetic runs. This was done because of the difficulties in dissolving the solid cobalt complex directly in the reaction cell where the perchlorate concentration was about 1 *M*.

Chromium(II) Reductions. The results for the chromium(II) reductions are summarized in Table I. Previously reported rate constants are listed in the third column for comparison with k_H. Structures of selected cobalt complexes are shown in Table II.

The reduction of the pyridinepentaamminecobalt(III) complex was studied on two different samples of deuterated complex: one had the lowest deuterium enrichment of all the complexes studied; the other had the highest enrichment. The results for the two samples agree within experimental error.

Many runs for the chromium(II) reduction of the isonicotinamide complex were done in an attempt to reduce the scatter in the results. No apparent reason was found for this lack of precision. The runs were done on two different deuterated complexes of about the same deuterium enrichment.

The rate law for the chromium(II) reduction of the 4-pyridinecarboxylatopentaamminecobalt(III) complex is known to be of the form[20] rate = $[k_0 + k_{-1}(H^+)^{-1}][(Co^{III})(Cr^{2+})]$. It had also been observed that 4-pyridinecarboxylic acid and the carboxyl-bound chromium(III) complex of this acid (one product in the above reduction) act as catalysts in several redox reactions. The catalysis rate law was shown to have a term proportional to $(H^+)^{-1}$ and one proportional to $(H^+)^{-2}$.[24] In the present study of the chromium(II) reduction of the 4-pyridinecarboxylatopentaamminecobalt(III) complex an acid range of 0.20–0.96 *M* was chosen in order that the acid concentration be high enough to avoid interference from autocatalysis. A plot of k_{obsd} vs. $1/(H^+)$ using four acid concentrations was found to be linear for both the deuterated and undeuterated complexes. Values of k_0 and k_{-1} are listed in Table I.

The chromium(II) reduction of the fumaratopentaamminecobalt(III) complex has a three-term rate law, one term independent of acid, one inverse in acid, and the third first order in acid.[9] The inverse acid path, however, appears only at acidities below 0.01 *M*. In this work the reaction was studied in an acid range of 0.1–0.9 *M* thus reducing the k_{obsd} to $[k_0 + k_{-1}(H^+)]$. For both the deuterated and undeuterated sets of reactions, the plot of k_{obsd} vs. (H^+) using four acid concentrations was found to be linear. The values of k_0 and k_{-1} are listed in Table I.

The reductions of both the deuterated and undeuterated aquopentaamminecobalt(III) complexes were followed at several different acid concentrations. For each complex the

Table III. Summary of k_H/k_D Ratios for the Vanadium(II) Reductions of Pentaamminecobalt(III) Complexes[a]

Ligand[b]	D atoms/ molecule	k_{lit}, M^{-1} sec^{-1}	k_H,[c] M^{-1} sec^{-1}	k_D, M^{-1} sec^{-1}	k_H/k_D[c]
Pyridine	14.23	0.24[d]	0.253 ± 0.002	0.171 ± 0.003	1.51 ± 0.03
Pyridine	12.01		0.252 ± 0.005	0.175 ± 0.002	1.57 ± 0.03
Nicotinamide	13.02		2.18 ± 0.02	1.58 ± 0.06	1.44 ± 0.06
Isonicotinamide	12.5		3.98 ± 0.04	3.53 ± 0.06	1.16 ± 0.02
Aquo	12.82	0.533[e]	0.549 ± 0.004	0.380 ± 0.006	1.54 ± 0.03
Azido	13.49	13[f]	11.6 ± 0.3	11.1 ± 0.3	1.04 ± 0.04
Isothiocyanato	13.96	0.3[f]	0.253 ± 0.003	0.183 ± 0.006	1.41 ± 0.05

[a] All reactions were done at 25°; ionic strength was 1.00 M. The k_H/k_D ratios have been corrected to represent an isotope effect where the enrichment of the deuterated complex is 15 D atoms/molecule. [b] The oxidant is the pentaamminecobalt(III) complex of this ligand. [c] Error limit is the standard deviation. [d] Reference 26. [e] Reference 27. [f] Reference 23.

plot of k_{obsd} vs. $1/(H^+)$ was found to be linear, and k_0 and k_{-1} were evaluated according to the expression $k_{obsd} = k_0 + k_{-1}(H^+)^{-1}$. For the undeuterated aquo complex the values found for k_0 and k_{-1} are 0.29 ± 0.27 M^{-1} sec^{-1} and 2.48 ± 0.09 sec^{-1}, respectively. For the deuterated complex k_0 and k_{-1} are 0.33 ± 0.29 M^{-1} sec^{-1} and 2.06 ± 0.10 sec^{-1}, respectively. In accordance with the work of Toppen and Linck[21] the acid independent term, k_0, probably arises from a medium effect. Therefore, only the inverse-acid path was considered for evaluating a k_H/k_D ratio. This ratio, based on the above values of k_{-1}, is 1.23 ± 0.07.

The hydroxo ligand acts as the bridging ligand in the inverse-acid path for reduction. It was therefore of interest to know the k_H/k_D ratio for the chromium(II) reduction of the hydroxopentaamminecobalt(III) complex. The rate constant for the hydroxo complex reduction is related to that for the inverse-acid aquo reduction by the expression

$$k_{OH} = k_{-1}/K$$

where K is the equilibrium constant for the equilibrium

$$Co(NH_3)_5OH_2{}^{3+} + H_2O = Co(NH_3)_5OH^{2+} + H_3O^+$$

K can be expected to have a somewhat altered value for the ammine-deuterated complexes. Tobias et al.[25] determined the equilibrium constants for the reactions

$$Co(NH_3)_5OD_2{}^{3+} + D_2O = Co(NH_3)_5OD^{2+} + D_3O^+ \quad (1)$$

$$Co(ND_3)_5OD_2{}^{3+} + D_2O = Co(ND_3)_5OD^{2+} + D_3O^+ \quad (2)$$

The ratio of the equilibrium constants, K_D/K_H, where K_D is for eq 2 and K_H is for eq 1, is 1.29. The magnitude of the isotope effect K_D/K_H would be expected to be nearly the same in H_2O as it is in D_2O. The rate constant ratio, k_H/k_D, for the chromium(II) reduction of the hydroxopentaamminecobalt(III) complex is then 1.58 ± 0.10.

In the study of the chromium(II) reduction of the trans-ammine-deuterated acetatopentaamminecobalt(III) complex it was necessary to demonstrate first that the cobalt complex was essentially only trans deuterated. Proton magnetic resonance spectra of the undeuterated and of the trans-ammine-deuterated acetato complex were obtained in DMSO-d_6 solutions made acidic with DCl. From the integration and on the basis of the methyl group having three hydrogens in each complex, about 12% of the trans-ammine hydrogens (0.36 atom) and about 88% of the cis-ammine hydrogens (10.6 atoms) were not deuterated in the trans-ammine-deuterated complex. The NMR spectra predict a deuterium enrichment of about 4.0 D atoms/molecule found. From the analyses enrichment result and the NMR spectra it is concluded that the trans-ammine hydrogens were essentially deuterated and that the cis-ammine hydrogens were predominantly undeuterated in this trans-ammine-deuterated complex.

The kinetics for the chromium(II) reduction of the trans-ammine-deuterated complex was done at the same acid concentration as for the totally deuterated and undeuterated complexes. The k_H/k_D ratio, again adjusted to represent the ratio for an enrichment of 15 D atoms/molecule, is 1.60 ± 0.07.

Vanadium(II) Reductions. The results for the vanadium(II) reductions are summarized in Table III. Previously reported rate constants are listed in the third column for comparison with k_H. For the azidopentaamminecobalt(III) complex it was known that the complex had a relatively large extinction coefficient at its visible region maximum (ϵ_{520} 265 cm^{-1} M^{-1})[23] and that the solutions of the complex were light sensitive.[15] In order to use low concentrations of cobalt without weighing out very small quantities of solid, fresh stock solutions of the azido complexes in dilute acid were prepared and aliquots of these were used for the kinetics. Because of its light sensitivity, solutions of the complex were kept out of direct light during all preparations.

Discussion

Chromium(II) Reductions. The observed k_H/k_D ratios for Cr^{2+} reductions range from 1.0 to about 1.6. Among those complexes with a large isotope effect are the pyridine complex, known to have an outer-sphere mechanism, and the acetate, nicotinamide, and hydroxo complexes, known to have predominating inner-sphere paths. It appears that the activation process at cobalt(III), as sensed by the ammine ligands, is similar for these inner- and outer-sphere reactions. This is to be expected since the reorganization requirement about cobalt(III) obtains in either case.

The low k_H/k_D ratio for the isonicotinamide complex compared to, say, the acetato or nicotinamide complex suggests that activation at the cobalt center is important to a lesser degree in its Cr^{2+} reduction. This is in agreement with the previous suggestion[8] that in this case the chemical mechanism obtains, where electron transfer from Cr^{2+} to the isonicotinamide ligand is the primary activation process. It would not be proper, however, to draw this conclusion without investigating another alternative.

In the formation of the precursor complex the reductant ion and its coordination sphere may displace water molecules from the second coordination shell and more distant coordination shells of the cobalt(III) ion. Since the water molecules of the second coordination shell of cobalt(III) are undoubtedly hydrogen bonded to the cobalt(III) ammine groups, an isotope effect in the precursor formation step can arise when the NH_3 groups are replaced by ND_3. The k_H/k_D ratio may be low for the isonicotinamide complex, compared to the acetato and nicotinamide complexes, simply because the more distant position of attack diminishes the precursor isotope effect. That this is not the case is inferred by the result for the 4-pyridinecarboxylato complex, where attack at the adjacent carboxyl is known to occur[18] and the isotope effect is only 11%. This sets the upper limit for k_H/k_D arising from the precursor formation step for a carboxylato complex and any other complex with a more distant site of Cr^{2+} attack.

It seems reasonable to conclude, therefore, that the low ratios for the isonicotinamide, the 4-pyridinecarboxylato, and the protonated fumarato complexes indicate little activation at the cobalt center, presumably because a chemical mechanism obtains. This supports previous conclusions for these systems.[8,18,28] The small ratio for the 4-pyridinecarboxylato inverse-acid path also agrees with the proposal for a chemical mechanism, but the error limit prohibits valid interpretation.

Conversely, the relatively high k_H/k_D for the acetato complex agrees with the previous conclusion[29] that a chemical mechanism is ruled out for the reduction of the acetato complex by Cr^{2+}. A resonance-transfer mechanism in which both metal centers undergo simultaneous activation would account for the acetato reduction. This type mechanism is also indicated for the reduction of the nicotinamide complex, for which no previous conclusion has been drawn.

The remaining complexes were included in this study to test the effect of the length of the bridging ligand upon the k_H/k_D ratio. Examination of molecular models[30] shows that the cobalt–chromium distance in the bridged activated complex increases along the following series: hydroxo (a one-atom bridge[4d]), acetato (with chromium at the carbonyl oxygen as indicated by a variety of experiments[31]), cyano (a two-atom bridge[22,32]), and isothiocyanato (a three-atom bridge[33]). With the latter complex especially, where various orientations are possible, the orientations giving the longer cobalt–chromium distances are assumed to be representative. For all of these complexes the chemical mechanism can be excluded on the same basis as has been done for the acetato.[29] Reference to the k_H/k_D ratios for these complexes shows an inverse correlation with the cobalt–chromium distance. This suggests that the formation of the precursor complex does make a contribution to the overall isotope effect. As would be expected, this effect is greatest for the hydroxo complex where the second coordination sphere of cobalt(III) would be disrupted to the greatest extent by the close approach of chromium. The observation that the isotope effect for the acetato complex is not as great as for the hydroxo complex serves as further evidence that Cr^{2+} attacks the carbonyl oxygen of acetato and not the lead-in oxygen.

The k_H/k_D ratio for the fumarato complex, 1.26 ± 0.05, is small compared to the ratios for the complexes discussed above where a chemical mechanism is unlikely and is larger than the ratios for complexes for which the chemical mechanism seems likely. Although the magnitude of the error range weakens this interpretation, the results for the fumarato complex can be understood in terms of a chemical mechanism in which the binuclear radical intermediate is present in a steady-state equilibrium. The chemical mechanism for the fumarato complex

$$(NH_3)_5Co^{III}fum + Cr^{2+} \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} (NH_3)_5Co^{III}f\dot{u}mCr^{III}$$

$$(NH_3)_5Co^{III}f\dot{u}mCr^{III} + 5H^+ \xrightarrow{k_b} Co^{2+} + fumCr^{III} + 5NH_4^+$$

would be expected to give a k_H/k_D ratio nearly equal to 1 if electron transfer to fumarato (step a) were rate determining ($k_{-a} << k_b$) because activation of the cobalt atom is unnecessary in this activation process. However, if k_{-a} becomes nearly equal to k_b (the radical intermediate returns to reactants nearly as often as it goes on to products), then a larger k_H/k_D ratio will appear because activation of the cobalt center is involved in step b. Perhaps the fumarato radical, being more reactive than its protonated form (which is stabilized by an additional positive charge), discriminates to a smaller extent between reducing cobalt(III) (step –a) and reducing chromium(III) (step b). Hence the fumarato complex would give a larger k_H/k_D ratio than its protonated form.

The trans-deuterated acetato complex gives a ratio (extrapolated to 15 deuterium atoms) which is almost within experimental error of the deuterated acetato complex. This result is in agreement with the finding of Green, Schug, and Taube[3] that $^{14}N-^{15}N$ fractionation is comparable in the cis and trans ammines in other pentaamminecobalt(III) reductions. This result does serve to provide further evidence that precursor formation does not give rise to a predominant k_H/k_D contribution in the Cr^{2+} reduction of carboxylato complexes. For steric reasons, such a contribution would involve the cis much more than the trans ammines and this is contrary to the observations.

Vanadium(II) Reductions. The observed k_H/k_D ratios for V^{2+} reductions range from about 1.54 to 1.04. For the pyridinepentaamminecobalt(III) system the nature of the oxidant demands that it react by an outer-sphere mechanism. The k_H/k_D ratio obtained for the pyridine is 1.54. The same ratio is obtained for the aquopentaamminecobalt(III) reduction, also thought to go by an outer-sphere mechanism.[4c,27]

In many inner-sphere reductions by vanadium(II), substitution to form the precursor complex rather than reorganization about the two metal centers is rate determining. When formation of the precursor complex is the rate-determining step of the redox reaction, a k_H/k_D ratio near 1 would be expected, since the Co^{III} undergoes no activation in the rate-determining step. Based on the indirect criteria of rate constants and activation parameters,[2] Price and Taube[34] suggested that the vanadium(II) reduction of the azidopentaamminecobalt(III) complex proceeds by an inner-sphere substitution-controlled mechanism. More recently, Hicks, Toppen, and Linck[35] have directly observed the inner-sphere product, VN_3^{2+}, of this reaction. The k_H/k_D ratio obtained for this system, 1.04, is in accord with the substitution-controlled nature of this reaction.

It has been proposed that the vanadium(II) reduction of the nicotinamide- and isonicotinamidepentaamminecobalt(III) complexes proceed in part by substitution-controlled inner-sphere paths as well as outer-sphere paths.[36] This proposal is based on the activation parameters and an analysis of solvent isotope effects for the reactions. The activation parameters for the isonicotinamide reaction are in good agreement with the values to be expected of a substitution-controlled reaction. The k_H/k_D ratios obtained for these two systems give concurring information. A pure outer-sphere path would give rise to a k_H/k_D ratio similar to that for the pyridine system, 1.54. The k_H/k_D ratio of 1.44 for the nicotinamide system can be associated with a major contribution from an outer-sphere path. For the isonicotinamide system, a small outer-sphere contribution to the overall reaction would explain why the ratio obtained (1.16) is larger than that observed (1.04) for a purely inner-sphere substitution-controlled reaction.

The mechanism for the vanadium(II) reduction of the isothiocyanatopentaamminecobalt(III) complex has not been directly established. The rate constant (0.253 M^{-1} sec^{-1}) is too low for this to be a substitution-controlled process, and the k_H/k_D ratio of 1.41 for this system also indicates that it is not substitution controlled.

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Registry No. Pyridinepentaamminecobalt(III), 31011-67-3; nicotinamidepentaamminecobalt(III), 50578-27-3; isonicotinamidepentaamminecobalt(III), 46372-30-9; 4-pyridinecarboxylatopentaamminecobalt(III), 40544-44-3; fumaratopentaamminecobalt(III), 17712-85-5; hydroxopentaamminecobalt(III), 16632-75-0; cyanopentaamminecobalt(III), 19529-81-8; isothiocyantopentaamminecobalt(III), 14970-18-4; acetatopentaamminecobalt(III), 16632-78-3; aquopentaamminecobalt(III), 14403-82-8; azidopentaamminecobalt(III), 14403-83-9; chromium(II), 22541-79-3; vanadium(II),

15121-26-3; deuterium, 7782-39-0; *trans*-[$Co(NH_3)_4(ND_3)O_2CCH_3](ClO_4)_2$, 55449-62-2.

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Chemical Behavior of Rhodium(II)–Ammine Complexes Generated by the Pulse Radiolytic One-Electron Reduction of Rhodium(III) Ammines

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The pulse radiolytic reduction of $Rh(NH_3)_5Cl^{2+}$, $Rh(NH_3)_5OH_2^{3+}$, $Rh(NH_3)_4Br_2^{+}$ by the hydrated electron has been examined. The first two ligands of the product rhodium(II) complex are eliminated very fast (<1 μsec), and the first intermediate identified is a $Rh(NH_3)_4^{2+}$ species. This further exchanges ammonia for water with $k = 3.5 \times 10^2$ sec^{-1} for the first NH_3 and with $k = 40$ sec^{-1} for the second NH_3. In addition, $Rh(NH_3)_4^{2+}$ appears to disproportionate with $k = 1.4 \times 10^7$ M^{-1} sec^{-1}. It reacts with oxygen with $k = 3.1 \times 10^8$ M^{-1} sec^{-1} forming a dioxygen adduct, $O_2Rh(NH_3)_4OH_2^{2+}$, which is relatively stable and has an absorption maximum at 265 nm with an absorptivity of 9200 M^{-1} cm^{-1}. The $Rh(NH_3)_4^{2+}$ reduction of $Rh(NH_3)_4Br_2^{+}$ results in a chain reaction that catalyzes the exchange of Br^- for H_2O in the rhodium(III) substrate.

Introduction

The d^7 electronic configuration is notoriously rare among monomeric transition metal complexes, with the known examples being overwhelmingly complexes of cobalt(II).[2,3] Among low-spin cobalt(II) complexes two different coordination geometries have been established: (a) five-coordinate as in $Co(CN)_5^{3-}$ [4] and (b) axially distorted six-coordinate as in $Co^{II}(N_4)X_2$ (N_4 = a cyclic tetraamine, porphyrin, etc.) species. In their solution chemistry, these low-spin cobalt(II) species are labile to substitution in one or more axial positions,[6] and they exhibit little affinity for binding of ligands in these labile axial positions.[6] Ammine complexes of cobalt(II) tend to be high spin and labile in all coordination positions;[7,8] however, one would expect the heavy-metal analogs, e.g., ammine complexes of rhodium(II), to be low spin and related in lability to one of the classes of low-spin cobalt(II) complexes.

A small number of rhodium(II) complexes have been investigated. The few rhodium(II) complexes which have been isolated as solids have been dimer, exhibiting a strong metal–metal bond,[2,9] thus providing no basis for discussing the solution chemistry of monomeric rhodium(II) species. On the other hand, monomeric rhodium(II) species have been postulated as transient intermediates in electron transfer[10] and photochemical[11,12] reactions of rhodium(III) complexes in aqueous solution.

The rhodium(II) species produced in photoredox reactions of rhodium(III) complexes tend to be very short-lived since they are good reducing agents, necessarily generated in the presence of radical oxidants.[11,13] As a consequence it is difficult to develop good criteria for the intermediacy of rhodium(II) in these systems, especially in the absence of definitive information concerning the chemistry of such species. In connection with their study of the photoredox chemistry of $Rh(NH_3)_5I^{2+}$, Kelly and Endicott suggested that rhodium(II) species were axially labile in two coordination positions, analogous to the axially distorted $Co^{II}(N_4)X_2$ species mentioned above. This suggestion was based on studies of the intermediates (I_2^-) and the products (tetraamminerhodium(III) species) resulting from photolysis of iodide solutions containing nonabsorbing amounts of $Rh(NH_3)_5OH_2^{3+}$; it was argued that the reactive rhodium(II) species were generated by rhodium(III) scavenging of the electrons from iodide photolysis, then oxidized by iodine radicals (or molecules). Thus these authors proposed that generation of tetraammine rhodium species was a necessary criterion for the intermediacy of rhodium(II). This proposal has been disputed by Basolo and