be evidence for an internal conjugate-base mechanism in which transfer of a proton from the secondary amine nitrogen to the coordinated hydroxide is a necessary preliminary to the act of aquation. A proper, quantitative kinetic study of the exchange is required in order to distinguish between these mechanisms and this is now under way. The exchange of the primary amine protons is far too slow to occur in the *trans*-aquochloro species and must be taking place in the hydroxoaquo or dihydroxo species. Since the pK_a of the *trans*-[Co(*R*,*S*-2,3,2-tet)OH(H_2O)]$^{2+}$ cation is 7.5 at 25 °C,[1] the data span the range of pH where the dominant species changes from the hydroxoaquo to the dihydroxo form and, again, a much more detailed study of the pH dependence of the rate of exchange is required.

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Registry No. β-*cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]Cl, 60409-16-7; β-*cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)CO_3]ClO_4, 52500-16-0; β-*cis*-[Co[*N*,*N*,*N′*,*N″*,*N‴*,*N‴*-$^2H_6$]-(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]Cl, 60384-65-8; β-*cis*-[Co[*N*,*N*,*N′*,*N″*,*N‴*,*N‴*-$^2H_6$]-(*R*,*R*(*S*,*S*)-2,3,2-tet)CO_3]ClO_4, 52500-19-3; β-*cis*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]$^+$, 60409-17-8; β-*cis*-[Co[*N*,*N*,*N′*,*N″*,*N‴*,*N‴*-$^2H_6$]-(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]$^+$, 60384-66-9; *trans*-[Co(*R*,*R*(*S*,*S*)-2,3,2-tet)Cl_2]$^+$, 46239-27-4.

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Effect of Pressure on the Isomerization Rate of the Diaquobis(ethylenediamine)cobalt(III) Ion

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In a 0.05 M perchloric acid medium, the isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ exhibits a pressure-dependent volume of activation, with $\Delta V_0^{\ddagger} = 14.3 \pm 0.2$ cm^3 mol^{-1} and $\Delta\beta^{\ddagger} = 0.010 \pm 0.002$ cm^3 mol^{-1} MPa^{-1}, together with $\Delta H^{\ddagger} = 131.4 \pm 1.2$ kJ mol^{-1} and $\Delta S^{\ddagger} = +103 \pm 5$ J K^{-1} mol^{-1}. A D mechanism with aquo ligand release to bulk solvent is proposed. In 1.0 M perchlorate media, the pressure dependence of the volume of activation is even more marked, with $\Delta V_0^{\ddagger} = 13.2 \pm 0.7$ cm^3 mol^{-1} and $\Delta\beta^{\ddagger} = 0.10 \pm 0.03$ cm^3 mol^{-1} MPa^{-1}, together with $\Delta H^{\ddagger} = 121.7 \pm 1.0$ kJ mol^{-1} and $\Delta S^{\ddagger} = +64 \pm 4$ J K^{-1} mol^{-1}. Dissociative aquo ligand release with extensive desolvation from secondary hydration zones around associated ions is proposed as the mechanism in high electrolyte concentrations. Two distinct dissociated transition states for isomerization and exchange[2] are revealed by the pressure studies.

Introduction

We have selected the diaquobis(ethylenediamine)cobalt(III) cation $Co(en)_2(OH_2)_2^{3+}$ as an appropriate substrate for the systematic evaluation of volumes of activation for anation reactions proceeding by ion-pair interchange mechanisms. As a basis for these studies, we report in this paper the volumes of activation and other activation parameters for the isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ to *cis*-$Co(en)_2(OH_2)_2^{3+}$. The succeeding paper by Tong, Krouse, and Swaddle[2] reports the volume of activation for the exchange of $H_2{}^{18}O$ with *trans*-$Co(en)_2(OH_2)_2^{3+}$ and in a third paper we report[3] volumes of activation for reactions of oxalate with *cis*-$Co(en)_2(OH_2)_2^{3+}$.

Kruse and Taube[4] have shown that whereas the stereoretentive exchange of an aquo ligand in *trans*-$Co(en)_2(OH_2)_2^{3+}$ is only 1.68 times faster, at 298 K, than the rate of the trans → cis interconversion, the rate of aquo ligand exchange in *cis*-$Co(en)_2(OH_2)_2^{3+}$ is 250 times faster than the rate of the cis → trans interconversion. These observations require the postulation of two distinct transition states (and probably two intermediates) for the exchange and isomerization reactions. However, on the basis of the data available, Kruse and Taube were unable to decide unambiguously on whether the presumed intermediates were generated by a dissociative mechanism or by an associative edge-displacement mechanism. We believe that the volumes of activation now reported for the exchange and isomerization reactions provide good evidence for two intermediates generated by dissociative release of an aquo ligand with extensive desolvation as one intermediate rearranges to the other intermediate.

Experimental Section

Materials. *trans*-[$Co(en)_2(OH_2)(OH)$]$(ClO_4)_2$ was prepared in 50% yield by the method of Kruse and Taube[4] and the product purified by recrystallization from dilute sodium perchlorate. Dissolution of this solid salt in perchloric acid yielded *trans*-$Co(en)_2(OH_2)_2^{3+}$ whose extinction coefficient (19.2 M^{-1} cm^{-1} at 492 nm) was in excellent agreement with published values.[5]

Perchloric acid of the desired molarity was prepared from concentrated Analar perchloric acid by dilution with doubly distilled water and was standardized against AR mercuric oxide and potassium iodide.

Sodium perchlorate (G. F. Smith Co.) was recrystallized twice from water and dried overnight at 120 °C.

High-Pressure Procedures. Two types of high-pressure vessels were employed: one from which samples could be withdrawn periodically for individual spectrophotometric analysis (the "sampling vessel") and the other (the "optical vessel") in which the pressurized reactant was monitored continuously in the beam of a Unicam SP800 spectrophotometer equipped with scale expansion facilities. The temperatures of the sampling vessel and the optical vessel were continuously regulated to within ±0.01 and ±0.05 K, respectively. Hydraulic pressures[6] in the range 10–200 MPa were maintained to within ±0.5 MPa. The reactant in the sampling vessel was contained within a Perspex (Lucite) cylinder provided with a floating Teflon

Table I. First-Order Rate Coefficients for the Interconversion of *trans*- → *cis*-$Co(en)_2(OH_2)_2^{3+}$ in 0.05 M $HClO_4$ at Atmospheric Pressure (0.1 MPa), Where $[Co(en)_2(OH_2)_2^{3+}] = 0.01$ M

Temp, °C	$10^5 k_{isom}$, s^{-1}	No. of runs	Temp, °C	$10^5 k_{isom}$, s^{-1}	No. of runs
34.5	7.85 ± 0.10	6	45.0	42.8 ± 0.28	3
35.0	8.18 ± 0.12	3	46.0	51.3 ± 0.52	4
40.0	19.1 ± 0.25	4	50.0	95.1 ± 1.1	3

Table II. First-Order Rate Coefficients for the Interconversion of *trans*- → *cis*-$Co(en)_2(OH_2)_2^{3+}$ in 1.0 M $HClO_4$ at Atmospheric Pressure (0.1 MPa), Where $[Co(en)_2(OH_2)_2^{3+}] = 0.01$ M

Temp, °C	$10^5 k_{isom}$, s^{-1}	No. of runs	Temp, °C	$10^5 k_{isom}$, s^{-1}	No. of runs
35.0	3.63 ± 0.05	3	50.0	34.4 ± 0.28	5
40.0	7.76 ± 0.08	4	50.5	37.0 ± 0.51	5
45.0	16.8 ± 0.15	6	55.0	69.3 ± 0.80	3

plunger and a Pt–Ir outlet tube. The reactant in the optical vessel was contained in a glass cuvette with a floating Teflon cap. Although these two pressure vessels presented different surfaces to the reaction solutions, no difference in reaction rates was detected.

Kinetic Procedures. A sampling procedure was used in the temperature variation studies at 0.10 MPa (1 atm) and also for pressure variation studies with the sampling vessel. A weighed quantity of *trans*-$[Co(en)_2(OH_2)OH](ClO_4)_2$ was dissolved in a known volume of perchloric acid and/or acidic sodium perchlorate and brought to the reaction temperature and pressure. Aliquot samples were withdrawn at regular time intervals and quenched in ice-chilled tubes and optical absorbances (A) were measured at 492 nm where the respective molar extinction coefficients for *cis*- and *trans*-$Co(en)_2(OH_2)_2^{3+}$ are 80.9 and 19.2 M^{-1} cm^{-1}, respectively. First-order rate coefficients, k_{isom}, were evaluated from the strictly linear variation of log $[(A_\infty - A_0)/(A_t - A_0)]$ with time. All reactions were followed over 2 half-lives and infinite-time absorbances, A_∞, were taken after at least 6 half-lives had elapsed.

In pressure studies with the optical vessel, the sample cuvette was filled with the reactant solution, as prepared above, and sealed with a Teflon cap. The cuvette was then located inside the optical vessel mounted within the cell compartment of the Unicam SP800 spectrophotometer. The pressure in the optical vessel was raised to the desired value and the reactant solution left at this pressure for 30 min to reestablish thermal equilibrium. (Subsequent measurements revealed that temperature rises of up to 4 °C occurred on pressurization but thermal equilibrium was reestablished within 10 min.) Optical absorbances were then recorded on a slave recorder linked to the scale expansion accessory of the spectrophotometer. In this case the Guggenheim method was employed. Isomerization rate coefficients, k_{isom}, were evaluated from the linear variation of log $(A_{t+\Delta} - A_t)$ with time where A_t and $A_{t+\Delta}$ denote the optical absorbances at times t and $(t + \Delta)$ and Δ is a fixed time increment of at least 2 reaction half-times.

Results

An equilibrium mixture of *cis*- and *trans*-$Co(en)_2(OH_2)_2^{3+}$ contains approximately 2 mol % of the trans isomer, the percentage being only slightly different in nitrate and perchlorate media.[5,7] The most accurate value of the equilibrium quotient K_{isom} (=[*cis*-$Co(en)_2(OH_2)_2^{3+}$]/[*trans*-$Co(en)_2(OH_2)_2^{3+}$]) is 58. Our measurements confirm that K_{isom} is invariant with temperature and no significant change in K_{isom} was detected at pressures up to 150 MPa.

The observed rate coefficient, k_{isom}, is the sum of the rate coefficients for the interconversions trans → cis (k_t) and cis → trans (k_c) but the value of K_{isom} establishes that k_c is only 1.7% of the value of k_t at all temperatures and pressures studied. Thus to an adequate approximation $k_{isom} = k_t$.

Temperature Variation of Isomerization Rate. The temperature variation of k_{isom} was evaluated between 34.5 and 55 °C at total ionic strengths of 0.05 (23 runs) and 1.0 M (26 runs). Ionic strengths were established with $HClO_4$ but our later pressure studies confirm that the pressure dependences of rates in media with either $HClO_4$ or $NaClO_4$ as supporting electrolytes are virtually equivalent. The data are summarized in Tables I and II where quoted values of k_{isom} represent the mean value of at least three determinations at each temperature and ionic strength. The standard deviation in individual k_{isom} values is equal to or less than 3% in all cases.

Table III. Effect of Pressure on the Rate of Isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ in 0.05 M $HClO_4$, Where $[Co(en)_2(OH_2)_2^{3+}] = 0.01$ M

Pressure, MPa	$10^5 k_{isom}$, s^{-1}	No. of runs	Pressure, MPa	$10^5 k_{isom}$, s^{-1}	No. of runs
34.5 ± 0.1 °C; Sampling Vessel Used with Perspex Surfaces					
0.10	7.85 ± 0.10	6	40.8	6.29 ± 0.05	6
13.6	7.31 ± 0.08	6	102	4.60 ± 0.08	6
27.2	6.74 ± 0.08	6			
46.0 ± 0.1 °C; Optical Vessel Used with Glass Surfaces					
0.10	51.3 ± 0.8	4	51.6	38.7 ± 0.6	5
17.2	46.7 ± 0.8	4	86.0	32.0 ± 0.3	5
34.4	42.6 ± 0.5	4			

Table IV. Effect of Pressure on the Rate of Isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ in 0.5 M $HClO_4$, Where $[Co(en)_2(OH_2)_2^{3+}] = 0.01$ M, $T = 48.0 \pm 0.1$ °C, and a Sampling Vessel Was Used with Perspex Surfaces

Pressure, MPa	$10^4 k_{isom}$, s^{-1}	No. of runs	Pressure, MPa	$10^4 k_{isom}$, s^{-1}	No. of runs
0.10	$2.38 \pm 0.04_5$	4	54.4	1.85 ± 0.04	5
13.6	$2.21 \pm 0.03_5$	5	102	1.60 ± 0.03	5
27.2	2.09 ± 0.04	5			

The following activation parameters were derived by least-squares analysis of the data: for ionic strength 1.0 M ($HClO_4$), $\Delta H^\ddagger = 121.7 \pm 1.0$ kJ mol^{-1} and $\Delta S^\ddagger = 64 \pm 4$ J K^{-1} mol^{-1}; for ionic strength 0.05 M ($HClO_4$), $\Delta H^\ddagger = 131.4 \pm 1.2$ kJ mol^{-1} and $\Delta S^\ddagger = 103 \pm 5$ J K^{-1} mol^{-1}. Both activation parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, therefore are significantly different in different ionic media.

The earlier work of Kruse and Taube[4] yielded values of $\Delta H^\ddagger = 107.1$ kJ mol^{-1} and $\Delta S^\ddagger = 17$ J K^{-1} mol^{-1} deduced from single measurements at three temperatures and in 1 M $HClO_4$. For the exchange of solvent water with the trans isomer in 0.8 M $HClO_4$, Kruse and Taube reported $\Delta H^\ddagger = 128.0$ kJ mol^{-1} and $\Delta S^\ddagger = 88$ J K^{-1} mol^{-1}.

Pressure Variation of Isomerization Rate. The rate of isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ was studied at pressures between 0.10 and 200 MPa and at electrolyte concentrations of 0.05, 0.50, and 1.0 M, using a reactant concentration of 0.01 M. The results are summarized in Tables III–V.

At the same reaction temperature, there was no detectable difference in the rates observed with the optical vessel (with glass surfaces) and the sampling vessel (with Perspex surfaces). A number of runs at each pressure revealed that the standard deviation of each mean value of k_{isom} was not greater than ±2%.

The variation of log k_{isom} with pressure is nonlinear especially at high electrolyte concentrations. This behavior implies that the volume of activation $\Delta V^\ddagger$ is itself pressure dependent and it is necessary to estimate the limiting value $\Delta V_0^\ddagger$ as $P \rightarrow 0$. In each series of runs, a curve was fitted to the experimental data by using a nonlinear least-squares multiple regression computer program. This program calculates for a set of data, the curve of best fit in the form of a polynomial of up to degree 4. Since these studies were directed to obtain reliable values for $\Delta V_0^\ddagger$ or the derivative $(\partial \log k_{isom}/\partial P)_T$, most values of k_{isom} were evaluated at relatively low pressures. On the basis of the statistical "t" test

Table V. Effect of Pressure on the Rate of Isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$ in 1 M $HClO_4$ or 1 M $NaClO_4$, Where $[Co(en)_2(OH_2)_2^{3+}] = 0.01$ M

Pressure, MPa	$10^4 k_{\mathrm{isom}}$, s^{-1}	No. of runs	Pressure, MPa	$10^4 k_{\mathrm{isom}}$, s^{-1}	No. of runs
45.0 ± 0.1 °C; 1 M $HClO_4$; Sampling Vessel Used with Perspex Surfaces					
0.10	1.68 ± 0.02	6 (glass)	34.5	$1.43 \pm 0.02_5$	6
0.10	$1.67 \pm 0.01_5$	4	69.0	$1.30 \pm 0.02_0$	6
13.9	$1.57 \pm 0.01_0$	6	103.5	$1.23 \pm 0.01_5$	6
27.8	$1.47 \pm 0.01_8$	6	138.00	$1.17 \pm 0.01_0$	6
50.5 ± 0.1 °C; 1 M $HClO_4$; Optical Vessel Used with Glass Surfaces					
0.10	$3.62 \pm 0.02_6$	4 (Perspex)	34.4	$3.16 \pm 0.03_5$	4
0.10	3.70 ± 0.03	5	51.6	$3.00 \pm 0.02_5$	4
17.2	3.37 ± 0.03	4	102	2.70 ± 0.03	5
45.0 ± 0.1 °C; 1 M $NaClO_4$; Sampling Vessel with Perspex Surfaces Used					
0.10	2.82 ± 0.05	4	54.4	2.27 ± 0.02	5
13.6	2.62 ± 0.03	5	102	2.08 ± 0.03	6
27.2	2.47 ± 0.03	5			

Table VI. Volumes of Activation at Zero Pressure ($\Delta V_0^{\ddagger}$) and Compressibility Coefficients of Activation ($\Delta\beta^{\ddagger}$) for the Isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$

Temp, °C	Electrolyte	$\Delta V_0^{\ddagger}$, cm^3 mol^{-1}	$10^2\Delta\beta^{\ddagger}$, cm^3 mol^{-1} MPa^{-1}
34.5	0.05 M $HClO_4$	14.3 ± 0.2	0.9 ± 0.2
46.0	0.05 M $HClO_4$	14.2 ± 0.2	1.0 ± 0.2
48.0	0.5 M $HClO_4$	14.2 ± 0.5	8 ± 2
45.0	1 M $HClO_4$	12.6 ± 0.8	10 ± 3
45.0	1 M $NaClO_4$	13.7 ± 0.7	10 ± 3
50.5	1 M $HClO_4$	13.7 ± 0.5	11 ± 3

for 95% confidence levels, it was found that the data in Tables III–V were best represented by a polynomial of the form

$$\log k_P = \log k_0 + bP + cP^2$$

where $\Delta V_0^{\ddagger} = -bRT$ and the compressibility coefficient of activation is $\Delta\beta^{\ddagger} = -(\partial\Delta V^{\ddagger}/\partial P)_T = 2cRT$.

Values of $\Delta V_0^{\ddagger}$ and $\Delta\beta^{\ddagger}$, together with their computed standard deviations, are summarized in Table VI. There is only a very slight decrease in $\Delta V_0^{\ddagger}$ with increasing electrolyte concentration but there is a marked increase in $\Delta\beta^{\ddagger}$ with increasing electrolyte concentration. There is no statistically significant difference between values derived for solutions of 1.0 M $HClO_4$ and 1.0 M $NaClO_4$ and there is no statistically significant variation in $\Delta V_0^{\ddagger}$ and $\Delta\beta^{\ddagger}$ with reaction temperature.

Discussion

Isomerization in Dilute Electrolyte Media. In 0.05 M $HClO_4$ media, the trans → cis isomerization exhibits a relatively large positive volume of activation, $\Delta V_0^{\ddagger} = +14.2$ cm^3 mol^{-1}, which is temperature independent. The isomerization is uncomplicated by changes in the electrostriction of the solvent since the reaction involves only the exchange of neutral water with no change in formal charge of the substrate complex ion. Under these circumstances, detailed arguments have already been presented[8,9] to suggest that a large positive $\Delta V_0^{\ddagger}$ value is strong evidence for a dissociative-type mechanism. In general an I_d mechanism, involving transfer of an aquo ligand to the immediate hydration sphere of an ion, would be expected to exhibit a lower $\Delta V_0^{\ddagger}$ value than a D mechanism, involving complete transfer of an aquo ligand into the bulk solvent. In the extreme limit a D mechanism might be expected[8] to yield $\Delta V_0^{\ddagger} \approx +18$ cm^3 mol^{-1}, i.e., the molar volume of water, but there are as yet insufficient reference systems to judge where a distinction between I_d and D can be drawn with lower values of $\Delta V_0^{\ddagger}$.

The measured value of the compressibility coefficient of activation, $\Delta\beta^{\ddagger} = -(\partial\Delta V^{\ddagger}/\partial P)_T = 0.010 \pm 0.002$, may be used in an attempt to distinguish between these I_d and D mechanisms, even though $\Delta\beta^{\ddagger}$ values are necessarily subject to relatively large statistical uncertainties. The I_d mechanism involves transfer of an aquo ligand between two zones in which water must have a very low compressibility and the expected value of $\Delta\beta^{\ddagger}$ should be very small. The D mechanism involves transfer of an aquo ligand from a region of low compressibility to a region of high compressibility and thus the expected value of $\Delta\beta^{\ddagger}$ should be relatively large. The magnitude of these expected values of $\Delta\beta^{\ddagger}$ can be estimated as follows.

We have proposed[8] a value of $\beta = 0.0012$ cm^3 mol^{-1} MPa^{-1} for the first hydration sphere about a spherical complex ion of formal charge 3+ and a radius of 350 pm. This was derived from an estimated internal pressure within the first hydration sphere of the complex ion of 3.2 GPa. Hamann[10] has pointed out that the best volumetric data for water[11] suggest an even lower value of $\beta = 0.0006$ at this pressure. The differences should not be emphasized too strongly however since this internal pressure is estimated from the classical electrostatics of a uniform spherical ion in a dielectric continuum and the pressure is likely to be an overestimate. The essential point is that the compressibility of water in the first hydration sphere will be small and comparable to that of the aquo ligand in the coordination sphere. For an I_d mechanism we can therefore predict that as a limit $\Delta\beta^{\ddagger} = (\beta_{\text{hyd sphere}} - \beta_{\text{coord sphere}}) \ll 0.0006$ cm^3 mol^{-1} MPa^{-1} and for all practical purposes $\Delta\beta^{\ddagger} \simeq 0$. However the ln k_P vs. P plot is curved and the observed value $\Delta\beta^{\ddagger} = 0.010 \pm 0.002$ is of a greater magnitude than that predicted for the I_d mechanism. On the other hand, the D mechanism should exhibit a limiting value $\Delta\beta^{\ddagger} = (\beta_{\text{bulk water}} - \beta_{\text{coord sphere}}) = (0.0084 - 0.0006) = 0.008$ which is similar in magnitude to the value observed, $\Delta\beta^{\ddagger} = 0.010 \pm 0.002$. We conclude, within the limitation imposed by the statistical uncertainty in $\Delta\beta^{\ddagger}$, that a D mechanism operates with the isomerization involving dissociation of an aquo ligand and the transfer of a water molecule to the bulk solvent.

This conclusion is supported by the quite large positive entropy of activation for isomerization, namely, $\Delta S^{\ddagger} = 103 \pm 5$ J K^{-1} mol^{-1}. The D mechanism must involve a cratic entropy contribution for release of 1 mol of water of +33 J K^{-1} mol^{-1}. Other contributions, which cannot be estimated with certainty, would include some positive translational and rotational contributions from the released aquo ligand and positive contributions from the enhanced flexibility of en chelate rings as the dissociated intermediate is formed.

Isomerization in Concentrated Electrolyte Media. The rate of isomerization is retarded when the concentration of "inert" electrolyte is increased in the reaction medium from 0.05 to 1.0 M. Not unexpectedly, there are slight differences in rate coefficients when 1.0 M $NaClO_4$ is substituted for 1.0 M $HClO_4$ but the values of the activation volume parameters are not statistically different in the two electrolytes. The effect may therefore be ascribed to a general electrolyte phenomenon rather than a specific acid retardation effect. The effect on rate coefficients is not drastic; for example, at 308 K, a retardation by 2.3 times occurs on increasing the $HClO_4$ concentration from 0.05 to 1.0 M. However, the effect on the thermal activation parameters is quite marked; $\Delta H^{\ddagger}$ is reduced by 9.7 kJ mol^{-1} while $\Delta S^{\ddagger}$ is less positive by 39 J K^{-1} mol^{-1} in the concentrated electrolytes. The overall retardation thus arises from the counterbalancing of a less favorable $\Delta S^{\ddagger}$ effect, amounting to +12.0 kJ mol^{-1} in $\Delta G^{\ddagger}$ at 308 K, by a more favorable contribution of −9.7 kJ mol^{-1} from $\Delta H^{\ddagger}$.

This electrolyte effect is also revealed by the activation volume parameters. The preferred values, derived by weighting appropriately the 97 individual runs conducted at 1.0 M electrolyte concentrations, are $\Delta V_0^\ddagger = 13.2 \pm 0.7$ cm^3 mol^{-1} and $\Delta\beta^\ddagger = 0.10 \pm 0.03$ cm^3 mol^{-1} MPa^{-1}. The volume of activation thus remains large and positive, although somewhat less than that for low electrolyte concentrations, and a D mechanism with aquo ligand release probably still operates. However, the ln k_P vs. P plots for concentrated electrolyte media are markedly more curved[12] than for low electrolyte media. The value $\Delta\beta^\ddagger = 0.10 \pm 0.03$ is some 10 times greater than that evaluated for low electrolyte concentrations and is very much greater than that expected ($\simeq 0.008$) for the release of a single aquo ligand into the bulk solvent water. This suggests that there is extensive desolvation occurring from hydration zones about the substrate cation when the transition state for isomerization is generated in concentrated electrolyte media.

The D mechanism described for isomerization in 0.05 M $HClO_4$ was uncomplicated by free energy barriers to motion within, and from, the hydration spheres surrounding the $Co(en)_2(OH_2)_2{}^{3+}$ cation. The mechanism was therefore expressed broadly as dissociative release of an aquo ligand to the bulk solvent. In finer detail, the release of an aquo ligand into a hole in the first hydration sphere will be accompanied by a sequence of cooperative diffusive displacements of other water molecules beyond the cation and deeper into the solvent so that a single water molecule is effectively transferred into the bulk solvent. Furthermore, the movement of en chelate rings about the cobalt(III) center, which is necessary to achieve stereochemical change, will not be hindered by the structure in the solvent zones around the cation at low electrolyte concentration.

In concentrated electrolyte media, the free energy balance changes because of the influence of ionic association. The ground state of the *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ cation in 1 M $HClO_4/NaClO_4$ media probably involves extensive ion association, of the solvent-separated ion-pair type, with a substantial proportion of solvent water bound to the various ionic types. The overall effect would be severely electrostricted hydration zones of the ionic aggregates. When a dissociative transition state is generated, there is a larger free energy barrier to creation of vacancies in the hydration sphere of the cation to accommodate the dissociating aquo ligand and the moving chelate rings. The large value of $\Delta\beta^\ddagger$ would suggest that these vacancies are created by a partial disordering of the hydrated ionic aggregates with the effective release of several water molecules to the remaining bulk solvent. The actual number of water molecules released cannot be estimated reliably since the known compressibility value for pure water ($\beta = 0.0084$) is unlikely to apply to bulk water with concentrated electrolyte solutes.

In summary, our pressure studies suggest that the trans → cis isomerization proceeds through a D mechanism with a large positive $\Delta V_0^\ddagger$ value in both high- and low-electrolyte media. Different activation parameters arise in these different media because of the increased importance of desolvation of the ion-associated transition state in high concentrations (1 M) of electrolyte. Our measurements of $\Delta\beta^\ddagger$ for 0.5 M $HClO_4$ indicate that desolvation is also quite important at this intermediate electrolyte concentration.

Intermediates for Exchange and Isomerization. The succeeding paper by Tong, Krouse, and Swaddle[2] reports $H_2{}^{18}O$ exchange studies with $Co(en)_2(OH_2)_2{}^{3+}$ (0.20 *m*) in 0.80 *m* $HClO_4$, a medium in which our studies would have suggested ionic association is operative. In contrast to the case of isomerization, for the exchange reaction $\Delta V_{ex}^\ddagger = +5.9 \pm 0.2$ cm^3 mol^{-1} and no pressure variation of $\Delta V_{ex}^\ddagger$ is observable. The transition states for exchange and isomerization are clearly different and an I_d mechanism is proposed[2] for exchange in contrast to the D mechanism proposed here for isomerization. The existence of two intermediates for exchange and isomerization as originally proposed by Kruse and Taube[4] is revealed by these different volumes of activation and it is clear that dissociated intermediates are involved rather than the alternative associative intermediates generated by edge displacement. If a tetragonal-pyramidal intermediate is proposed for the aquo exchange and a trigonal-bipyramidal intermediate for the trans → cis interconversion, then the need for desolvation of the secondary hydration sphere in high-electrolyte media must arise partly from motion of the en chelate rings as the trigonal bipyramid is formed from the tetragonal-pyramidal structure. We will show in a subsequent paper[3] that oxalate anions can compete with water for the tetragonal-pyramidal intermediate.

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