CONTRIBUTION FROM THE WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1, ENGLAND

Mechanisms and Steric Course of Octahedral Aquation. XIV.[1] The Activation Parameters and Steric Course of Aquation of *trans*-Chloro- and *trans*-Bromoazidobis(ethylenediamine)cobalt(III) Cations

BY V. RICEVUTO[2] AND M. L. TOBE

Received February 18, 1970

The rates and steric course of aquation of *trans*-$[Co(en)_2N_3Cl]ClO_4$ have been reexamined over a 50° range of temperature. At 25.0°, $[H^+] = 0.01\ M$, $k = 2.6 \times 10^{-4}$ sec^{-1}, $\Delta H^{\ddagger} = 20.7 \pm 0.3$ kcal/mol, and $\Delta S^{\ddagger} = -6 \pm 2$ eu. The corresponding bromo complex has been prepared and examined for the first time. At 25.0°, $[H^+] = 0.01\ M$, $k = 8.5 \times 10^{-4}$ sec^{-1}, $\Delta H^{\ddagger} = 20.0 \pm 0.5$ kcal/mol, and $\Delta S^{\ddagger} = -6 \pm 2$ eu. In all cases, after correction for subsequent isomerization, it is shown that aquation occurs with complete retention of configuration. The specific rate of approach to equilibrium of *cis*- and *trans*-$Co(en)_2N_3OH^{2+}$ was also measured over a 30° temperature range. At 25.0°, $[H^+] = 0.010\ M$, $k = 9.6 \times 10^{-5}$ sec^{-1}, $\Delta H^{\ddagger} = 32.0 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = +30 \pm 3$ eu. The equilibrium composition (43% *trans*) is independent of temperature over this range. The steric course of spontaneous and Hg^{2+}-catalyzed aquation of *cis*-$Co(en)_2N_3Cl^+$ has also been reexamined. It has been shown conclusively that both processes give identical amounts of the *cis*- and *trans*-aquoazido products and there is reasonable evidence to suggest that some 15% of the initial reaction product has the *trans* configuration. This is the first example of stereochemical change in the spontaneous aquation of a *cis*-$Co(en)_2AX^{n+}$ complex.

Introduction

It has been suggested recently that a relationship exists between the occurrence of steric change in octahedral substitution and the entropy of activation of the process.[3] For reactions of the type

$$trans\text{-}MLACl^{n+} + H_2O \longrightarrow MLAH_2O^{(n+1)} + Cl^-$$

where M = Cr(III), Co(III), or Rh(III) and L represents $(NH_3)_4$, $(en)_2$, or a range of quadridentate amines, the entropy of activation when the product was exclusively *trans* ($-12 \rightarrow 0$ cal deg^{-1} mol^{-1}) was significantly lower than that found when the product also contained the *cis* isomer ($0 \rightarrow +20$ cal deg^{-1} mol^{-1}). It was suggested that this relationship allowed one to distinguish between a square-pyramidal and trigonal-bipyramidal form of the five-coordinate intermediate of a dissociative process. The case where $A = N_3$ ($\Delta S^{\ddagger} \approx 0$; product contains 20% *cis* isomer) seemed to merit reexamination for a number of reasons. There were reports in the literature[4,5] that the spectra used for the product analysis in the original work[6] were in error and that the Hg^{2+}-catalyzed aquation of the *trans*-chloroazido complex was stereoretentive. Furthermore, the azido group, in principle, has the ability to act both as a π donor, like Cl or OH, or as a π acceptor, like CN and NO_2. We wondered whether this might constitute a system where both forms of the intermediate were possible. Thus we have examined the rate and steric course of aquation of *trans*-$Co(en)_2N_3X^+$ (X = Cl, Br) over as wide a range of temperature as possible in order to see whether the steric course and entropy of activation are significantly temperature dependent.

Experimental Section

trans-Diazidobis(ethylenediamine)cobalt(III) perchlorate was prepared by the air oxidation of $Co(ClO_4)_2$, ethylenediamine, and sodium azide according to the method of Buckingham, *et al.*[5]

trans-Chloroazidobis(ethylenediamine)cobalt(III) perchlorate was prepared from the *trans*-diazidoperchlorate by the method of Buckingham, *et al.*[5] Unless the reaction conditions are carefully controlled, the main product of the reaction is *cis*-$[Co(en)_2Cl_2]ClO_4$. This, incidentally constitutes an extremely useful method for making this complex. The initial product was recrystallized a number of times from warm acidified water.

***trans*-Bromoazidobis(ethylenediamine)cobalt(III) Perchlorate.**—*trans*-$[Co(en)_2(N_3)_2]ClO_4$ (11 g) was added to freshly distilled, bromine-free hydrobromic acid (60 ml, 48%) at room temperature and stirred until a blue-green solution was obtained (15–20 sec). Solid sodium perchlorate (20 g) was then added and the mixture was quickly cooled to just above its freezing point. Crystallization was induced by scratching the walls of the beaker and after 10 min the crude product was filtered off, washed with small portions of ethanol and then ether, and dried. The solid was extracted with small portions of cold water until only the yellow-green *trans*-$[Co(en)_2Br_2]ClO_4$ impurity remained on the filter. The complex was recovered from the filtrate by adding a large excess of sodium perchlorate. The filtered-off solid was extracted with acetone and the filtrate was evaporated to dryness under vacuum. Two further recrystallizations from cold water gave an analytically and kinetically pure sample. The final yield (5%), however, was very low. *Anal.* Calcd for $C_4H_{16}N_7O_4BrClCo$: C, 12.0; H, 4.0; N, 24.5; total halogen, 28.8. Found: C, 12.0; H, 4.0; N, 23.2; total halogen, 28.8.[7]

cis-Diazidobis(ethylenediamine)cobalt(III) nitrate was prepared by the method of Buckingham.[5]

cis-Chloroazidobis(ethylenediamine)cobalt(III) chloride was prepared by the method of Buckingham[5] and recrystallized from ethanol–water at least five times. *Anal.* Calcd for $C_4H_{16}N_7Cl_2Co$: C, 16.4; H, 5.5; N, 33.6. Calcd for $C_4H_{16}N_7Cl_2Co \cdot H_2O$: C, 15.5; H, 5.8; N, 31.6. Found: C, 16.1; H, 5.5; N, 31.9.

cis-Aquoazidobis(ethylenediamine)cobalt(III) sulfate was pre-

---

(1) Part XIII: E. Campi, J. Ferguson, and M. L. Tobe, *Inorg. Chem.*, **9**, 1781 (1970).

(2) On leave from Istituto di Chimica-Fisica, University of Messina, Messina, Italy.

(3) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

(4) D. A. Loeliger and H. Taube, *ibid.*, **4**, 1032 (1965).

(5) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *ibid.*, **6**, 1807 (1967).

(6) P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4812 (1960).

(7) Halide was estimated gravimetrically. This figure is calculated on the assumption that the silver halide precipitate contained equimolar amounts of the chloride and bromide.

pared by the method of Buckingham[5] and recrystallized to constant spectrum. *Anal.* Calcd for $C_4H_{18}N_7O_5CoS \cdot H_2O$: C, 13.6; H, 5.7; N, 27.8. Calcd for $C_4H_{18}N_7O_5CoS$: C, 14.3; H, 5.4; N, 29.2. Found: C, 14.0; H, 5.0; N, 29.4.

All other reagents were Analar grade.

Kinetics.—All reactions were followed spectrophotometrically using a Unicam SP800 recording spectrophotometer. For the reactions at 0°, the solutions were made up with precooled dilute perchloric acid and kept in the thermostat. Samples were withdrawn at the appropriate times and the spectrum was immediately measured at room temperature. At higher temperatures the spectrophotometer cell served as the reaction vessel. Temperature control (±0.1°) was achieved by circulating water from a thermostat and the reaction temperature was determined at the end of the run by a thermometer actually placed in the reaction mixture. In all but the fastest reactions the solutions were prepared by adding a known volume of dilute perchloric acid (previously brought to the reaction temperature) to a weighed amount of solid complex in the spectrophotometer cells. In the fastest runs, the solvent was brought to reaction temperature in the spectrophotometer and the reaction was started by adding the complex by a small spatula and stirring the solution rapidly with a small platinum paddle that could be retracted out of the light path. The fastest reactions were followed by clamping the spectrophotometer at a fixed wavelength and allowing the recorder bed to move at a known constant rate.

Spectrophotometric Analysis.—By fitting optical density data at three suitable wavelengths into the appropriate expressions for concentration derived from the solution of the three simultaneous Beer's law equations it was possible to determine the concentrations of *trans*-$Co(en)_2N_3X^+$ and *cis*- and *trans*-$Co(en)_2N_3H_2O^{2+}$ at various stages of the reaction. The extinction coefficients used are given in Table I.

TABLE I
MOLAR EXTINCTION COEFFICIENTS (cm^{-1} M^{-1})
USED IN THE CALCULATIONS

	580 nm	550 nm	500 nm
trans-$Co(en)_2N_3Cl^+$	237	187	45
trans-$Co(en)_2N_3Br^+$	240	140	38
trans-$Co(en)_2N_3H_2O^{2+}$	191	230	103
cis-$Co(en)_2N_3H_2O^{2+}$	109	193	293

In the faster reactions, where a significant amount of reaction took place within the time necessary to scan the spectrum (2 min), it was necessary to make certain that the three optical densities fed into the equations related to the same moment in time. This was done by plotting the optical density as a function of the corrected time ($t + \Delta t$, where t is time recorded at the start of the scan and Δt is the time needed for the recorder to reach the appropriate wavelength) at each of these wavelengths and obtaining the necessary data.

Results

Aquation of *trans*-Chloro- and *trans*-Bromoazidobis(ethylenediamine)cobalt(III) Cations.—Spectrophotometric studies of the changes in the spectra of solutions initially containing *trans*-$Co(en)_2N_3Cl^+$ confirm the two stages reported by Staples and Tobe[8] and identified as a solvolytic displacement of Cl^- and the subsequent *trans* ⇌ *cis* isomerization of the aquoazido product. The *trans*-bromoazido complex behaves in a similar way. The extent to which the second stage interferes with the first depends upon the nature of the substrate and upon the temperature. Interference is least at the lowest temperatures and with the more labile bromo substrate. The second stage, which has also been studied independently (see below), is characterized by an isosbestic point at 543 nm and therefore the rate of aquation was measured by following the change of optical density at this wavelength. Good linear plots were obtained for log $(D_\infty - D_t)$ against time, where D_t and D_∞ are the optical densities at 543 nm at time t and after 10 half-lives, respectively. The first-order rate constants obtained in this way are collected in Table II. In those runs where the concentrations of the three components were determined by spectrophotometric analysis, it was also possible to determine the rate constant from the slope of the plot of log $[Co(en)_2N_3X^+]$ against time. These are also collected in Table II.

TABLE II
FIRST-ORDER RATE CONSTANTS FOR THE AQUATION OF
trans-$Co(en)_2N_3X^+$ IN 0.01 M PERCHLORIC ACID;
[COMPLEX] = 1.2×10^{-3} M

X	Temp, °C	10^4k_a, sec^{-1}	X	Temp, °C	10^4k_a, sec^{-1}
Cl	0.3	0.092[a]	Cl	41.5	17.1
Cl	10.5	0.435	Cl	49.5	45
Cl	10.1	0.322[b]	Cl	49.5	41
Cl	25.0	2.20[b]	Cl	51.0	53[a]
Cl	26.0	2.90	Cl	58.7	92[a]
Cl	31.5	6.00	Br	15.6	2.8
Cl	35.0	8.70[b]	Br	26.5	10.4
Cl	40.0	13.4	Br	31.0	17.7
Cl	40.2	15.5	Br	40.5	46.5
Cl	40.6	16.7	Br	49.0	109

[a] By a sampling method. [b] Data from ref 8.

The Kinetics of Isomerization of *cis*- and *trans*-Aquaoazidobis(ethylenediamine)cobalt(III) Cations.—This reaction has previously been studied only at 25.0°[5,8] and, in order to correct for subsequent isomerization of the product in the determination of the steric course of the aquation, it was necessary to determine the position of, and rate of approach to, equilibrium over a range of temperature.

When acidified aqueous solutions (pH 2) of *trans*-$Co(en)N_3X^+$ (X = Cl, Br) or *cis*-$Co(en)_2N_3Cl^+$ were allowed to stand until no further change in spectrum was observed, the final spectrum was independent of the nature of the starting material and fully in agreement with that expected for a mixture of *cis*- and *trans*-$Co(en)_2N_3H_2O^{2+}$ containing 57% of the *cis* isomer (Table II). The composition did not vary significantly with temperature over the range studied. There was no evidence for the displacement of the azido group under these conditions. Since, in the regions where it was convenient to study the reaction, the rate of the isomerization reaction was never much more than an order of magnitude different from the solvolytic reaction, it was inconvenient to use this method to examine the second step. Although it was possible to remove the coordinated chloride or bromine rapidly and stereospecifically with Hg^{2+}, the presence of excess mercuric ions in the solution affected the subsequent isomerization process. An alternative method of generating the aquo complexes rapidly made use of the

---

[8] P. J. Staples and M. L. Tobe, *J. Chem. Soc.*, 4803 (1960).

fact that the composition of the product of base hydrolysis of *trans*-$Co(en)_2N_3Cl^+$ ($\leq 10\%$ *cis*-hydroxoazido complex) was different from that of the equilibrium aquo mixture. Solutions of the *trans*-chloroazido complex were brought to the reaction temperature and treated with 10-fold excess of sodium hydroxide solution. After the appropriate time (30 sec at 25° to ~1 sec at the highest temperature) the solutions were acidified to pH 2 and the subsequent spectrophotometric changes followed. The base hydrolysis of the azidohydroxo isomers is sufficiently slow compared to that of the chloroazido complex to allow the first reaction to be complete before the second interferes. The conversion of the hydroxo to the aquo complex takes place without any change in configuration. The specific rate constants for approach to equilibrium $k_{sp} = k_c + k_t$ were determined from the slope of log $(D_\infty - D_t)$ against time where the D terms represent the optical densities at 500 nm. k_c and k_t were individually determined using the relationship $[cis]/[trans]$ at equilibrium $= K = k_t/k_c$. These values are collected in Table III. When this research was nearly complete, it was necessary to prepare pure *cis*-$[Co(en)_2N_3H_2O]SO_3 \cdot H_2O$. The rate of isomerization of this complex is also reported.

TABLE III

RATE CONSTANTS FOR THE ISOMERIZATION REACTION[a]

$$cis\text{-}Co(en)_2N_3H_2O^{2+} \underset{k_t}{\overset{k_c}{\rightleftharpoons}} trans\text{-}Co(en)_2N_3H_2O^{2+}$$

Temp, °C	10^3k_{sp}, sec^{-1}	10^3k_c, sec^{-1}	10^3k_t, sec^{-1}
25.0	0.100[b]	0.043	0.057
26.0	0.120	0.052	0.068
31.5	0.340	0.146	0.194
38.5	1.10[c]	0.47	0.63
40.0	1.42	0.61	0.81
49.5	5.70	2.45	3.25
58.7	22.5	9.7	12.8

[a] $[H^+] = 0.01$ *M*; $\mu = 0.02$ *M*. [b] Data from ref 8. [c] Using pure *cis*-$[Co(en)_2N_3H_2O]SO_4 \cdot H_2O$.

The Steric Course of Aquation of *trans*-$Co(en)_2N_3X^+$.—On adding excess mercuric perchlorate solution to freshly prepared acidified (pH 2) aqueous solutions of *trans*-$Co(en)_2N_3X^+$ (X = Cl, Br) the spectrum changes rapidly to one identical with that reported by Buckingham, *et al.*, for the *trans*-$Co(en)_2N_3H_2O^{2+}$ cation.[5] This confirms their observation that the Hg^{2+}-catalyzed aquation of the *trans*-chloroazido complex gives 100% *trans* product and shows that the bromo complex is likewise converted in a stereoretentive fashion.

At temperatures below 35° for the chloroazido complex and 55° for the bromoazido complex the initial part of the aquation reaction is characterized by sets of isosbestic points (nm) at 565 (223), 432 (110) and 572 (213), 458 (68), respectively (molar extinction coefficients in parentheses). These isosbestic points correspond exactly to the crossing points of the spectra of the *trans*-chloro- and *trans*-bromoazido complexes with that of the pure *trans*-$Co(en)_2N_3H_2O^{2+}$ complex. Owing to the relative positions of the spectra, this method would be sensitive to the presence of 3% *cis*-aquoazido complex when derived from the chloro complex. At higher temperatures, when the isomerization of the product was fast enough to interfere with this simple method, a complete spectrophotometric analysis was carried out. The fraction of aquoazido complex present in the *trans* form (f) was plotted against the fraction of the complex in the aquo form (F_a) and the correction for subsequent isomerization was made by extrapolating the curve back to zero reaction. The extrapolation was guided by the calculated expression

$$\frac{f - f_\infty}{f_0 - f_\infty} = \frac{k_a}{k_{sp} - k_a}\left\{\frac{F_a - F_a^{k_{sp}/k_a}}{F_a}\right\}$$

where k_a and k_{sp} are the first-order rate constants for aquation and isomerization and f_∞ is the fraction of the complex in the *cis* form at isomerization equilibrium. f_0 is the fraction of *trans* isomer in the direct product of the aquation. The data gathered at 40.5 and 51.0° are shown in Figure 1, together with the results of an experiment carried out at 0.3° in order to compare the results of this elaborate analysis with the simple method. In all cases it is clear that aquation takes place with >95% retention of configuration.

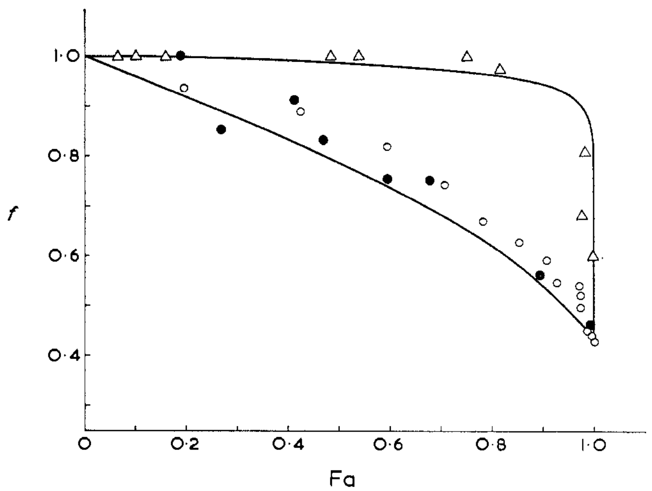

Figure 1.—Fraction of aquoazido product in the *trans* form (f) as a function of the fraction of aquation completed (F_a). Experimental points: △, 0.3°; ○, 49.5°; ●, 58.7°. Calculated lines are for 0.3 and 58.7°, assuming no *cis*-aquoazido complex is formed directly (*i.e.*, $f_0 = 1.00$).

The Steric Course of Aquation of *cis*-$Co(en)_2N_3Cl^+$.—Knowing that the rate of isomerization of the *cis*- and *trans*-aquoazido products was very much less than the rate of aquation of the *cis*-chloroazido complex at 0° (from the extrapolation of the data in ref 8), it seemed worthwhile examining the steric course of the reaction at this low temperature when the second stage did not interfere. The spectrum of a solution originally containing *cis*-$[Co(en)_2N_3Cl]Cl$ was measured after 93 hr at 0.0°. By this time most of the *cis*-chloroazido complex had aquated (k_a(extrapolated to 0°) $\approx 1.2 \times 10^{-5}$ sec^{-1}) and the spectrum was quite close to that of the immediate product of the mercury-catalyzed aquation of *cis*-$Co(en)_2N_3Cl^+$. After a further 24 hr, the similarity was even closer. After this the spectrum change was as expected for the *cis* ⇌ *trans* isomerization of the aquoazido product (k_{sp}(extrapolated to 0°) ≈ 6×10^{-1} sec^{-1}). The spectrum, measured after 117 hr at 0°, is compared in Figure 2 with that obtained by adding excess mercuric perchlorate to a freshly prepared solution of *cis*-[Co(en)$_2$N$_3$Cl]Cl. The spectrum of the *cis*-chloroazido complex is also shown for comparison. All three solutions were made up from aliquot portions of a single stock solution and have identical concentrations. The difference between the spectra of the Hg^{2+}-induced reaction and the spontaneously aquated solution is fully accounted for by the subsequent isomerization step. Considering this as two consecutive first-order reactions

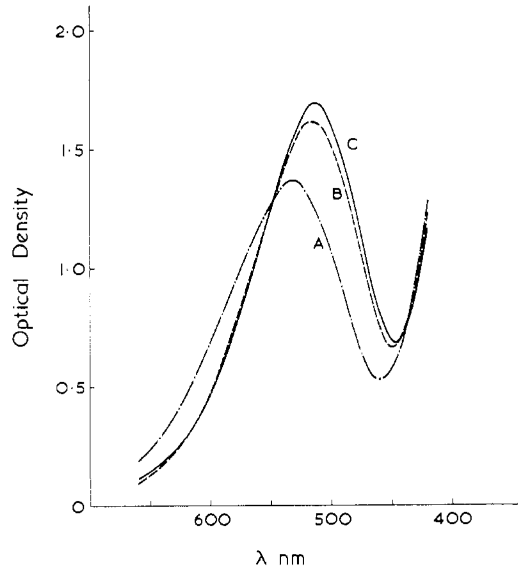

Figure 2.—Visible absorption spectra of aliquots of a single solution of *cis*-[Co(en)$_2$N$_3$Cl]Cl: (A) in 0.01 *M* HClO$_4$, measured immediately; (B) in 0.01 *M* HClO$_4$, measured after 117 hr at 0°; (C) in 0.01 *M* HClO$_4$, after addition of Hg(ClO$_4$)$_2$ (0.1 *M*). Final concentration of all solutions 1.67×10^{-3} *M* in total complex (assuming the original complex is anhydrous); cell length 4 cm.

$$A \xrightarrow{k_a} B \xrightarrow{k_{sp}} C$$

where A = *cis*-Co(en)$_2$N$_3$Cl$^+$ and B = *cis*- + *trans*-Co(en)$_2$N$_3$H$_2$O^{2+} in the ratio produced by aquation and C = *cis*- + *trans*-Co(en)$_2$N$_3$H$_2$O^{2+} in the equilibrium ratio (57% *cis*), it is possible to calculate that with $k_a = 1.2 \times 10^{-5}$ sec^{-1} and $k_{sp} = 6 \times 10^{-7}$ sec^{-1} less than 1% of the chloro complex should remain after 117 hr. The fraction of the complex in the form of B is

$$B = [B]/[A_0] = \frac{k_a}{k_{sp} - k_a}(e^{-k_a t} - e^{-k_{sp} t}) = 0.81$$

and so [C]/[A$_0$] = 0.18 by difference. If B = 100% *cis* (*i.e.*, the reactions were stereoretentive), the amount of *cis*-aquo complex present after 117 hr should be (100 × 0.81 + 57 × 0.18) = 92%, but if the composition of B was the same as that of the product of the Hg^{2+}-induced reaction, 85% *cis*, then the amount of *cis*-aquo complex after 117 hr should be (85 × 0.81 + 57 × 0.18) = 80%. The spectra shown in Figure 2 are fully consistent with the latter figure.

Discussion

This reexamination of the kinetics and steric course of the spontaneous aquation of *trans*-Co(en)$_2$N$_3$X$^+$ (X = Cl, Br) has shown quite conclusively that, contrary to previous reports,[8] the reaction takes place with complete retention of configuration and this retention is observed over the whole of the range of temperature studied (0–60°). We had searched particularly for any change of steric course and entropy of activation with temperature in the belief that azide was a ligand that could, in principle, act as a π donor as well as a π acceptor and therefore might promote a square-pyramidal intermediate (retention of configuration, low entropy of activation, relatively low activation energy) at low temperatures and a trigonal-bipyramidal intermediate (stereochemical change, high entropy of activation, relatively high activation energy) at higher temperatures. We could find no evidence for curvature in the plot of log (k/T) against $1/T$ in the 60° range of temperature examined (Figure 3). The rates, activation parameters, and steric course (where relevant) of the reactions studied are collected in Table IV. The new value for the entropy of activation (−6 cal deg^{-1} mol^{-1}) is well within the range associated with the retention of configuration and so the anomaly of the *trans*-azido complex is removed and N$_3$ falls into the same category as NO$_2$ and CN, in both acid and base hydrolyses.

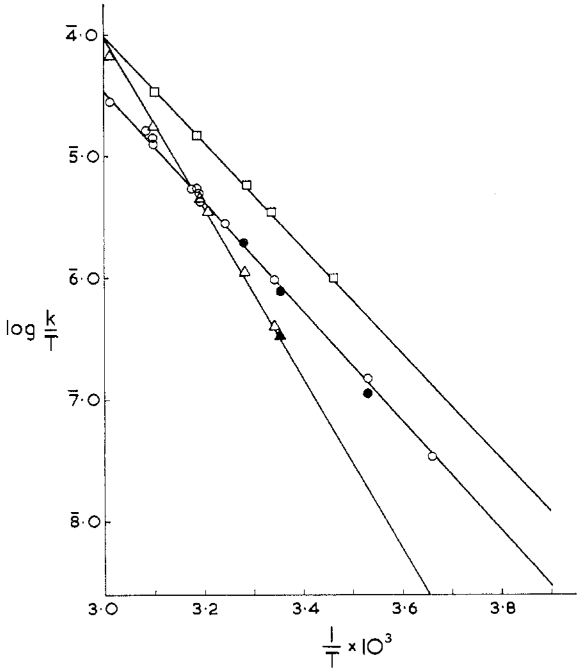

Figure 3.—Arrhenius plots for the aquation of *trans*-[Co(en)$_2$N$_3$Br]ClO$_4$ (□) and *trans*-[Co(en)$_2$N$_3$Cl]ClO$_4$ (○) and for the isomerization of *cis*- and *trans*-[Co(en)$_2$N$_3$H$_2$O^{2+} (△). (Filled symbols are data from ref 8.)

The stereoretentive nature of the aquation of the *trans* complexes caused us to reexamine the steric

TABLE IV

STERIC COURSE AND ACTIVATION PARAMETERS FOR THE AQUATION AND ISOMERIZATION OF SOME AZIDO COMPLEXES IN 10^{-2} *M* PERCHLORIC ACID

Complex	$10^4k_{25°}$, sec^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	% steric change
trans-$Co(en)_2N_3Cl^+$	2.6	20.7 ± 0.3	−6 ± 2	<3
trans-$Co(en)_2N_3Br^+$	8.5	20.0 ± 0.5	−6 ± 2	<3
cis-$Co(en)_2N_3Cl^+$	2.0[a]	21.3 ± 0.5[a]	−4 ± 2	15
$Co(en)_2N_3H_2O^{2+}$ [a]	0.96	32.0 ± 0.5	+30 ± 3	

[a] Data from ref 8.

course of the aquation of the *cis*-$Co(en)_2N_3Cl^+$ cation. The report[5] that the Hg^{2+}-catalyzed aquation, like the NO^+-induced aquation of *cis*-$Co(en)_2(N_3)_2^+$,[3] gave 15% stereochemical change, would, if correct, make this the first system in which the *trans* complex reacted with retention of configuration while its *cis* isomer underwent some stereochemical change. Buckingham[5] had confirmed, by an indirect method, the original work of Staples, *et al.*,[8] who claimed that the spontaneous aquation occurred with complete retention of configuration, but, since the original data were the result of spectrophotometric analysis based on inaccurate spectra, we felt that this too could merit reexamination. Making use of the fact that at 0° the aquation of *cis*-$Co(en)_2N_3Cl^+$ is some 20 times faster than the isomerization of its products, it was possible to show that the spectrum of the product, after correction for subsequent isomerization, was identical with that of the product of mercuric-catalyzed aquation. It seemed likely to us at this stage that these were the spectra of the pure aquoazido complex and that there was possibly some error in the spectrum published by Buckingham, *et al.*[5] We therefore repeated their preparation and obtained a material which, after adequate recrystallization, was identical with the one they described. Assuming that the complex is the monohydrate, we obtained a spectrum identical with theirs (ϵ_{508} 303). However, some slight discrepancy appears in the analysis; the agreement for C is reasonable, 14.0 (13.8), but the nitrogen values differ considerably 29.4 (27.9). Buckingham's values are in parentheses. It might, therefore, be possible to formulate the complex as the aquo complex without the water of crystallization. This will then lower the molar extinction coefficients by some 5% (ϵ_{508} 289) but the decrease is not enough to account for the spectrum of the product of Hg^{2+}-catalyzed aquation of *cis*-$Co(en)_2N_3Cl^+$ (ϵ_{508} 260). The spectrum of a solution in 0.01 *M* perchloric acid changed with time in a way that was fully consistent with a *cis* ⇌ *trans* isomerization and there was no indication of any other preliminary reaction. The final spectrum agreed closely with those obtained when *trans*-chloro- or *trans*-bromoazidobis(ethylenediamine)cobalt(III) salts had been allowed to equilibrate. The approach to equilibrium was first order and the rate constant agreed fully with those determined from the *trans* side of the equilibrium. An immediate precipitate of $BaSO_4$ is obtained when barium chloride solution is added to a fresh solution of the sulfate.

We also examined the *cis*-$[Co(en)_2N_3Cl]Cl$ complex closely in case impurity here was causing the discrepancy but our spectrum agrees closely with those reported elsewhere.

We therefore conclude that, unless there is some impurity in the *cis*-chloro- or *cis*-aquoazido complex that we have been unable to detect, the spontaneous aquation of *cis*-$Co(en)_2N_3Cl^+$ takes place with the formation of some *trans*-aquoazido product which may be as much as 15%. This does not agree with previous reports that this reaction gives 100% *cis* but does indicate that the spontaneous and Hg^{2+}-induced aquation give the same distribution of product.

This is the only example to date of a spontaneous aquation of a *cis*-$Co(en)_2ACl^+$ complex that is not fully stereoretentive and we are not able to suggest a plausible reason why the *cis*-chloroazido complex should behave in this way.

We have also, in passing, reexamined the steric course of base hydrolysis of these halogenoazido complexes. Using the method of Staples and Tobe[8] and the purified material we find that *cis*-$Co(en)_2N_3Cl^+$ gives 50 ± 2% *cis* and 50 ± 2% *trans* product, *trans*-$Co(en)_2N_3Cl^+$ gives 8 ± 2% *cis* and 92 ± 2% *trans* product, and *trans*-$Co(en)_2N_3Br^+$ gives 17 ± 2% *cis* and 83 ± 2% *trans* product. Although the primary spectroscopic data in the original determination differ markedly from our new results, the errors seem to cancel out in the calculation and these revised figures do not differ markedly from those originally published (*cis*-chloroazido gives 51% *cis; trans*-chloroazido gives 13% *cis*[8]).

Acknowledgment.—V. R. acknowledges a grant from the Consiglio Nazionale delle Ricerche, Rome, Italy.