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The Kinetics and Stereochemistry of Spontaneous Aquation of *trans*$[Co(en)_2Cl_2]^+$ and *trans*$[Co(en)_2Br_2]^+$

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The rates and steric course of spontaneous hydrolysis of trans$[Co(en)_2X_2]^+$ *in 0.1* M CF_3SO_3H *at 25 °C are recorded:* $X = Cl$, $k_s = (4.2 \pm 0.1)\ 10^{-5}\ s^{-1}$, *74 ± 1.5%* trans$[Co(en)_2(OH_2)Cl]^{2+}$ *product, 79 ± 1%* cis *at equilibrium;* $X = Br$, $k_s = (4.13 \pm 0.07)\ 10^{-4}\ s^{-1}$, *84.5 ± 1.5%* trans$[Co(en)_2(OH_2)Br]^{2+}$ *product, 74.0 ± 1.5%* cis *at equilibrium. The hydrolysis rate for the bromo complex and the steric course data for both complexes differ significantly to earlier values. The rate of isomerisation of* trans *and* cis$[Co(en)_2(OH_2)Br]^{2+}$ *have been measured in 0.01–1.0* M $HClO_4$ *and 0.1* M CF_3SO_3H *at 25 °C and the result* ($k_i = (2.32 \pm 0.07)\ 10^{-4}\ s^{-1}$) *is independent of the anion and ionic strength.*

Introduction

The mechanism of aquation of octahedral Co(III) complexes continues to come under scrutiny. In recent years there have been efforts to more precisely determine the effect of the leaving group on the steric course of aquation of $[Co(en)_2AX]^{n+}$ complexes [1–3]. These studies include both the so-called spontaneous and induced processes. Recent work on a range of *cis* isomers [1] has substantially altered the earlier and long-standing picture, and there was this expectation for the *trans* series. New data for *trans*$[Co(en)_2N_3X]^{n+}$ [4] and *trans*-$[Co(en)_2Cl(Me_2SO)]^{2+}$ [5] have since been documented, and herein we describe the rates and steric course of spontaneous aquation for *trans*$[Co(en)_2Cl_2]^+$ and *trans*$[Co(en)_2Br_2]^+$. Rate and equilibrium data for *trans*/*cis*$[Co(en)_2(OH_2)Br]^{2+}$ isomerisation, required for the *trans*$[Co(en)_2Br_2]^+$ aquation study, are given also. The corresponding $[Co(en)_2(OH_2)Cl]^{2+}$ results have appeared [5].

This report was prompted by some substantial and surprising differences between the present and earlier results [6–13], for both the rates and stereochemistry.

Experimental

Complexes

The salts *trans*- and *cis*$[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$ were from batches used in concurrent work. Full characterisation is given elsewhere [5]. *Trans*-$[Co(en)_2(OH_2)Br]S_2O_6 \cdot H_2O$ and *cis*$[Co(en)_2(OH_2)Br_2 \cdot H_2O$ were synthesised as described [14]. *Anal.* Calcd for $[Co(C_4H_{16}N_4)(OH_2)Br]S_2O_6 \cdot H_2O$: C, 10.55; H, 4.43; N, 12.31; S, 14.09; Br, 17.55. Found: C, 10.77; H, 4.85; N, 12.25; S, 14.21; Br, 17.46. Calcd. for $[Co(C_4H_{16}N_4)(OH_2)Br]Br_2 \cdot H_2O$: C, 10.56; H, 4.43; N, 12.32; Br, 52.71. Found: C, 10.81; H, 4.54; N, 12.25; Br, 52.99%. Vis. spectra: *trans*, ϵ_{606}^{max} 35.5, ϵ_{518}^{min} 10.4; *cis* ϵ_{531}^{max} 90.9, ϵ_{444}^{min} 19.0 (0.01 *M* $HClO_4$). These compare closely with previous values [3, 11, 14].

Trans$[Co(en)_2Cl_2]Cl \cdot HCl \cdot 2H_2O$ [15] was oven dried to afford the crude acid free chloride salt. Some was prepared from the perchlorate salt (obtained from the acid chloride by metathesis in water using aqueous $HClO_4$) by crystallisation from Me_2SO or DMF using LiCl. The perchlorate of the *trans* isomer is very soluble and the chloride salt sparingly soluble in these solvents, the reverse of water (*cf.* Cr(III) analog [16]). The product was recrystallised twice from water by careful dilution with acetone to afford deep green needles of the anhydrous material (air-dried). This procedure ensured the absence of the *cis* isomer, and was confirmed by chromatography on Sephadex [1]. *Anal.* Calcd for $[Co(C_4H_{16}N_4)Cl_2]Cl$: C, 16.83; H, 5.65; N, 19.63; Cl, 37.25. Found: C, 16.95; H, 5.56; N, 19.56; Cl, 37.37%.

Trans$[Co(en)_2Cl_2]Cl$ was recrystallised twice from water using cold triflic acid (CF_3SO_3, 3 *M*) or sodium triflate to afford needles of *trans* $[Co(en)_2Cl_2]CF_3SO_3$. *Trans*$[Co(en)_2Br_2]CF_3SO_3$ was obtained similarly from *trans*$[Co(en)_2Br_2]Br$

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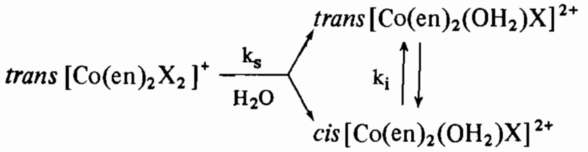
[3, 14]. The triflate salts were washed with cold ethanol followed by ether, and air dried to provide the anhydrous salts. *Anal.* Calcd for $[Co(C_4H_{16}N_4)Cl_2]CF_3SO_3$: C, 15.05; H, 4.04; N, 14.04; F, 14.28; Cl, 17.76. Found: C, 15.22; H, 4.33; N, 14.00; F, 13.95; Cl, 17.87. Calcd for $[Co(C_4H_{16}N_4)Br_2]CF_3SO_3$: C, 12.31; H, 3.31; N, 11.48; S, 6.57; F, 11.68; Br, 32.75. Found: C, 12.34; H, 3.48; N, 11.21; S, 6.57; F, 11.81; Br, 33.16. Vis. spectra: *trans*-Cl_2^+, ϵ_{620}^{max} 37.9, ϵ_{525}^{min} 4.8, ϵ_{400}^{sh} 36.9; *trans*-Br_2^+, ϵ_{659}^{max} 51.7, ϵ_{542}^{min} 3.7 (0.01 *M* CF_3SO_3H).

Kinetics

The aquation rates of *trans*$[Co(en)_2Br_2]^+$ and *trans*$[Co(en)_2Cl_2]^+$ in 0.1 *M* CF_3SO_3H or 0.01 *M* $HClO_4$ at 25.00 ± 0.05 °C were determined spectrophotometrically on a Cary 118C instrument using the techniques described previously [1, 3, 5]. Both reactions occur stepwise, exhibiting the usual biphasic kinetics:



$$\begin{tikzcd} & trans[Co(en)_2(OH_2)X]^{2+} \arrow[d, shift left, "k_i"'] \\ trans[Co(en)_2X_2]^+ \arrow[ur, "k_s"] \arrow[dr, "H_2O"'] & \\ & cis[Co(en)_2(OH_2)X]^{2+} \arrow[u, shift left] \end{tikzcd}$$

The first order aquation rate constants k_s were determined in the usual way from absorbance–time data covering 3–4 $t_{1/2}$ which were collected at wavelengths corresponding to one or more of the several *cis/trans*-$[Co(en)_2(OH_2)X]^{2+}$ isosbestic points. This procedure avoided interference from the secondary $[Co(en)_2(OH_2)X]^{2+}$ isomerisation reaction, of comparable rate (see Results), and from the slow loss of the second X^- group which becomes prominent at ~5 $t_{1/2}$ of the primary aquation reaction. The aquation rate constants were determined also at other wavelengths (X = Cl, 510 nm; X = Br, 530 nm), from a non-linear least squares analysis of the D, t data for consecutive first-order reactions [1, 5, 17]. The subsequent isomerisation constants k_i were fixed at their known (independently measured) [5] values in these analyses. The accuracy of the results was assessed from the agreement between k_s values obtained by this procedure and from the analyses employing data collected at one or more of the $[Co(en)_2(OH_2)X]^{2+}$ isosbestic points. As a further check on the results, the 510 nm D, t data for *trans*$[Co(en)_2Cl_2]^+$ and 530 nm data for *trans*$[Co(en)_2Br_2]^+$ were treated by the least squares procedure using both k_s and k_i as parameters. Data covering times corresponding to at least 90% conversion to the equilibrium $[Co(en)_2(OH_2)X]^{2+}$ isomer distribution were used in these analyses, for the reasons given elsewhere [1, 17]. This was particularly important for *trans*$[Co(en)_2Br_2]^+$ where $k_s \sim 2k_i$. The agreement between the k_s and k_i values obtained in this way were compared with those determined independently for the separate primary and secondary reactions. This gave a clear indication of the accuracy of the results.

The rates of isomerisation of $[Co(en)_2(OH_2)Br]^{2+}$ in 0.01, 0.1 and 1.0 *M* $HClO_4$ and 0.1 *M* CF_3SO_3H at 25 °C were determined at 530 and 550 nm where absorbance changes are large [3, 11]. The D, t data accurately followed a first-order rate law over 4–5 $t_{1/2}$. At longer reaction times, slow Br^- loss from $[Co(en)_2(OH_2)Br]^{2+}$ was observed, particularly at the lowest acid concentration employed (0.01 *M*) where the contribution to the hydrolysis from the labile $[Co(en)_2(OH)Br]^+$ ions ($pK_a \sim 7$) was apparent.

Equilibria and Steric Course of Aquation

The visible spectra after complete hydrolysis of *trans*$[Co(en)_2X_2]^+$ and isomerisation of *cis*- and *trans*$[Co(en)_2(OH_2)X]^{2+}$ (X = Cl, Br) were recorded; slightly better were the infinite time spectra extrapolated from the 4–5 $t_{1/2}$ hydrolysis and isomerisation reaction D, t data; these spectra are corrected for the subsequent loss of the second Br^- or Cl^-, albeit slight. The *cis/trans* isomer distributions were determined at 510 nm for X = Cl^- and 530 nm for X = Br^-. At these wavelengths the spectra of *cis*- and *trans*$[Co(en)_2(OH_2)X]^{2+}$ differ most.

Repetitive absorption spectra for reacting solutions of *trans*$[Co(en)_2Br_2]^+$, *trans*$[Co(en)_2Cl_2]^+$ and *trans*$[Co(en)_2(OH_2)Br]^{2+}$ were recorded over close intervals of time to obtain isosbestic point data. For *trans*$[Co(en)_2Br_2]^+$, subsequent isomerisation (~2 fold slower) of the first formed $[Co(en)_2(OH_2)Br]^{2+}$ product did not interfere at the early reaction times sufficient to define these points (up to ~20 min, 25 °C). For *trans*$[Co(en)_2Cl_2]^+$, subsequent $[Co(en)_2(OH_2)Cl]^{2+}$ isomerisation proved too fast (~3-fold faster) to permit their accurate definition, while for *trans*$[Co(en)_2(OH_2)Br]^{2+}$ sharp isosbestic points were maintained for essentially the complete reaction (up to ~4–5 $t_{1/2}$).

The steric course of *trans*$[Co(en)_2X_2]^+$ aquation was determined as described in detail for *trans*-$[Co(en)_2Cl(Me_2SO)]^{2+}$ [5] and *cis*$[Co(en)_2AX]^{n+}$ [1]. The method is accurate provided the subsequent $[Co(en)_2(OH_2)X]^{2+}$ isomerisation step is not much faster (<factor of 5) than the primary aquation step; this conditions is met for both *trans*$[Co(en)_2Cl_2]^+$ (factor ~ 2.5) and *trans*$[Co(en)_2Br_2]^+$ (factor ~ 0.5). The essential strategy was to follow the reactions at wavelengths corresponding to the maximum difference in the *cis*- and *trans*$[Co(en)_2(OH_2)X]^{2+}$ spectra (X = Br, 530 nm; X = Cl, 510 nm), and to determine the extinction coefficient (ϵ_B) of the first formed *cis* + *trans*$[Co(en)_2(OH_2)X]^{2+}$ product corrected for subsequent *trans* to *cis* isomerisation. Thus D, t data were analysed by non-linear least analysis by fitting to the appropriate equation for consecutive first order reactions, of the form

TABLE I. Isosbestic Point Data for the Spontaneous Aquation of *trans*$[Co(en)_2Br_2]^+$ and Isomerisation of $[Co(en)_2(OH_2)Br]^{2+}$ in Dilute Acid at 25 °C.

Observed		Calculated[a,b]	
λ; nm	ε, M^{-1} cm^{-1}	λ, nm	ε, M^{-1} cm^{-1}
618.5	32.6(2)	620	33.1
474	26.3(2)	472	26.3
trans$[Co(en)_2(OH_2)Br]^{2+} \rightleftarrows$ *cis*$[Co(en)_2(OH_2)Br]^{2+}$			
Observed		Calculated	
605.5	35.5(4)	606	35.7
462.5	28.7(4)	463	30.0

[a] λ,ε recorded not especially sensitive to the proportion of *trans* product; molar extinction coefficients for *cis* and *trans*-$[Co(en)_2(OH_2)Br]^{2+}$ used for the calculation were: ϵ^{620}_{trans} = 34.6, ϵ^{620}_{cis} = 24.4; ϵ^{472}_{trans} = 24.5, ϵ^{472}_{cis} = 36.5 M^{-1} cm^{-1}. [b] Calculated for 84.5% *trans*, 15.5% *cis* product.

$$\epsilon = A_1 e^{-k_s t} + A_2 e^{-k_i t} + \epsilon_\infty$$

where A_1, A_2 are constants which are functions of k_s, k_i, ϵ_o, ϵ_B, and ϵ_∞. The better results were obtained using k_i and ϵ_∞ fixed at their known values. However it was found that for the completely parameterised problem using accurate D, t data covering ~90% reaction, calculated k_i and ϵ_∞ came out close to their known values, lending strong support to the analysis.

Results and Discussion

Isomerisation

The *trans* ⇄ *cis*$[Co(en)_2(OH_2)Br]^{2+}$ rates and equilibria were required to determine the steric course of aquation of *trans*$[Co(en)_2Br_2]^+$ under identical conditions (0.1 *M* CF_3SO_3H). The non-coordinating triflate media were employed because of the greatly improved solubility of the *trans*-dibromo (and dichloro) complexes. The corresponding $[Co(en)_2(OH_2)Cl]^{2+}$ data were reported recently [5]. The bromo-aqua isomerisation rates and equilibria have been measured previously in 0.2 *M* $HClO_4$ [3] and 0.01 *M* HNO_3 [11] using $[Co(en)_2(OH)Br]Br$, $[Co(en)_2(OH_2)Br]Br_2$ and $[Co(en)_2(OH_2)Br]SO_4$ salts. It has been shown that the isomerisation rate and equilibrium position for the analogous *trans* ⇄ *cis*$[Co(en)_2(OH_2)N_3]^{2+}$ reaction differ significantly in SO_4^{2-} compared with ClO_4^- or $S_2O_6^{2-}$ containing media. Therefore the bromoaqua system has been reexamined using the non-coordinating $S_2O_6^{2-}$ salt of the *trans* isomer in both $HClO_4$ and CF_3SO_3H media.

Sharp isosbestic points in the expected positions (Table I) endured for up to 4–5 $t_{1/2}$ of the *trans*- to *cis*$[Co(en)_2(OH_2)Br]^{2+}$ isomerisation reaction. Small and slower subsequent changes in absorption spectra correspond to loss of Br^- from *cis*/*trans*

TABLE II. Equilibrium Data.

trans$[Co(en)_2(OH_2)Br]^{2+} \rightleftarrows$ *cis*$[Co(en)_2(OH_2)Br]^{2+}$			
Starting Material	Medium	ϵ_∞[a]	% cis_e[b]
trans$[Co(en)_2Br_2]CF_3SO_3$	0.1 *M* CF_3SO_3H	70.2, 71.5	75.0
	0.01 *M* $HClO_4$	69.8	73.5
trans$[Co(en)_2(OH_2)Br]S_2O_6 \cdot H_2O$	0.1 *M* $HClO_4$	71.2, 71.5	75.5
cis$[Co(en)_2(OH_2)Br]Br_2 \cdot H_2O$	0.1 *M* $HClO_4$	69.8, 70.9	74.0
$[Co(en)_2(OH_2)Br]^{2+}$[c]	0.2 *M* $HClO_4$		75
	0.01 *M* $HClO_4$		76
trans$[Co(en)_2)OH_2)Cl]^{2+} \rightleftarrows$ *cis*$[Co(en)_2(OH_2)Cl]^{2+}$			
trans$[Co(en)_2Cl_2]CF_3SO_3$	0.10 *M* $HClO_4$	70.4	79.5
	0.1 *M* CF_3SO_3H	70.9, 71.2	80.0
trans$[Co(en)_2(OH_2)Cl]S_6O_6 \cdot H_2O$[d]	0.1 *M* $HClO_4$	69.8	78.5
cis$[Co(en)_2(OH_2)Cl]S_2O_6 \cdot H_2O$[d]	0.1 *M* $HClO_4$	71.0	80.0

[a] Br, 530 nm. Cl, 510 nm. [b] Calculated from ϵ_∞(ave) using the relation: % $cis_e = 10^2 (\epsilon_\infty - \epsilon_{trans})/(\epsilon_{cis} - \epsilon_{trans})$ and the following molar extinction coefficients: Br, ϵ^{530}_{cis} = 90.9, ϵ^{530}_{trans} 11.4; Cl, ϵ^{510}_{cis} 86.3, ϵ^{510}_{trans} 9.6 M^{-1} cm^{-1}. [c] Data from refs. 3 and 11. [d] Data from ref. 5.

TABLE III. Rate Constants for $[Co(en)_2(OH_2)Br]^{2+}$ Isomerisation at 25.0 °C

$$trans \underset{k_{ct}}{\overset{k_{tc}}{\rightleftharpoons}} cis$$

$k_i = k_{tc} + k_{ct}$

	$10^4\ k_i$, s^{-1}			$10^4\ k_i$, s^{-1}	
	530 nm	550 nm		530 nm	550 nm
0.01 *M* $HClO_4$[a]	2.32	2.35	0.1 *M* CF_3SO_3H[a]	2.17	2.22
	2.31	2.28		2.32	2.34
	2.28	2.24			
	Av:	2.30 ± 0.04		Av:	2.26 ± 0.08
0.1 *M* $HClO_4$[a]	2.28	2.35	1 *M* $HClO_4$[a]	2.39	2.40
	2.24	2.25		2.43	2.51
				2.37	2.39
	Av:	2.28 ± 0.05		Av:	2.42 ± 0.05
0.2 *M* $HClO_4$[c]	2.04				
0.01 *M* HNO_3[b]	2.14				

[a] Starting complex *trans*$[Co(en)_2(OH_2)Br]S_2O_6 \cdot H_2O$. [b] Starting complexes, *trans*$[Co(en)_2(OH)Br]Br \cdot H_2O$ and *cis*$[Co(en)_2(OH_2)Br]Br_2 \cdot H_2O$ (Ref. 11). [c] Starting complexes as b; also *trans*$[Co(en)_2(OH_2)Br]SO_4$ (Ref. 3).

equilibrated $[Co(en)_2(OH_2)Br]^{2+}$. Commencing with either isomer, final spectra (Table II) corresponded to 75 ± 1% *cis*, 25 ± 1% *trans*$[Co(en)_2(OH_2)Br]^{2+}$.

The rate data are recorded in Table III. It is clear that the nature of the complex anion (Br^-, SO_4^{2-} or $S_2O_6^{2-}$), medium (ClO_4^- or $CF_3SO_3^-$) or ionic strength ($\mu = 0.01-1.0$ *M*) significantly affect neither the isomerisation rate nor the equilibrium position as found for the chloro system. Moreover the results ($\mu = 0.1$ *M*; $k_i = k_{tc} + k_{ct} = (2.27 \pm 0.08) \times 10^{-4}$ sec^{-1}, 75% *cis* at equilibrium; $K = 75/25 = k_{tc}/k_{ct}$, hence $k_{tc} = 1.70 \times 10^{-4}$ s^{-1} and $k_{ct} = 5.7 \times 10^{-5}$ s^{-1}; 25 °C) agree quite closely with earlier data [3, 11].

Included in Table III are equilibrium data derived from the *trans*$[Co(en)_2X_2]CF_3SO_3$ starting materials, and it can be seen that the common result pertains to both the bromo and chloro systems, *i.e.*, the observed equilibrium position is independent of starting material also. It is clear that these aquation reactions go to completion.

Spontaneous Aquation of trans*[Co(en)$_2$Cl$_2$]$^+$*

The rate of Cl^- loss was directly determined spectrophotometrically by following the reaction at 586 and 356 nm, two of the four isosbestic points in the spectra of *cis*- and *trans*$[Co(en)_2(OH_2)Cl]^{2+}$ for which an appreciably absorbance change could be obtained. Thus the D, t data followed a single exponential function since subsequent *trans* to *cis* isomerisation did not interfere. The common result ($k_s = (4.2 \pm 0.1)\ 10^{-5}\ s^{-1}$, 0.1 *M* CF_3SO_3H, 25 °C) was obtained at both wavelengths and may be compared with numbers for several other determinations by various methods [6–10], $k_s = (2.7–4.9)\ 10^{-5}$ s^{-1}. A value around 3.5×10^{-5} s^{-1} best fits the previous results obtained under conditions sufficiently acidic to eliminate a rate contribution from the especially fast base hydrolysis reaction of the *trans*-dichloro complex ($k_{OH} = 3200$ M^{-1} s^{-1}, 25 °C); our value, ~20% greater, is not alarmingly different.

The steric course was determined by the same method used in several recent aquation studies [1, 5]. The relative merits of this and earlier procedures have been discussed. The present procedure amounts to calculating the spectrum of the first formed product B arising in the consecutive reaction scheme

$$A \xrightarrow{k_x} B \xrightarrow{k_i} C,$$

where B is the *cis*/*trans*$[Co(en)_2(OH_2)Cl]^{2+}$ mixture directly formed from *trans*$[Co(en)_2Cl_2]^+$ (A), and C is the equilibrium isomer mixture. The spectrophotometric result is accurate provided k_i is not very much greater than k_s ($k_i/k_s \lesssim 5$), which is the present case ($k_i/k_s \cong 2.5$), and of course provided ϵ_{cis} and ϵ_{trans} for $[Co(en)_2(OH_2)Cl]^{2+}$ differ significantly at the wavelength chosen (at 510 nm, $\epsilon_{cis} = 86.3$, $\epsilon_{trans} = 9.6$). The ϵ, t data fitted to the appropriate function by standard non-linear least squares analysis yielded $k_s = 3.8 \times 10^{-5}$ s^{-1} and

TABLE IV. Rate Constants and Steric Course for Spontaneous Aquation of *trans*[Co(en)$_2$Br$_2$]$^+$ and *trans*[Co(en)$_2$Cl$_2$]$^+$ in 0.1 *M* CF$_3$SO$_3$H at 25 °C.

		trans[Co(en)$_2$Br$_2$]$^+$			
10^3[Co], *M*	λ, nm	10^4 k$_s$, s^{-1} [c]	10^4 k$_i$, s^{-1} [c]	ϵ_B [a]	% *trans* product [h]
6.76	530	3.68 ± 0.11	(2.27)[d]	24.7	83.5
6.66	530	4.03 ± 0.09	(2.27)[d]	23.4	85.0
6.66	530	3.70 ± 0.43	2.33 ± 0.12	(26.0)	(81.5)
[b]	606[e]	4.12 ± 0.07	–	–	–
[b]	461[e]	4.14 ± 0.07	–	–	–
7.16[g]	530	4.31 ± 0.29	(2.27)[d]	23.3	85.0
7.16	606[e]	4.10 ± 0.38	–	–	–
		trans[Co(en)$_2$Cl$_2$]$^+$			
6.46	510	0.382 ± 0.004	(1.04)[d]	29.8	73.5
6.46	510	0.392 ± 0.015	0.96 ± 0.09	(30.3)	(73.0)
6.61	510	0.384 ± 0.005	(1.04)[d]	28.6	75
6.61	510	0.382 ± 0.016	1.05 ± 0.12	(28.5)	(75.5)
[b]	586[f]	0.433 ± 0.037	–	–	–
[b]	356[f]	0.412 ± 0.010	–	–	–

[a] Molar extinction coefficient for the first formed product, calculated from a least squares analysis of D, t data using the appropriate function (see ref. 17). [b] [Co] ≅ (5–12) 10^{-3} *M*; 'spoon' method, unweighed complex (see Experimental). [c] Standard deviations given are those obtained from the least squares analysis; single runs. [d] Bracketed values refer to least squares analysis for which k$_i$ was fixed at its known (independently measured) value; $k_i = k_{tc} + k_{ct}$ = rate constant for approach of the *trans* ⇄ *cis*[Co(en)$_2$(OH$_2$)X]$^{2+}$ (X = Br, Cl) equilibrium. [e] Wavelength corresponding to one of the isosbestic points in the *trans* ⇄ *cis*[Co(en)$_2$(OH$_2$)Br]$^{2+}$ subsequent isomerisation step. [f] Wavelength corresponding to one of the isosbestic points in the *trans* ⇄ *cis*[Co(en)$_2$(OH$_2$)Cl]$^{2+}$ subsequent isomerisation step. [g] Medium, 0.01 *M* HClO$_4$. [h] Calculated from ϵ_B using the relation % *trans* = $10^2 (\epsilon_B - \epsilon_{cis})/(\epsilon_{trans} - \epsilon_{cis})$ and the following molar extinction coefficients: X = Br, ϵ_{cis}^{530} 90.9, ϵ_{trans}^{530} 11.4; x = Cl, ϵ_{cis}^{510} = 86.3, ϵ_{trans}^{510} = 9.6 M^{-1} cm^{-1}.

ϵ_B = 29.2 ± 0.6(2), which corresponds to 74 ± 1% first formed *trans* product (Table IV). In this fit, k$_i$ (= 10.4 × 10^{-5} s^{-1}) was held constant at its independently determined value while ϵ_c was fixed at its measured value. Note that the k$_s$ value so obtained is in close agreement with the directly and independently determined number (4.1 ± 0.1) 10^{-5} s^{-1}. In least squares analyses on the same ϵ, t data but in which k$_s$, k$_i$, ϵ_c were *all* used as parameters, remarkably similar results were obtained (Table IV), although of course the standard deviations are greater. The pertinent result, 74 ± 1.5% *trans* product is greater than a previously recorded number, 65 ± 5% *trans* [6], and it could be considered more accurate. Another earlier determination of the steric course (80% *cis* product) [7] appears to be spurious.

Spontaneous Aquation of trans*[Co(en)$_2$Br$_2$]$^+$*

The results (Table IV) were obtained as described for the *trans*-dichloro complex. In contrast, well-defined isosbestic points were obtained since the subsequent *trans*- to *cis*[Co(en)$_2$(OH$_2$)Br]$^{2+}$ isomerisation is slower (~2-fold) than the aquation step. These data are however not diagnostic of the steric course because the spectra of *cis*- and *trans*[Co(en)$_2$(OH$_2$)Br]$^{2+}$ do not differ appreciably at the observed isosbestic pts, 618 and 474 nm. Nonetheless the result obtained (Table I) is consistent with the 84.5 ± 1.0% *trans* product calculated from the kinetic data (530 nm, Table IV).

Our values for k$_s$ ((4.13 ± 0.07) × 10^{-4} s^{-1}) obtained at the 461 and 606 nm *cis*/*trans*[Co(en)$_2$(OH$_2$)Br]$^{2+}$ isosbestic points, agree well; the k$_s$ value obtained from the analysis of the 530 nm data for consecutive reactions, where k$_i$ was either fixed at its known value (2.27 × 10^{-4} s^{-1}) or used as a parameter (giving k$_i$ = (2.33 ± 0.12) × 10^{-4} s^{-1}) also agrees (Table IV). Yet the common k$_s$ result is alarmingly different to earlier values k$_s$ = 1.4 × 10^{-4} s^{-1}, determined titrimetrically and spectrophotometrically [11, 12] and different to a very recent value (1.56 × 10^{-4} s^{-1}) [13] determined polarigraphically. There is no obvious reason for the differences. It cannot reside in temperature differences, since our k_i determined from the *same* (530 nm) data for which a k_s value was obtained agrees very closely with the two previous [3, 11] k_i values for 25 °C. And the problem is unlikely to reside in differences in media, since we find $k_s = 4.1 \times 10^{-4}$ s^{-1} for 0.1 *M* CF_3SO_3H and (4.3 ± 0.3) 10^{-4} s^{-1} for 0.01 *M* $HClO_4$; indeed, aquation rates are insensitive to the nature of the (inert) anion and ionic strength in general. We are strongly inclined to accept the present k_s value; it is different to otherwise account for the agreement between the results obtained at several wavelengths (Table IV), despite the purely statistical (3:1) weight [11–13] against our result.

The steric course number (84.5% *trans* product) is significantly greater than the (single) previous determination [11], 70% ± 2 *trans* product. This new result is better discussed in the context of revised steric course data for the induced aquation reactions *trans*$[Co(en)_2Br_2]^+$ and Hg^{2+} and *trans*$[Co(en)_2BrN_3]^+$ + NO^+. There exist some previously unrecognized problems in the determination of the induced aquation steric course for both the bromo and chloro complexes, and since the effect of the leaving group on the stereochemical outcome is crucially important in deciding the stoichiometric mechanism, further discussion is deferred until all these data become available.

The new data for *trans*$[Co(en)_2Cl_2]^+$ brings the steric course result for spontaneous aquation more into line with the results [5] for other *trans*$[Co(en)_2ClX]^{n+}$ (71% *trans* product). For the spontaneous aquation of *trans*$[Co(en)_2BrX]^{n+}$, there is only the one well-defined result, *trans*$[Co(en)_2Br_2]^+$ (84% *trans*), and it remains to be seen if the steric course is independent of the leaving group. We note that the current steric course data available for the induced aquation reactions supports the case for a common intermediate for the hydrolysis of *trans*$[Co(en)_2ClX]^{n+}$, but as yet not *trans*$[Co(en)_2BrX]^+$.

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