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Kinetics of Aquo Exchange of Diaquobis(ethylenediamine)cobalt(III) Ion in Acidic Aqueous Solution. Pressure Effect and Mechanism

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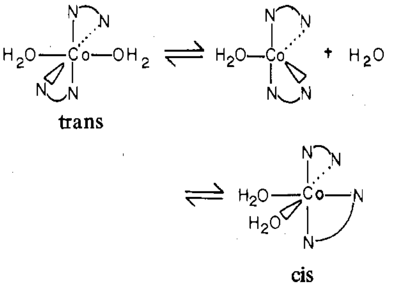
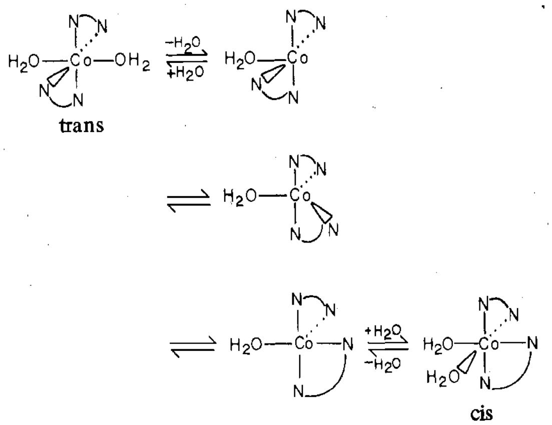
The volume of activation for aquo exchange in *trans*-$Co(en)_2(OH_2)_2^{3+}$ in aqueous $HClO_4$ (ionic strength 2.0 mol kg^{-1}, 308 K) is +5.9 ± 0.2 cm^3 mol^{-1} and is independent of pressure over the range 0.1–300 MPa at least. These observations, taken together with those of Stranks and Vanderhoek (preceding paper), for the isomerization of *trans*-$Co(en)_2(OH_2)_2^{3+}$, are interpreted in terms of a dissociative interchange mechanism involving a tetragonal-pyramidal intermediate for aquo exchange and a dissociative mechanism with a trigonal-bipyramidal intermediate for the isomerization.

Kruse and Taube[2] showed that, in the isomerization of *trans*-diaquobis(ethylenediamine)cobalt(III) ion in aqueous solution, one aquo ligand is exchanged with solvent and that stereoretentive aquo exchange in the trans isomer is faster (by some 70%, at 298 K in 1 *m* $HClO_4$) than isomerization. These data suggest, but do not prove, a dissociative (D) or dissociative interchange (I_d) mechanism for both processes. Kruse and Taube[2] pointed out that their kinetic data for the isomerization and aquo exchange of *cis*- and *trans*-$Co(en)_2(OH_2)_2^{3+}$ cannot be explained on the basis of a single five-coordinate intermediate having trigonal-bipyramidal geometry (mechanism I) but suggested one in which aquo exchange occurs mainly via a primary tetragonal-pyramidal intermediate which may also rearrange to trigonal-bipyramidal geometry and so permit isomerization on recombination with water (mechanism II).[3]



(I)



(II)

We now present data on the effect of pressure on the rate of the aquo-exchange reaction of the trans isomer, which, taken in conjunction with corresponding measurements by Stranks and Vanderhoek[4] on the kinetics of the isomerization reaction and anation processes, indicate that dissociative mechanisms are indeed involved, that the rearrangement of the presumed five-coordinate intermediate in isomerization is accompanied by extensive desolvation in the transition state, and that stereoretentive aquo exchange does not involve the same rearranged intermediate as does isomerization.

Experimental Section

Preparation of *trans*-$[Co(en)_2(OH_2)(OH)](ClO_4)_2$. *trans*-$[Co(en)_2Cl_2]Cl$ was made by a standard method[5] and recrystallized from aqueous HCl. A mixture of this product (10 g), silver oxide (12.2 g), and water (8 cm^3) was stirred well and filtered. The filtrate was ice-cooled and acidified carefully with 71% $HClO_4$ (1.2–1.8 cm^3). The precipitated mixture of *cis*- and *trans*-$[Co(en)_2(OH_2)_2](ClO_4)_3 \cdot xH_2O$ was filtered, washed with acetone, and air-dried (1.66 g). This material was redissolved in 28 cm^3 of water, the pH was adjusted to 7.58–7.66 with 4 *m* NaOH, Norit charcoal (0.3 g) was added, and the mixture was set aside at room temperature for 14 h. The filtered solution was treated with $NaClO_4$ to precipitate *trans*-$[Co(en)_2(OH)(OH_2)](ClO_4)_2$, which was filtered, washed with acetone, and dried in vacuo over P_2O_5; yield 0.5 g. Anal. Calcd for $CoN_4C_4H_{19}Cl_2O_{10}$: N, 13.56. Found: N, 13.40. The visible spectrum agreed well with that reported[6] for the trans isomer. The $H_2{}^{18}O$-labeled salt was made in the same way, using 1.5% $H_2{}^{18}O$ water as solvent in the conversion of the dichloro complex.

Kinetic Measurements. A solution (0.2 *m*) of $H_2{}^{18}O$-labeled *trans*-$[Co(en)_2(OH)(OH_2)](ClO_4)_2$ in 0.8 *m* $HClO_4$ was prewarmed and then pressurized (±0.5 MPa) in the thermostated (±0.01 K) pressure apparatus previously described;[7] it was established that the outlet capillary of tantalum could be replaced by one of stainless steel without affecting the reaction rate. Samples (about 1.5 cm^3) were withdrawn periodically (rejecting "hold-up"), chilled with ice water, and treated with just enough concentrated HCl (1.0–1.6 cm^3) to precipitate *trans*-$[Co(en)_2(OH_2)_2]Cl_3$, which was filtered, washed with acetone, and dried in vacuo over P_2O_5 for at least 18 h. The coordinated water was recovered on a vacuum line by heating the salt at 363–413 K and was converted to CO_2 as described previously[8] for mass spectrometric analysis to determine the ^{18}O abundance.

Kruse and Taube[2] precipitated the *trans*-$Co(en)_2(OH_2)_2^{3+}$ ion to the exclusion of the cis isomer by addition of hexachlorothallate(III) ion in aqueous HCl and reported that the precipitate contained two molecules of water of crystallization as well as two aquo ligands per cobalt atom. In our hands, the Kruse–Taube procedure yielded mainly *trans*-$[Co(en)_2(OH_2)_2]Cl_3$, and the above procedure was therefore adopted as being simpler and yielded a product free of both the cis isomer and lattice water. Nevertheless, the exchange kinetics were not in general followed beyond 50% completion, since the effectiveness of the procedure was reduced thereafter by accumulation of the isomerized complex in solution. Other potential non-oxygen-containing precipitants which were investigated included HBr (which precipitated both the cis and the trans isomers together) and $NaBF_4$ and HBF_4 (which gave no precipitate).

Results and Discussion

First-order rate coefficients k_{ex} for the aquo-exchange reaction at 307.97 K and ionic strength $I = 2.0$ *m* are collected in Table I. The datum for atmospheric pressure (ca. 0.1 MPa) was obtained using ordinary laboratory glassware and agreed well with the value of 6.33×10^{-5} s^{-1} extrapolated from measurements made in the pressure assembly and with 6.32×10^{-5} s^{-1} interpolated from the data of Kruse and Taube[2] (which yield $\Delta H^* = 126._2$ kJ mol^{-1} and $\Delta S^* = 84._2$ J K^{-1}

Table I. First-Order Rate Coefficients k_{ex} for the Exchange of $H_2{}^{18}O$ between *trans*-$Co(en)_2({}^{18}OH_2)_2{}^{3+}$ and Solvent Water as a Function of Pressure at 307.98 K[a]

Pressure, MPa	10^5k_{ex}, s^{-1}	Pressure, MPa	10^5k_{ex}, s^{-1}
0.1[b]	6.29 ± 0.38[c]	201.3	4.17 ± 0.17
6.4	6.27 ± 0.24	250.0	3.52 ± 0.14
102.5	4.90 ± 0.18	301.9	3.09 ± 0.16
102.5	5.20 ± 0.31	301.9	3.23 ± 0.08
152.4	4.23 ± 0.27		

[a] $[Co(en)_2(OH_2)_2(ClO_4)_3] = 0.200$ *m*; $[HClO_4] = 0.80$ *m*. Rate data refer to exchange of *both* aquo ligands. [b] In ordinary glass vessels. [c] Standard errors cited refer to uncertainties within individual kinetic runs.

mol^{-1} for the exchange of both aquo ligands, under the same conditions).

A plot of ln k_{ex} vs. pressure is linear within the experimental uncertainty (which is somewhat larger than usual because the reaction could be followed only over the first 50%) and so yields a *pressure-independent* volume of activation $\Delta V^* = +5.9 \pm 0.2$ cm^3 mol^{-1}. It follows that there is predominant Co–OH_2 bond breaking with little or no change in solvation on going to the transition state of this simple, symmetrical reaction, since significant solvational changes manifest themselves in a pressure dependence of the volume of activation.[9–11] Thus, the mechanism is I_d or D; the numerical value of $\Delta V_{ex}{}^*$ is too large to accommodate extreme arguments (as in footnote 10 of ref 11) for an I_a or A process. This result again illustrates the anomalous behavior in substitution of Co(III) complexes among cationic octahedral complexes of the trivalent transition metals, which in general yield negative values of $\Delta V_{ex}{}^*$ in solvent-exchange reactions, implying an I_a mechanism.[8,9,11]

This result lends support to Hunt and Taube's[12] interpretation of their value of $\Delta V^* = +1.2$ cm^3 mol^{-1} for aquo exchange in aqueous $Co(NH_3)_5OH_2{}^{3+}$. The larger $\Delta V_{ex}{}^*$ value for *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ probably reflects in part relaxation of the greater steric compressions which are presumably present in the initial state vis-à-vis $Co(NH_3)_5OH_2{}^{3+}$, by analogy[9] with Foxman's observations[13] on $Co(NH_2CH_3)_5Cl^{2+}$, but could also contain a contribution from reaquation of the trigonal-bipyramidal species of mechanism II to the trans configuration. Stranks and Vanderhoek[4] found, for the isomerization of *trans*-$Co(en)_2(OH_2)_2{}^{3+}$, $\Delta V_{iso}{}^*$ (at zero pressure) = +14.3 and +13.2 cm^3 mol^{-1} at $I = 0.05$ and 1.0 M, respectively; this isomerization presumably proceeds via the trigonal-bipyramidal species of mechanism II, there being no indication of Co–N bond fission, and so the very large size of $\Delta V_{iso}{}^*$ relative to $\Delta V_{ex}{}^*$ precludes the possibility that a significant fraction of aquo exchange goes through the trigonal-bipyramidal intermediate. Furthermore, $\Delta V_{iso}{}^*$ is strongly pressure dependent, with $-(\partial\Delta V^*/\partial P)_T = 0.01$ and 0.1 cm^3 mol^{-1} MPa^{-1} at $I = 0.05$ and 1.0 M, respectively,[4] whereas no pressure dependence of $\Delta V_{ex}{}^*$ can be detected up to 300 MPa. In any event, the isomerization equilibrium lies heavily in favor of the cis isomer in acidic solution;[2] that is, reaquation of the trigonal-bipyramidal intermediate to the trans configuration is not favored.

Thus, aquo exchange in *trans*-$Co(en)_2(OH_2)_2{}^{3+}$ proceeds almost exclusively via a tetragonal-pyramidal five-coordinate intermediate without significant solvational change. This mechanism is best described as I_d rather than D, since the lack of significant pressure dependence of $\Delta V_{ex}{}^*$ shows that the second coordination sphere (solvation sheath) does not relax before six-coordination is regained.[9–11] The isomerization reaction must involve rearrangement of the tetragonal-pyramidal intermediate to trigonal bipyramidal, with extensive concomitant desolvation which is reflected in the strong pressure dependence of $\Delta V_{iso}{}^*$; this mechanism should therefore be classified as D.[9] Desolvation during the rearrangement of a tetragonal-pyramidal intermediate to trigonal bipyramidal also provides a rationale[9] for Tobe's observation[14] that ΔS^* is usually much more positive for aquations of complexes of the type of $CoLACl^{n+}$ (where L = $(en)_2$, trien, cyclam, etc., and A is an "inert" ligand) when there is marked steric change than when the reaction is stereoretentive. Finally, the closeness of the value of $\Delta V_{ex}{}^*$ to the volumes of activation obtained by Stranks and Vanderhoek[15] for stereoretentive anation within ion pairs of the type $Co(en)_2(OH_2)_2{}^{3+},X^{n-}$ indicates that both anation and solvent exchange proceed by I_d mechanisms in $Co(en)_2(OH_2)_2{}^{3+}$.

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Registry No. *trans*-$[Co(en)_2(OH_2)(OH)](ClO_4)_2$, 14099-22-0; *trans*-$Co(en)_2(OH_2)_2{}^{3+}$, 19314-32-0; *trans*-$[Co(en)_2Cl_2]Cl$, 14040-33-6; H_2O, 7732-18-5.

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