higher dielectric constant of the hydrate telescopes the electron-trapping levels, and hence release of electrons requires less energy. Electron emission has been observed to accompany dehydration of salts.[59]

Such annealing reactions generally take place with retention of configuration.[60,61] However, neutron-irradiated *cis*- or *trans*-[$Co(NH_3)_4(NO_2)_2$](NO_3)$_2$ has been found to give rise to a considerable percentage of the other isomer.[26]

Since electron transfer can lead to isomerization and since electron transfer may be important in the solid-phase reactions discussed above, it appears possible that the isomerization of *trans*-[$Co(pn)_2Cl_2$](H_5O_2)Cl_2 involves electron transfer. Within the framework of this mechanism it is easy to see how ligand exchange occurs faster for the "hydrated" form, but it is not evident why isomerization should occur only while water is present or why *trans*-[$Co(en)_2Cl_2$](H_5O_2)Cl_2 should not also isomerize. Therefore, at the present time the mechanism developed by analogy to solution reactions gives the most ready explanation of the isomerization and ligand-exchange behavior of *trans*-[$Co(pn)_2Cl_2$](H_5O_2)Cl_2.

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The Kinetics and Steric Course of the Spontaneous Aquation of the *cis*-Dibromobis(ethylenediamine)cobalt(III) Cation

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The aquation of the complex cation *cis*-dibromobis(ethylenediamine)cobalt(III) has been reexamined kinetically and the steric course of substitution determined. A complete spectrophotometric analysis of the system has revealed both *cis*- and *trans*-$Co(en)_2OH_2Br^{2+}$ in the initially formed products. At 25° and an ionic strength of 0.1 the complex aquates directly to give 72% *cis*- and 28% *trans*-$Co(en)_2OH_2Br^{2+}$. Close examination of the substitution processes showed that the observed products do not result from 100% stereoretentive aquation followed by rapid isomerization. Rate constants for the aquation of *cis*-$Co(en)_2Br_2^+$ and the isomerization of the products have been determined over a 25° temperature range. While the values found for the latter are in good agreement with those already reported,[1] the rates presented below for the aquation process are somewhat lower than those previously found.[2] Activation parameters have been calculated for the aquation. The temperature independence of the equilibrium constant for the isomerization of the products has been confirmed; the value found for the constant agrees with the literature figures.[1] The sensitivity of the steric course to temperature and the nonstereoretentivity of the aquation of this complex are discussed.

Introduction

It is now generally agreed that the mechanism of hydrolysis of Werner-type complexes of cobalt(III) is basically dissociative.[3-5] One interesting observation is that while trans Co(III) substrates with anionic leaving groups often display steric change during spontaneous aquation only in one case has a cis complex been previously reported to do so.[6] Recently we have found another cis Co(III) complex, the *cis*-dibromobis(ethylenediamine)cobalt(III) cation, where the acid hydrolysis of its anionic leaving group leads initially to both cis and trans products. It was found impossible to reconcile the spectra observed during its aquation with the published rates of aquation[2] and isomerization of product(s)[1] and the assumed stereoretentivity of the reaction. Thus the rates of the processes involved and the equilibrium constant for the isomerization were redetermined. We now report our results for these together with the steric course of the aquation and the temperature dependence of this course.

Experimental Section

Preparation of Compounds.—All the complexes prepared were stored either in a vacuum desiccator over anhydrous magnesium perchlorate or in tightly sealed tubes. Due to the inability to store some of the compounds without decomposition, freshly prepared materials were generally used; light was excluded as a routine precaution. Carbonatobis(ethylenediamine)cobalt(III) chloride was prepared by the method of Dwyer, *et al.*,[7] and recrystallized as the bromide from water. Conversion of this complex to *cis*-$Co(en)_2Br_2^+$, *cis*-$Co(en)_2OH_2Br^{2+}$, and *trans*-$Co(en)_2Br_2^+$ salts was effected by minor modifications of the methods of Werner.[8]

cis-[$Co(en)_2Br_2$]BrH_2O was recrystallized from water as the bromide. *trans*-[$Co(en)_2Br_2$]Br was recrystallized from water and then from well-dried methanol to remove traces of tris(ethylenediamine)cobalt(III). *cis*-[$Co(en)_2OH_2Br$]Br_2H_2O was purified by recrystallization from very dilute acid as the bromide.

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TABLE I

ELEMENTAL ANALYSES

	% C		% H		% N		% Br		% S	
Complex	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
cis-$[Co(en)_2Br_2]BrH_2O$	11.0	11.2	4.15	4.16	12.8	12.6	54.9	55.1		
trans-$[Co(en)_2Br_2]Br$	11.5	11.6	3.85	3.82	13.4	13.3	57.2	56.9		
cis-$[Co(en)_2OH_2Br]Br_2H_2O$	10.6	10.5	4.43	4.45	12.3	12.3	52.7	52.8		
trans-$[Co(en)_2OHBr]BrH_2O$	12.9	13.1	5.12	5.09	15.0	14.7	42.8	42.8		
trans-$[Co(en)_2OH_2Br]SO_4$	12.9	12.9	4.88	4.76	15.0	15.0	21.4	21.6	8.6	8.4

trans-$[Co(en)_2OHBr]BrH_2O$ was prepared as described by Chan and Tobe,[9] with the following modifications. *trans*-$[Co(en)_2Br_2]Br$ was treated with diethylamine–ice–water as outlined, and the crude product was recycled with fresh amine mixture; 15 min at 0° was allowed for each treatment. The *trans*-$[Co(en)_2OHBr]BrH_2O$ thus produced was filtered off and washed with 7:3 ethanol–water and then ethanol. Recrystallization was accomplished by washing 10 g of this material placed on a large sintered-glass filter with 10 ml of ice water. Under suction, the solution passed into 25 ml of ethanol precooled in an ice–salt mixture. At this stage, crystals often appeared. The solution was quickly filtered again and the glass vessel containing the deep blue filtrate was vigorously scratched to induce crystallization. After 5 min at ice–salt temperature the pure product was filtered off. Further fractions were contaminated with pink *cis*-$[Co(en)_2OH_2OH]Br_2H_2O$.

As this work neared completion, the solid bromoaquo species *trans*-$[Co(en)_2OH_2Br]SO_4$ was successfully isolated. Essentially the same methods as used for the chloro analog were employed.[7,10] The compound fractionally crystallized from ice-cold aqueous ethanol as the most soluble fraction. Its spectral properties were identical with those of the *trans*-$Co(en)_2OHBr^+$ complex in acid solution.

cis-Dibromobis(ethylenediamine)cobalt(III) bromide was also prepared by another, more convenient method.[11] *cis*-Diazidobis(ethylenediamine)cobalt(III) perchlorate[6,12,13] readily produces the dibromo complex in excellent yield after standing in concentrated hydrobromic acid for approximately 1 hr (prefiltering through a fine-porosity sintered-glass filter is recommended). Recrystallization from room-temperature water as the bromide readily frees the cis complex from traces of trans impurity. Using *trans*-diazidobis(ethylenediamine)cobalt(III) perchlorate,[13] the trans dibromo complex may be similarly prepared. These same techniques have also been recently employed to synthesize the corresponding dichloro complexes.[6]

Characterization of Compounds.—Elemental analyses and agreement of the electronic and infrared spectra with the best literature data available were used to indicate the analytical and isomeric purity of our complexes.[9,14,15] (Tables I and V include some of the relevant data.) Infrared spectra were measured by the KBr disk or Nujol mull method. Visible absorption spectra were generally measured in dilute aqueous acid or the less reactive dimethyl sulfoxide (DMSO). In some cases, spectra were measured on successive fractions of complexes fractionally crystallized.

Instrumentation.—Infrared spectra were recorded on a Perkin-Elmer Model 457 IR spectrophotometer, and visible absorption spectra on a Hitachi Model EPS-3T recording instrument. A Hilger Watts Uvispek manual spectrophotometer was also used for some kinetic measurements. Matched 1- or 4-cm silica cells were used for visible absorption spectra. A Haake thermostat pump controlled the temperature of the cell blocks.

Analyses (C, H, N, S, Br, Cl) were performed by the Australian Microanalytical Service. See Table I for results.

Kinetic Studies.—The aquation reaction was followed spectrophotometrically. The reaction temperature was maintained constant within ±0.05°. Initial difficulty in obtaining reproducible rate constants at temperatures below 25° was traced to incomplete dissolution of the compound which, in association with its limited solubility, is slow to dissolve. Thus for runs at and below 25° excess solid was shaken with solvent previously brought to the required temperature in the water bath and the resulting solution passed rapidly through a fine-porosity sintered-glass filter. The reaction mixture was then introduced into a spectrophotometric cell already thermally equilibrated in the cell block. Because of the relatively slow rate of reaction at the temperatures concerned, some minutes could then be allowed to ensure that a steady temperature was attained before measurements were commenced. At temperatures above 25° where the increased rate of reaction reduces the time available for preliminary treatment the increase in temperature also markedly increases the rate of dissolution of the solid. This allowed the solution to be prepared in the cell. An amount of reactant which could be rapidly dissolved and which led to a convenient optical density was added to solvent already at a constant temperature in the cell. A Pasteur pipet was used to agitate the solution.

The rate of approach to equilibrium of *cis*- or *trans*-$Co(en)_2OH_2Br^{2+}$ was also investigated using this last technique.

Results

Aquation of *cis*-Dibromobis(ethylenediamine)cobalt(III) Cation.—The solvents used were 10^{-1} *M* nitric acid and 10^{-2} *M* perchloric acid. At least two determinations of the rate constant were made in each of these solvents. It has previously been shown that the rate is independent of initial concentration of reactant and ionic strength over a wide range.[2] Our observations support this. Partly because of the inconsistent nature of early results mentioned above both a manual and a recording spectrophotometer were used to obtain rate data. The manual instrument was used to measure optical density changes at 606.5 nm, this being the wavelength found in our work for an isosbestic point in the spectra of the products. The previous study[2] employed 606 nm. The double-beam instrument was used to record optical density changes by repetitive scanning over the range 440–660 nm for runs at and below 25°. At higher temperatures the constant-wavelength mode was employed to record optical density changes at 606.5 nm. For both instruments at 25° and higher temperatures the reaction was followed for a period corresponding to 3 half-lives and the optical density at "infinite time" (D_∞) was measured after 10 half-lives. At lower temperatures the reaction was followed for 5 half-lives and Guggenheim plots were used to calculate rate constants. The constant-wavelength recordings at 606.5 nm established that at temperatures up to and including 40°, D_∞ could be safely measured even after 10 half-lives. The values found at the temperatures studied are presented in Table II and a plot of log (k/T) *vs.* $1/T$ is given in Figure 1. Although our value at 15° agrees with that previously reported, those at higher temperatures are lower.[2] The activation parameter plot is linear over the 25° range of temperature investigated. The enthalpy of activation found from this is 21.3 ± 0.3 kcal mol^{-1} and the entropy of activation is -1.0 ± 1 cal deg^{-1} mol^{-1}. The confidence limits were determined from the two extremes of the "line of best fit." The

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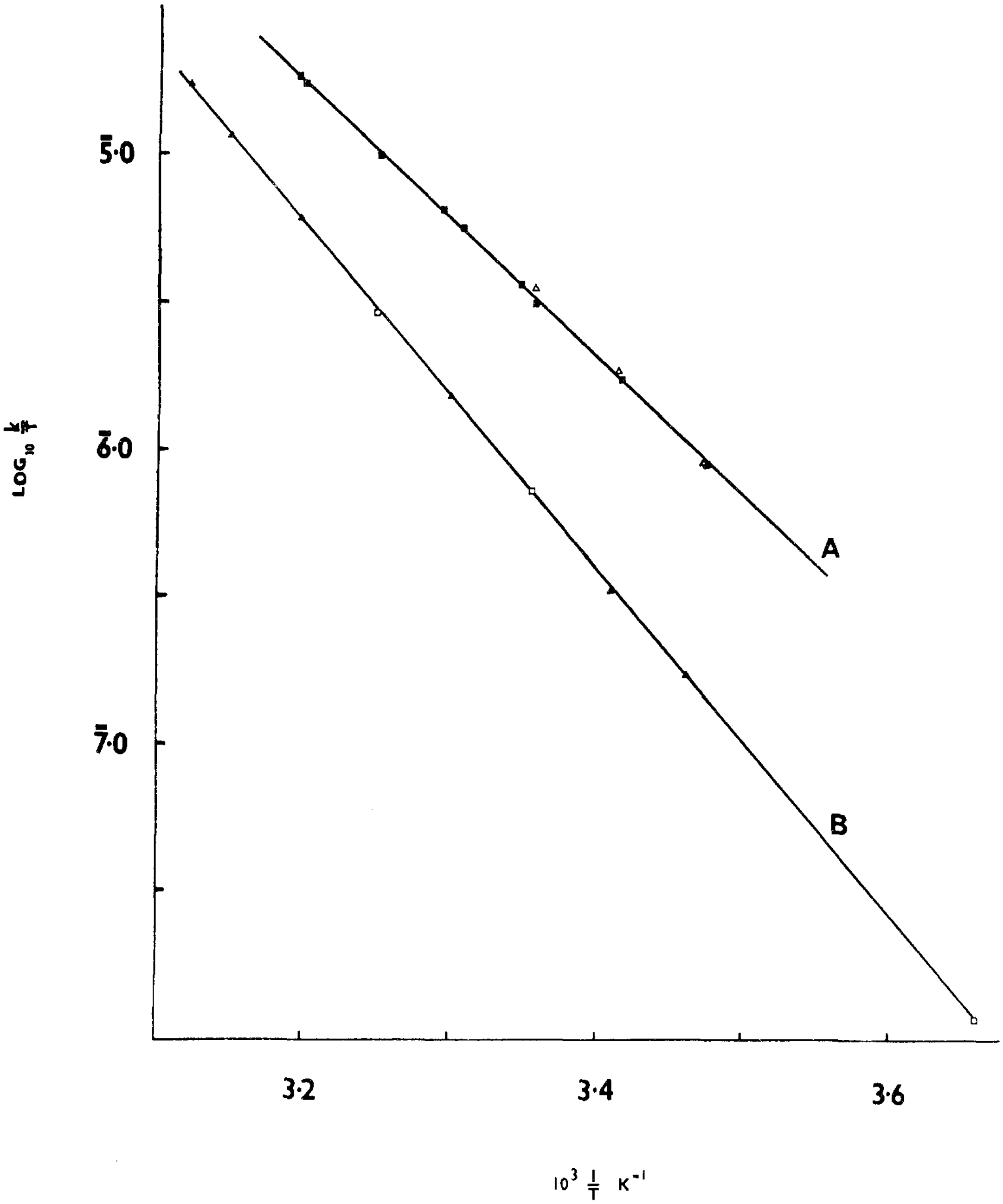

Figure 1.—Activation energy plots for the aquation of *cis*-$Co(en)_2Br_2^+$ (A) and for the isomerization of *cis*- and *trans*-$Co(en)_2OH_2Br^{2+}$ (B). Filled symbols represent data from this work; open symbols represent data from previously published results.[2,1]

TABLE II[a]

FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF *cis*-$Co(en)_2Br_2^+$ IN 0.1 M NITRIC ACID AND 0.01 M PERCHLORIC ACID WHERE [COMPLEX] $\approx 1 \times 10^{-2}$ M

Temp, °C	10^4k, sec^{-1}	Temp, °C	10^4k, sec^{-1}
14.9	2.60 ± 0.05	30.6	20.2 ± 0.4
19.9	5.13 ± 0.10	34.8	30.1 ± 0.6
25.0	9.33 ± 0.20	39.7	54.0 ± 1.0
25.9	10.9 ± 0.2	40.1	57.4 ± 1.1
29.4	17.0 ± 0.3		

[a] The values quoted are the mean and range of at least four determinations at each temperature.

above values are not within the limits of experimental error of those previously calculated (23.8 ± 0.9 kcal mol^{-1}, +5.0 ± 3 cal deg^{-1} mol^{-1}, respectively).[2]

The Kinetics of Isomerization of *cis*- and *trans*-Aquobromobis(ethylenediamine)cobalt(III) Cation. The trans isomer was employed in all cases but one since this provides a larger change in optical density. A sample of *trans*-$[Co(en)_2OHBr]Br \cdot H_2O$ was added to 0.2 M perchloric acid contained in a cell using procedures already described. The hydroxo species was instantly and stereoretentively converted to the aquo form.[1] Changes in optical density were recorded at 530 nm. The reaction was followed for ~3 half-lives and D_∞ read after 10 half-lives. The rate constants for the approach to equilibrium calculated from these data are presented in Table III. The plot of log (k/T) *vs.* $1/T$ (Figure 1) shows the good agreement between our results and those previously reported.[1] This present study extends the temperature range over which the reaction has been investigated.

The Equilibrium Constant for the Isomerization of *cis*- and *trans*-Aquobromobis(ethylenediamine)cobalt(III) Cations.—Spectrophotometric studies have

TABLE III

RATE CONSTANTS FOR THE ISOMERIZATION REACTION[a]

$$cis\text{-Co(en)}_2\text{OH}_2\text{Br}^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} trans\text{-Co(en)}_2\text{OH}_2\text{Br}^{2+}$$

Temp, °C	$10^4(k_1 + k_{-1})$, sec^{-1}	10^4k,[b] sec^{-1}	10^4k_{-1},[b] sec^{-1}
15.6	0.493 ± 0.010	0.126	0.367
20.2	0.935 ± 0.020	0.240	0.695
30.1	4.53 ± 0.09	1.16	3.37
39.6	18.6[c] ± 0.4	4.77	13.8
44.5	36.6 ± 0.8	9.38	27.2
47.3	55.2 ± 1.1	14.1	41.1

[a] $[H^+] = 0.2$ *M*. The values quoted are the mean and range of duplicate determinations at each temperature. [b] Calculated using the equilibrium constant K_e (see Table IV). [c] Using pure *cis*-$[\text{Co(en)}_2\text{OH}_2\text{Br}]\text{Br}_2\text{H}_2\text{O}$.

shown[1] that the equilibrium constant is effectively independent of temperature over the range 0–35°. In this present work the position of equilibrium over the range 19.6–48.7° was investigated and a similar independence of temperature was noted. A solution of known concentration of the trans isomer in 0.2 *M* perchloric acid was allowed to equilibrate in a thermostated cell. The optical density at 530 nm was observed until a maximum was reached. Throughout the reaction a check was kept on the constant optical density at the two isosbestic points. The extinction coefficients of the two isomers (see Table V) are very different at 530 nm thus allowing a reliable estimate to be made of the fraction of each isomer present at equilibrium. The percentage of the cis isomer found at five temperatures is presented in Table IV. Duplicate determinations agreed to within ±1.5%. The values are within experimental error of those already reported.[1]

TABLE IV

EQUILIBRIUM CONSTANTS FOR THE ISOMERIZATION REACTION[a]

$$cis\text{-Co(en)}_2\text{OH}_2\text{Br}^{2+} \rightleftharpoons trans\text{-Co(en)}_2\text{OH}_2\text{Br}^{2+}$$

Temp, °C	% cis isomer at equil	Temp, °C	% cis isomer at equil
19.6	74.7	40.0	74.2
29.5	74.7	48.7	74.0
38.8	74.2		

[a] Average value of K_e = [trans]/[cis] = 0.345.

Steric Course of Aquation of *cis*-Dibromobis(ethylenediamine)cobalt(III) Cation.—The spectra of weighed samples of the reactant and the two products were recorded at 10° in 0.1 *M* HClO_4 over the range 430–680 nm. A nitrogen purge was used to prevent cell fogging. In the case of *cis*-$[\text{Co(en)}_2\text{Br}_2]\text{BrH}_2\text{O}$ 4-cm cells were used to overcome solubility and dissolution problems. Extinction coefficients were calculated at 5-nm intervals, extrapolation to zero reaction time being used where necessary. The values presented are the average of at least three determinations (see Figure 2 and Table V). Agreement with previously reported data is satisfactory.[9,14,15]

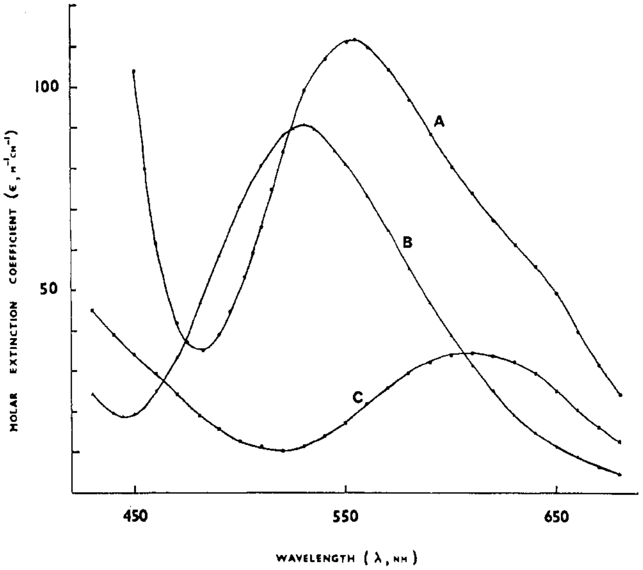

Figure 2.—Visible absorption spectra in 0.1 *M* HClO_4 of *cis*-$\text{Co(en)}_2\text{Br}_2^+$ (A), *cis*-$\text{Co(en)}_2\text{OH}_2\text{Br}^{2+}$ (B), and *trans*-$\text{Co(en)}_2\text{OH}_2\text{Br}$ (C).

TABLE V

EXTINCTION COEFFICIENTS OF REACTANT AND PRODUCTS AT SIGNIFICANT WAVELENGTHS

Wavelength, nm	*cis*-$\text{Co(en)}_2\text{Br}_2^+$	*cis*-$\text{Co(en)}_2\text{OH}_2\text{Br}^{2+}$	*trans*-$\text{Co(en)}_2\text{OHBr}^{2+}$
445[a]		18.7	
463.5[c]		27.9	27.9
474[d]	38.0	38.0	
477[e]	36.3	41.9	21.2
482[a]	35.0		
490[f]	39.2	58.4	15.8
506[e]	59.3	77.7	11.7
520[a]			10.3
524[d]		89.5	
530[b]		90.7	11.5
554[b,f]	112.0	78.4	19.0
606.5[c]		34.4	34.4
610[b]			34.6
650[f]	49.2	11.6	25.1

[a] Local minimum. [b] Local maximum. [c] Isosbestic point in spectra of products. [d] Isosbestic point in spectra of reactant and cis product. [e] Isosbestic point found during aquation at 25°. [f] Used in solution of simultaneous equations.

TABLE VI

STERIC COURSE OF THE SPONTANEOUS AQUATION OF *cis*-$\text{Co(en)}_2\text{Br}_2^+$

	Calcd from data at isosbestic points			
Temp, °C	Wavelength of isosbestic, nm	% cis isomer initially produced	Calcd by soln of simultaneous equations	Av % cis isomer
15	476	79	78	67
	509	77		
20	476.5	77		75.5
	507.5	74		
25	477	73	72	72.2
	506	72		
30	478	69		69.5
	505	70		
35	478.5	66		67
	504	68		
40	479	64	64	65
	502	67		

During the aquation of *cis*-$\text{Co(en)}_2\text{Br}_2^+$ two isosbestic points occur. The wavelengths of these vary with temperature (Table VI). At temperatures below 30° where the rates of aquation and isomerization of products are relatively low the isosbestic points become well defined. At higher temperatures there is only sufficient time for several scans to be recorded before isomerization of the products causes departure from the initially observed points. At all temperatures studied the wavelengths at which the isosbestic points occur and the extinction coefficients involved preclude any possibility that the aquation is stereoretentive. For example, at 15° the points occur at 476 and 509 nm (see Figure 3).

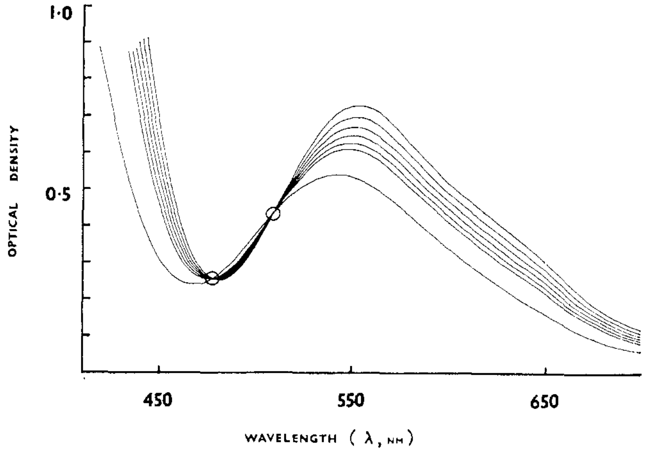

Figure 3.—Visible absorption spectra observed during the aquation of *cis*-$Co(en)_2Br_2^+$ in 0.1 *M* HNO_3 at 15°. Initial concentration ~5 × 10^{-3} *M;* cell length 1 cm. The seven scans were recorded over a period of ~60 min.

This indicates only 78% of the cis isomer in the initial products. The rate of aquation[2] of *cis*-$Co(en)_2Br_2^+$ and the rate of isomerization[1] of *cis,trans*-$Co(en)_2OH_2Br^{2+}$ previously reported and checked in this study show that the latter proceeds at only about one-fourth of the rate of the former at 25°. This excludes a mechanism by which aquation yields 100% cis aquo complex as the initial product and rapid isomerization reduces this to 78%. The isosbestic point method of calculation was used to determine the percentage of the cis product at 5° intervals from 15 to 40° (Table VI). It is interesting to observe that at 25° where the initial kinetically determined proportions of the two products are very close to the thermodynamic equilibrium proportions the isosbestic points persist for almost 100% of the aquation reaction. However at lower temperatures where the initial isosbestic points are further apart than at 25° and at higher temperatures where they are closer together scans run at later times show that isomerization has altered the kinetically controlled cis: trans ratio toward that required by thermodynamics. This is particularly apparent at the higher temperatures where the rate of isomerization shows a relatively greater increase (Figure 1).

Results for steric course found by the above method were confirmed at three temperatures by determining the concentration of the three species involved from the solution of three simultaneous equations.[16] Duplicate determinations at each temperature were carried out using weighed samples. The wavelengths used were 490, 554, and 605 nm. The appropriate extinction coefficients at these wavelengths are given in Table V. Agreement between the two methods is good (Table VI). The reliability of this latter approach can be tested by noting that the total concentration found at various stages of the reaction by solving the equations remains constant and agrees with the known value for the solution examined. Further, rate constants for the reaction were determined from the concentration of *cis*-$Co(en)_2Br_2^+$ calculated at various times and were found to agree with those determined from optical density changes at 606.5 nm. At 40° where the increased reaction rates prevent a number of scans from being recorded before isomerization of the products becomes significant, the direct calculation of the initial percentage of the cis isomer is unreliable. Thus the percentage of cis isomer present was plotted against per cent reaction and a calculated expression was used to guide the extrapolation back to zero reaction time. This method has been widely used.[16]

Discussion

Until recently all cis Co(III) complexes investigated with anionic leaving groups were found to aquate stereoretentively. The reexaminations of the aquation of *cis*-$Co(en)_2N_3Cl^+$ [6] and *cis*-$Co(en)_2Br_2^+$ have shown departures from this pattern. Before regarding this behavior as anomalous, it would be well to consider the steric course of other actions of cis complexes.

Studies on water exchange[17] and aquation of solvento species[18] provide examples of cis complexes aquating with steric change, albeit with neutral leaving groups. Base hydrolyses[19,20] and induced aquations[10,13] often take place with considerable steric change. If these reactions are viewed as simple aquation with the reactive complex species being a modified version of the substrate, then it is seen that steric change is as common for cis substrates as it is for trans. In this context the occurrence of steric change in the aquation of cis-$Co(en)_2Br_2^+$ does not seem extraordinary.

It is unusual, however, in that the closely analogous complexes *cis*-$Co(en)_2Cl_2^+$ and *cis*-$Co(en)_2ClBr^+$ both aquate with retention of configuration.[1] Tobe[21] has recently suggested that for aquation of these and related complexes the energy difference between the two basic forms of the reduced coordination number intermediate is not large. Thus subtle changes in the nature of solvent, leaving group or nonparticipating group are sufficient to determine whether the trigonal-bipyramidal or the tetragonal-pyramidal intermediate is generated. The former can lead to steric change; the second precludes it. It could simply be that the small differences between *cis*-$Co(en)_2Br_2^+$ and the above analogs are enough to tip the balance. The possibility that both forms of the intermediate can occur in the one reaction was investigated in the aquations of *trans*-$Co(en)_2N_3X^+$ (X = Cl, Br)[6] and *cis*-$Co(en)_2Br_2^+$. In no case was there any evidence for curvature in the plots of log (k/T) against $1/T$ over a wide temperature range.

Such plots are of course also used to calculate entropy of activation. A correlation between this parameter and steric course has been found with a chloride leaving group and a trans substrate.[21] In such cases the entropies of activation for reactions occurring with steric change are significantly higher than those for stereoretentive aquations. From the limited data available a similar correlation is indicated[22] for bromide as the leaving group from a trans complex. However it would seem that the relation cannot be extended to include cis substrates. *cis*-$Co(en)_2OHBr^+$ and *cis*-$Co(en)_2ClBr^+$ aquate stereoretentively but the reactions have higher entropies of activation than does the aquation of Co-

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$(en)_2Br_2^+$ which takes place with change of configuration.

In all careful studies so far reported where a cis substrate aquates with change of configuration (principally base hydrolysis[19,20] and induced aquation[10,13] studies) the steric course has provided evidence of a genuine five-coordinate intermediate. The spontaneous and induced aquation of *cis*-$Co(en)_2N_3Cl^+$ [6] give the same distribution of isomeric products. However current work in this department[23] indicates that the Hg^{2+}-induced aquation of *cis*-$Co(en)_2Br_2^+$ leads to only 58% of the cis aquobromo isomer at 20°. This contrasts with the 76% obtained by spontaneous aquation. It seems then that *cis*-$Co(en)_2Br_2^+$ is the first example of a nonstereoretentive aquation of a cis complex possibly not proceeding through a true five-coordinate intermediate. Also, *cis*-$Co(en)_2Br_2^+$ and *cis*-$Co(en)_2N_3Cl^+$ are the only cases reported in which the cis isomer displays more steric change than the trans during aquation.

It has been suggested[19] that a comparison of the temperature dependence of steric course for induced and spontaneous aquations would be useful in establishing the occurrence of a five-coordinate intermediate. Table VI shows that in the aquation of *cis*-$Co(en)_2Br_2^+$ there is a decrease from 78 to 65% in the fraction of cis isomer initially produced for a rise of 25° in temperature. This range includes the statistically determined amount (67%) predicted for one of the possible trigonal-bipyramidal intermediates.[3,4] However it should be realized that this simple theory applies strictly only to the symmetrical intermediates and neglects the now well-established effect of the nonparticipating groups[10,13] on the position of water attack. Further, it implies that there would be no variation of the proportion with temperature. Comparison of spontaneous and induced aquations indicates that the lifetime of the intermediate is another factor bearing on the stereochemistry of these reactions.[24]

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A Reactivity Trend Seen in the Reduction of Transition Metal Complexes by Outer-Sphere Reactants Verified for Hydrated Electron Reactions; Pulse Radiolysis Studies of Cobalt(III) Complexes

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Hydrated electrons (e_{aq}^-) generated in the pulse radiolysis of aqueous solutions of cobalt(III) cyanide complexes react with the cobalt solute at rate constants in the 10^9–10^{10} M^{-1} sec^{-1} region. Of particular interest is a correlation between the rate constant for $e_{aq}^- + Co(CN)_5X^{3-}$ and the magnitude of the ligand field splitting parameter (Δ) of the heteroligand X^-. Within the standard outer-sphere–inner-sphere terminology, an attempt is made to provide a useful way of looking at the transition state consisting of e_{aq}^- and the metal complex.

Introduction

The reactivity trend relating outer-sphere rates of reduction of transition metal complexes at a dropping-mercury electrode (dme) with the ligand field splitting parameter (Δ) was first recognized by Vlček.[2] Candlin, Halpern, and Trimm[3] subsequently showed the same trend to be operative in the outer-sphere reduction of cobalt(III) complexes[4] by the outer-sphere reductants V^{2+} and $Cr(bipy)_3^{2+}$. An indication of such a trend in the reduction of cobalt(III) cyanide ($Co(CN)_5X^{3-}$) complexes can be seen in some early pulse radiolysis data of Baxendale, Fielden, and Keene.[6] The results of this work on additional complexes do in fact confirm the correlation between Δ and the rate of reduction of $Co(CN)_5X^{3-}$ by e_{aq}^-.

Pulse radiolysis experiments were carried out on aqueous solutions of some cobalt(III) cyanide complexes and rate constants for the reaction of the hydrated electron with the $Co(CN)_5X^{3-}$ solutes measured ($X^- = \mathit{C}N^-, H^-, OH^-, \mathit{N}CS^-, I^-$, the italic letter indicating which atom is bonded to cobalt). These studies were originally undertaken to explore the possibility of generating a reaction sequence of the type

$$Co(CN)_6^{3-} + e_{aq}^- \longrightarrow Co(CN)_6^{4-} \longrightarrow Co(CN)_5^{3-} + CN^- \quad (1)$$

While the experimental results[7] reveal pentacyanoco-

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