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Kinetics and Steric Course of the Aquation of Dibromo- and Bromoaquobis(propylenediamine)chromium(III) Cations¹

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The kinetics and steric course of aquation of *cis*- and *trans*-Cr(pn)₂Br₂⁺ have been investigated in acid solution over a temperature range. The replacement of bromide by H₂O occurs with essentially complete retention of configuration. In 0.1 *N* HNO₃ at 25.0 ± 0.04° the first-order rate constants for the aquation reactions, activation energies, and entropies of activation are $k_{\text{aq}} = (25.7 \pm 1.5) \times 10^{-4} \text{ sec}^{-1}$, $E_a = 19.4 \pm 1.2 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -7.4 \pm 3.6 \text{ cal deg}^{-1}$ for *cis*-Cr(pn)₂Br₂⁺; $k_{\text{aq}} = (3.92 \pm 0.27) \times 10^{-4} \text{ sec}^{-1}$, $E_a = 21.9 \pm 0.9 \text{ kcal mol}^{-1}$, and $\Delta S^\ddagger = -2.7 \pm 3.0 \text{ cal deg}^{-1}$ for *trans*-Cr(pn)₂Br₂⁺. In 0.4 *N* HClO₄ at 25.0 ± 0.04° *cis*-Cr(pn)₂(OH₂)Br²⁺ has $k_{\text{aq}} = (1.60 \pm 0.2) \times 10^{-4} \text{ sec}^{-1}$ and gives essentially *cis*-Cr(pn)₂(OH₂)₂³⁺ as the directly formed product. The aquation of *trans*-Cr(pn)₂(OH₂)Br²⁺ in 2.0 *N* HNO₃ is complicated by other concurrent processes (possible Cr-N bond rupture and/or isomerization). At 25.0 ± 0.04° the bromide release rate constant for this species is $(2.45 \pm 0.30) \times 10^{-5} \text{ sec}^{-1}$. A mechanism is suggested to account for these data.

Introduction

A comparison of the first-stage aquation rates of *cis*- and *trans*-Co(pn)₂Cl₂⁺ at 25° reveals that these cations react 1.7 and 1.8 times faster than their en analogs.² We have recently observed that the pn/en rate ratio at 35° for the corresponding *trans*-dichloro Cr(III) cations is 1.4.³ Esparza and Garner² reported that *cis*-Cr(pn)₂Cl₂⁺ and *cis*-Cr(en)₂Cl₂⁺ react at the same rate at 25°. The present study was undertaken to examine the influence of the C-methyl group on the rates and steric course of aquation of *cis*- and *trans*-dibromo- and -bromoaquochromium(III) complexes and to determine whether Cr-N bond breaking competes significantly with Cr-halide bond breaking as was found in the *trans*-dichloro systems.^{3,4}

Experimental Section

Preparation of Complexes. *cis*-[Cr(en)₂Br₂]Br was prepared according to the method of Garner.⁵ *cis*-[Cr(en)₂(OH₂)Br]Br₂·H₂O was prepared by the method of Pfeiffer⁶ and recrystallized by dissolving a 2-g sample in 10 ml of water, adding 10 ml of 48% HBr, filtering, and cooling the filtrate for 2 hr. The resulting crystals were washed with acetone and ether and dried at room temperature under vacuum for 9 hr. *Anal.* Calcd for [Cr(en)₂(OH₂)Br]Br₂·H₂O: C, 10.72; H, 4.50; N, 12.51; Br, 53.52. Found: C, 10.65; H, 4.47; N, 12.31; Br, 53.55.

cis- and *trans*-[Cr(pn)₂Br₂]Br were prepared by procedures we have previously reported^{7,8} except the final purification step of the latter complex included washing with acetone and ether before drying.

trans-Cr(pn)₂(OH₂)Br²⁺ was prepared in solution by dissolving 50–60 mg of *trans*-[Cr(pn)₂Br₂](H₂O)₂Br₂⁸ in 50 ml of 0.1 *N* HNO₃ and allowing the solution to aquate for ca. 3 half-lives in the dark. The solution was absorbed on a cooled, prewashed cation-exchange resin (Dowex AG 50W-X8, 100–200 mesh, H⁺ form, 30 × 9 mm). The unreacted *trans*-dibromo complex was eluted with 1.0 *N* HNO₃ and the *trans*-bromoaquo band was moved to the bottom of the column with 1.4 *N* HNO₃. The top portion of the resin was removed by pipet and discarded and the desired *trans*-bromoaquo species was eluted with 2.0 *N* HNO₃ into a flask cooled in an ice-salt bath. The Cr/Br atom ratio of this species is 1.00.

(1) Abbreviations used: en, ethylenediamine; pn, propylenediamine = 1,2-diaminopropane.

(2) M. Esparza and C. S. Garner, *J. Inorg. Nucl. Chem.*, **29**, 2377 (1967).

(3) R. R. Barona and J. A. McLean, Jr., *Inorg. Chem.*, **10**, 286 (1971).

(4) D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, **83**, 4152 (1961).

(5) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **9**, 1348 (1964).

(6) P. Pfeiffer, *Z. Anorg. Allg. Chem.*, **56**, 279 (1908).

(7) J. A. McLean, Jr., and N. A. Maes, *Inorg. Nucl. Chem. Lett.*, **8**, 147 (1972).

(8) J. A. McLean, Jr., and R. I. Goorman, *Inorg. Nucl. Chem. Lett.*, **7**, 9 (1971).

cis-Cr(pn)₂(OH₂)Br²⁺ was prepared from the *cis*-dibromo complex in aged 0.1 *N* HClO₄ solutions and isolated on a 15 × 9 mm column using the above technique except that 1.0 *N* HClO₄ was used to elute the unreacted *cis*-dibromo and 3.5 *N* HClO₄ was used to elute the *cis*-bromoaquo. The spectrum was recorded in 0.4 *N* HClO₄ and was in agreement with that previously reported.⁷

cis-Cr(en)₂(OH₂)₂³⁺ was obtained by acidifying *cis*-[Cr(en)₂-OH(OH₂)]S₂O₈·H₂O prepared by Woldbye's method and its purity was confirmed by comparing its spectrum with the reported values.⁹ The corresponding pn complex was prepared by an analogous procedure. *Anal.* Calcd for [Cr(pn)₂(OH)(OH₂)S₂O₈·H₂O]: Cr, 12.59; C, 17.43; H, 6.10; N, 13.56. Found: Cr, 12.64; C, 17.53; H, 6.09; N, 13.37. The spectrum of this compound was unchanged when a dilute acidic solution was passed through an anion-exchange column (Dowex 1-X2, 100–200 mesh, NO₃⁻ form).

Kinetic Measurements. In all spectrophotometric runs solutions were prepared and the spectrum was quickly scanned repeatedly from 640 to 360 nm. Some runs were made at constant wavelength. The kinetic data were plotted as $-\ln(A_t - A_\infty)$ vs. t , where A_t and A_∞ are the absorbancies (at a given wavelength) at time t and of the product, respectively. The temperature was maintained at the required temperature ± 0.04°, with a thermostatically controlled water bath. Sample preparation for solid compounds involved dissolving a sufficient quantity of complex in 0.1 *N* HClO₄ or HNO₃ to give ca. a 10⁻³ *M* solution and quickly transferring it to a 10-cm cell. It was necessary to modify this technique in studying *cis*-[Cr(en)₂Br₂]Br because of the limited solubility of this salt. Approximately 20–25 mg of complex was rapidly stirred in 40 ml of 0.1 or 0.01 *N* HNO₃ and quickly filtered into a 10-cm cell (both dissolution and filtration were performed at reaction temperature).

Rate data for *cis*-Cr(pn)₂(OH₂)Br²⁺ were obtained by isolating this species in 3.5 *N* HClO₄ and diluting with double distilled water to adjust the acid concentration to 0.4 *N*. The solution was then quickly warmed to the desired temperature.

Rate data for the disappearance of *trans*-Cr(pn)₂Br₂⁺ and halide release of this complex were obtained by chromatographic and potentiometric titration techniques reported earlier.³

Analytical Methods. Visible absorption spectra were obtained with a Cary Model 14 spectrophotometer using matched quartz cells. Spectra were recorded at 0° (immediately after dissolution for solid samples). Chromium analyses on solid samples as well as chromatographic fractions were performed by methods previously described.³

Results

Aquation rates and Arrhenius activation parameters have been determined for *cis*- and *trans*-Cr(pn)₂Br₂⁺ and *cis*-Cr(en)₂Br₂⁺. Quinn and Garner⁵ have reported rate data at 25° for the last complex and we have simply extended their study over a range of temperatures. The bromoaquo species corresponding to the three cations were synthesized and investigated under aquation conditions to determine (1) whether first-stage aquation could be studied without

(9) F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

Table I. Absorption Maxima and Minima (nm) of Cis and Trans pn- and en-Cr^{III} Complexes in Acidic Solutions^a

Complex	Acid	λ_{\max}	λ_{\min}	λ_{\max}	λ_{\min}	λ_{\max}
<i>cis</i> -Cr(pn) ₂ Br ₂ ⁺ ^b	0.1 N HNO ₃	537 (85.6)	463 (27.4)	410 (79.8)		
<i>cis</i> -Cr(en) ₂ Br ₂ ⁺ ^c	0.1 N HNO ₃	537 (80.3)	463 (25.9)	409 (76.5)		
<i>cis</i> -Cr(pn) ₂ (OH ₂)Br ₂ ²⁺ ^b	2 N HClO ₄	518 (75.6)	443 (22.4)	390 (62.9)		
<i>cis</i> -Cr(en) ₂ (OH ₂)Br ₂ ²⁺ ^e	0.04 N HNO ₃	519 (72.2)	446 (21.0)	387 (60.5)		
<i>cis</i> -Cr(pn) ₂ (OH ₂) ₂ ³⁺ ^d	2 N HNO ₃	487 (71.6)	417 (18.6)	370 (45.5)		
<i>cis</i> -Cr(en) ₂ (OH ₂) ₂ ³⁺ ^{e, f}	0.1 N HClO ₄	484 (67.0)	417 (17)	367 (42.5)		
<i>trans</i> -Cr(pn) ₂ Br ₂ ⁺ ^g	0.1 N HNO ₃	606 (35.3)	527 (4.6)	~460 sh (25.0)		410 (30.9)
<i>trans</i> -Cr(en) ₂ Br ₂ ⁺ ^e	0.1 N HClO ₄	607 (34.9)	530 (5.2)	~460 sh (24)		406 (30.7)
<i>trans</i> -Cr(pn) ₂ (OH ₂)Br ₂ ²⁺ ^d	2 N HNO ₃	560 (23.1)	502 (12.8)	445 (26.6)	432 (26.0)	384 (47.7)
<i>trans</i> -Cr(en) ₂ (OH ₂)Br ₂ ²⁺ ^e	1.4 N HNO ₃	561 (23.2)	504 (14.2)	455 (24.9)	444 (24.7)	384 (44.8)
<i>trans</i> -Cr(pn) ₂ (OH ₂) ₂ ³⁺ ^h	0.1 N HNO ₃	505 sh (24.3)		448 (31.2)	408 (21.2)	365 (41.3)
<i>trans</i> -Cr(en) ₂ (OH ₂) ₂ ³⁺ ^{e, f}	1.4 N HNO ₃	508 sh (22.5)		442 (29.3)	404 (20.0)	361 (39.2)

^a Values inside parentheses are the molar absorptivity indices a_m defined by $A = \log(I_0/I) = a_m c d$ in $M^{-1} \text{ cm}^{-1}$. ^b Reference 7. ^c The a_m values reported here for *cis*-Cr(en)₂Br₂⁺ are lower than those reported in ref 5. In the prior study, slow dissolution of the complex requires 1.6 half-lives before spectral data could be obtained to extrapolate back to zero reaction time. We believe our more rapid sample preparation technique permits a more accurate extrapolation of the spectral data back to zero reaction time. ^d This work. ^e Reference 5. ^f Reference 2. ^g The previously reported a_m values for this cation in ref 8 were not sufficiently accurate to permit calculation of the experimental spectra as a function of aqution time. Therefore, it was necessary to carefully redetermine these values. ^h R. R. Barona, Ph.D. Thesis, University of Detroit, 1970.

interference from the second stage and (2) the steric course of the primary aquation reactions. Quinn and Garner⁵ used a modification of the Pfeiffer method to synthesize *cis*-[Cr(en)₂(OH₂)Br]Br₂·H₂O for possible kinetic studies. These authors experienced erratic kinetic results in the aquation of this compound and consequently used the bromoaquo species prepared by chromatographic isolation from *cis*-[Cr(en)₂Br₂]Br aquation mixtures. We found that the product prepared by the original Pfeiffer⁶ synthesis, without modification, gives kinetic results identical to their chromatographic product; therefore, the solid compound prepared by the Pfeiffer method was used in our study.

The spectra obtained for the solid complexes by dissolving and recording at 0° were identical with those obtained from spectral kinetic runs extrapolated back to zero time in all cases except *cis*-[Cr(en)₂Br₂]Br. The second method is required for spectral characterization of this compound because of its limited solubility.

In spectrophotometric rate determinations wavelengths were chosen at which absorbance changes with time were optimum. All rate plots were linear over 50–80% reaction; rate constants were obtained from kinetic data by the method of least squares. The spectra, first-order rate constants determined at various temperatures, and Arrhenius activation parameters are presented in Tables I–III, respectively.

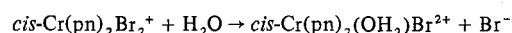
Discussion

Studies which have been carried out on the synthesis and properties of Cl₂-(en)₂-Co(III) and Cl₂-(pn)₂-Co(III) complexes indicate that (1) these compounds are similar in chemical behavior but differ in solubility (*trans* > *cis* for en system; *cis* > *trans* for pn system), (2) the introduction of alkyl groups into the carbon skeleton has a relatively small effect on the frequencies and molar absorptivity indices of d–d transitions, and (3) faster aquation rates and lower activation energies are observed for pn complexes.¹⁰

The present study shows that the first two above statements are valid for the corresponding Cr(III) analogs; however, the data in Table III indicate that the third generalization does not apply to all Cr(III) complexes of this type. A discussion and comparison of the pn and en Cr(III) complexes follows.

Aquation of *cis*-Cr(pn)₂Br₂⁺. A_∞ (at a given wavelength) could not be observed experimentally for first-stage aqua-

tion due to the second stage at long reaction times. Therefore, A_∞ 's were calculated assuming aquation to 100% *cis*-Cr(pn)₂(OH₂)Br₂²⁺. Plots of this logarithmic function of the absorbancies at the two absorption peaks of the *cis*-dibromo complex (537 and 410 nm) vs. t gave rates of (25.5 ± 1.2) and $(25.0 \pm 1.5) \times 10^{-4} \text{ sec}^{-1}$, respectively, at 25°. These rates were linear over 55–60% reaction and three sharp isosbestic points¹¹ were observed over the same period at 518 (75.5), 457 (29.0), and 391 (62.7). The theoretical isosbestic points for the *cis*-Cr(pn)₂Br₂⁺-*cis*-Cr(pn)₂(OH₂)Br₂²⁺ system are 519 (75.8), 458 (28.3), and 391 (62.8) which agree within experimental error with the observed. These agreements of rate data at two wavelengths and experimental and theoretical isosbestic points support the conclusion that first-stage aquation proceeds as



The data in Table II are based on averages for all kinetic runs under a given set of conditions and show that there is agreement with the 25° rate constants determined in 0.1 N HNO₃ and 0.1 N HClO₄ for this complex.

The 25° aquation studies of Quinn and Garner⁵ were extended to obtain Arrhenius activation parameters for *cis*-Cr(en)₂Br₂⁺. We used a modified sample preparation technique (see Experimental Section) which permitted spectral scanning to begin in *ca.* 60 sec after mixing. The linearity of our rate plots was similar (50–80% reaction) and k_{aq} at 25° agreed with the prior study. Tables II and III show that there are no significant differences in the rates or Arrhenius activation parameters of the en and pn *cis*-dibromo systems.

Aquation of *cis*-Cr(pn)₂(OH₂)Br₂²⁺. The A_∞ values used for rate plots were calculated from the experimental spectra of *cis*-Cr(pn)₂(OH₂)₂³⁺ whose spectrum is invariant over the acid concentration range used in the kinetic studies. On the other hand, Table II shows that the rate data in 3 N acid are different from that obtained in more dilute acid and furthermore are different in 3 N HNO₃ and 3 N HClO₄ (the former accelerates and the latter retards the rate). The rate is independent of the acid concentration in the 0.1–0.4 N range and the bulk of our data was obtained at the latter acid concentration. This particular [H⁺] was chosen because solutions for kinetic studies could be prepared by dilution of chromatographic eluates, thereby

(10) S. C. Chan, C. L. Chik, and B. Hui, *J. Chem. Soc.*, 607 (1967).

(11) The first numbers are wavelengths in nm and the numbers in parentheses are molar absorptivity indices in $M^{-1} \text{ cm}^{-1}$.

Table II. First-Order Rate Constants for Hydrolysis of *cis*- and *trans*-Cr(AA)₂Brⁿ⁺ in Acidic Solutions

Compound	Temp, °C	Acid	10 ⁴ k, sec ⁻¹	Method ^a
<i>cis</i> -Cr(pn) ₂ Br ₂ ⁺ ^b	25.0	0.1 N HClO ₄	24.8 ± 1.5	S
		0.1 N HNO ₃	25.7 ± 1.5	S
	20.0	0.1 N HNO ₃	14.7 ± 1.5	S
<i>cis</i> -Cr(en) ₂ Br ₂ ⁺ ^b	15.0	0.1 N HNO ₃	8.22 ± 0.70	S
	25.0	0.01–0.1 N HNO ₃	23.0 ± 3.0	S
	20.0	0.01 N HNO ₃	13.1 ± 1.5	S
	15.0	0.01 N HNO ₃	7.48 ± 0.70	S
<i>cis</i> -Cr(pn) ₂ (OH) ₂ Br ²⁺ ^b	25.0	0.1 N HClO ₄	1.70 ± 0.20	S
	25.0	0.4 N HClO ₄	1.60 ± 0.20	S, H
	25.0	3 N HClO ₄	0.92 ± 0.15	S
	25.0	3 N HNO ₃	2.55 ± 0.40	S
	25.0	0.4 N HClO ₄	1.70 ± 0.20	S
<i>cis</i> -Cr(en) ₂ (OH) ₂ Br ²⁺ ^{b,c}	25.0	0.4 N HClO ₄	1.70 ± 0.20	S
	24.8	0.06–0.14 N HNO ₃ or HClO ₄	1.8 ± 0.2	
<i>cis</i> -Cr(pn) ₂ Cl ₂ ⁺ ^d	25.0	0.1 N HClO ₄	3.5 ± 0.3	
<i>cis</i> -Cr(en) ₂ Cl ₂ ⁺ ^e	25.0	0.1 N HNO ₃	3.30	
<i>trans</i> -Cr(pn) ₂ Br ₂ ⁺ ^b	30.0	0.1 N HNO ₃	7.08 ± 0.70	S
	25.0	0.1 N HNO ₃	3.92 ± 0.27	S
<i>trans</i> -Cr(en) ₂ Br ₂ ⁺ ^{f,c}	20.0	0.1 N HNO ₃	4.00 ± 0.21	H
		0.1 N HNO ₃	4.03 ± 0.24	C
	25.0	0.1 N HNO ₃	2.05 ± 0.20	S
	25.0	0.1 N HNO ₃	3.26	
	24.8	0.01–0.1 N HClO ₄	3.2 ± 0.2	
	25.0	2.0 N HNO ₃	0.245 ± 0.030	H
	25.0	1.4 N HNO ₃	0.030 ± 0.002	
<i>trans</i> -Cr(pn) ₂ (OH) ₂ Br ²⁺ ^b	25.0	0.1 N HNO ₃	3.35 ± 0.27	
<i>trans</i> -Cr(en) ₂ (OH) ₂ Br ²⁺ ^c	25.0	0.1 N HNO ₃	2.25 ± 0.03	
<i>trans</i> -Cr(pn) ₂ Cl ₂ ⁺ ^g	25.0	0.1 N HNO ₃		
<i>trans</i> -Cr(en) ₂ Cl ₂ ⁺ ^h	25.0	0.1 N HNO ₃		

^a Method used in monitoring the reaction: C, chromatographic; H, bromide release; S, spectrophotometric. ^b This work. ^c Reference 5. ^d Reference 2. ^e J. Selbin and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, 79, 4285 (1957). ^f A. M. Weiner and J. A. McLean, Jr., *Inorg. Chem.*, 3, 1469 (1964). ^g R. R. Barona and J. A. McLean, Jr., *ibid.*, 11, 1443 (1972). ^h D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, 18, 219 (1961).

Table III. Activation Parameters for *cis*- and *trans*-Cr(AA)₂Br₂⁺

Compound	Acid	10 ⁴ k- (25°), sec ⁻¹	E _a , kcal mol ⁻¹	ΔS [‡] , cal deg ⁻¹ mol ⁻¹
<i>cis</i> -Cr(pn) ₂ Br ₂ ⁺ ^a	0.1 N HNO ₃	25.7	19.4 ± 1.2	-7.4 ± 3.6
<i>cis</i> -Cr(en) ₂ Br ₂ ⁺ ^a	0.01 N HNO ₃	23.0	19.2 ± 0.9	-8.3 ± 3.0
<i>trans</i> -Cr(pn) ₂ Br ₂ ⁺ ^a	0.1 N HNO ₃	3.92	21.9 ± 0.9	-2.7 ± 3.0
<i>trans</i> -Cr(en) ₂ Br ₂ ⁺ ^b	0.1 N HNO ₃	3.26	22.4	-1

^a This work. ^b Footnote f, Table II.

avoiding errors introduced by reducing [H⁺] with anion-exchange resin in the OH⁻ form.⁵

The aquation kinetics in 0.4 N HClO₄ at 25° were studied at 390, 410, 518, and 538 nm. The rate constants at these four wavelengths were found to be linear over 50–60% reaction and in excellent agreement as the average value at each wavelength is within the range of the *k* value ((1.60 ± 0.2) × 10⁻⁴ sec⁻¹) reported in Table II.

The rate constant in 0.1 N HClO₄ was estimated by following the aquation of *cis*-Cr(pn)₂Br₂⁺ over sufficiently long reaction times to permit the loss of both halide ions and making a first-order plot of the data obtained after 6 half-lives of the first-stage aquation (ca. 1800 sec). It is seen that the value obtained by this method is within acceptable agreement of data obtained directly in 0.4 N acid.

Three well-defined isobestic points¹¹ were maintained over at least 50% reaction at 497 (66.3), 436 (25.7), and 369 (45.5). The theoretical isobestic points for the *cis*-Cr(pn)₂(OH)₂Br²⁺–*cis*-Cr(pn)₂(OH)₂³⁺ system are 498 (67.3), 434 (25.5), and 369 (45.1).

The agreement of theoretical and experimental isobestics as well as rate constants at four different wavelengths suggests that *cis*-bromoquo aquates to give essentially a *cis*-diaquo product. The limits of spectrophotometric accuracy (errors could be as high as 10%⁵) preclude the conclusion that this reaction proceeds with complete steric retention of configuration. It is interesting to note that

the 6-half-life spectrum of this reaction does not agree with the experimental *cis*-diaquo spectrum. This is not surprising since we have found that the postulated *cis*-diaquo complex is not stable to aquation. The solid *cis*-diaquo complex in 2 N HNO₃ was found to aquate (*t*_{1/2} ca. 21 hr at 25°) to give a product tentatively characterized as the tetraquo species on the basis of its spectral features.³

The aquation rate of *cis*-Cr(en)₂(OH)₂Br²⁺ was determined using *cis*-[Cr(en)₂(OH)₂Br]Br₂·H₂O in 0.4 N HClO₄ and found to be (1.70 ± 0.20) × 10⁻⁴ sec⁻¹ which is in excellent agreement with the previously determined value⁵ in 0.06–0.14 N HNO₃. All other features of this system were analogous to the prior study. This leads to the inescapable conclusion that there is no difference in the aquation rates of *cis*-bromoquo pn and en analogs of Cr(III) complexes at 25°.

See Figure 1 for visible absorption spectra of the *cis* complexes.

Aquation of *trans*-Cr(pn)₂Br₂⁺. First-stage aquation rate constants for this species were determined by three independent methods.

Bromide release data were obtained from potentiometric titration³ and plotted as ln(*a*/(*a* - *x*)) vs. *t*, where *a* is half of the total coordinated bromide and *x* is the concentration of bromide released at time *t*. Data in this form gave a straight line up to ca. 55% reaction.

Chromatographic data were obtained by a modification of the method previously reported.³ Aliquots were removed from the reacting solution, immediately quenched at time *t*, and absorbed on a chromatographic column at 0°, and the unreacted *trans*-Cr(pn)₂Br₂⁺ was eluted with 1 N HNO₃. This higher acid concentration accelerates separation and elution of this species sufficiently to preclude reaction on the column which occurs at lower acid concentration. The first-order rate constant for the disappearance of *trans*-Cr(pn)₂Br₂⁺ was obtained from a linear plot of ln(*C*₀/*C*_{*t*}) vs. *t*, where *C*₀ and *C*_{*t*} are the complex

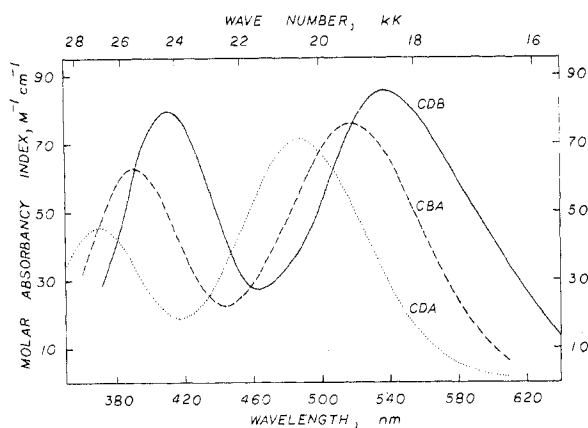


Figure 1. Visible absorption spectra at 0°: CDB, *cis*-Cr(pn)₂Br₂⁺ in 0.1 *N* HNO₃; CBA, *cis*-Cr(pn)₂Br(OH₂)₂²⁺ in 2.0 *N* HClO₄; CDA, *cis*-Cr(pn)₂(OH₂)₂³⁺ in 2.0 *N* HNO₃.

concentration at zero time and time *t*, respectively. The first-order rate plots obtained were linear over at least 60% reaction.

Spectrophotometric data were plotted using A_{∞} 's calculated from chromatographically isolated *trans*-Cr(pn)₂(OH₂)Br²⁺. The spectrum of the reacting system continually changes and never comes to an equilibrium during first-stage aquation. Kinetic plots are linear over 1.5 half-lives and three isosbestic points¹¹ were observed at 572 (21.8), 449 (26.5), and 416 (30.8) over the same period. The theoretical isosbestic points for the *trans*-Cr(pn)₂Br₂⁺-*trans*-Cr(pn)₂(OH₂)Br²⁺ system are 573 (22.1), 450 (26.9), and 415 (31.6) which are seen to be in excellent agreement with the observed.

Rate data collected at 384 and 606 nm gave constants within the error limits of the value reported in Table II. This agreement as well as the agreement between actual and predicted isosbistics indicate that the product of the first-stage aquation has the *trans* configuration. Further evidence to support this conclusion is the fact that the spectrum of chromatographically isolated *trans*-bromoquo complex does not change when allowed to aquate through 3 *cis*-bromoquo half-lives and rechromatographed to remove the possible *cis*-diaquo complex.

Aquation of *trans*-Cr(pn)₂(OH₂)Br²⁺. This cation was isolated chromatographically and studied in 2 *N* HNO₃ at 25.0°. We were unable to follow this rate spectrophotometrically since A_{∞} could not be observed experimentally and spectral changes indicated a mixture of products which we were unable to isolate or to identify. Two slightly broadened isosbestic points were observed over a 180-min reaction period at 547 and 437 nm. Although Figure 2 shows that these isosbistics are in the approximate wavelength range expected for *trans*-bromoquo and *trans*-diaquo complexes, the experimental spectrum does not fit this two-component system nor a three-component system including the *cis*-diaquo species. Preliminary studies of the spectra of the *trans*-diaquo compound showed that this species reacts to give more than one product under the above experimental conditions.

Due to the complexity of the aquation reaction of the *trans*-bromoquo complex, only the rate of bromide release was determined. The half-life of this reaction corresponded to ca. 470 min and the rate plots were linear over 50% reaction. Table II shows that this bromide release rate constant is $(2.45 \pm 0.30) \times 10^{-5} \text{ sec}^{-1}$ which is ca. 8 times greater than the corresponding en analog.

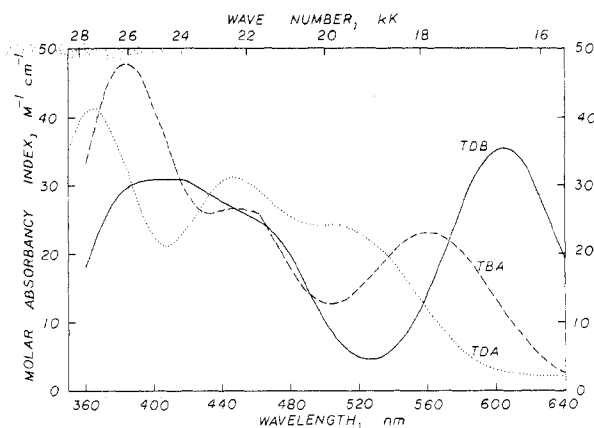


Figure 2. Visible absorption spectra at 0°: TDB, *trans*-Cr(pn)₂Br₂⁺ in 0.1 *N* HNO₃; TBA, *trans*-Cr(pn)₂Br(OH₂)₂²⁺ in 2.0 *N* HNO₃; TDA, *trans*-Cr(pn)₂(OH₂)₂³⁺ in 2.0 *N* HNO₃.

The scheme shown in Figure 3 summarizes the possible reaction paths involved in the aquation of *cis*- and *trans*-Cr(pn)₂Br₂⁺ in acidic medium at 25° in the absence of light.

Comparison of Co(III) and Cr(III) Systems. Data which are available for comparison of aquation rates of Co(III)-pn and -en complexes are summarized in Table IV. It is seen that pn/en ratios range from 36 to 1.7. Furthermore, a considerable number of kinetic data have been collected for *cis*- and *trans*-Co(en)₂AXⁿ⁺ systems, where X is the leaving group.¹² It is generally found that *cis* isomers aquate with retention of configuration whereas most *trans* isomers aquate with steric change. The results of Co(III) studies are consistent with a unimolecular dissociative mechanism where (1) pn causes faster rates due to steric crowding of the C-methyl group and (2) a square-pyramidal intermediate (D) or transition state (I_d) is postulated in stereoretentive aquations and a trigonal-bipyramidal geometry (D or I_d) for aquations where change in configuration is observed.

In contrast the results of Cr(III) presented in this study show that there are no distinct differences in the aquation rates of pn and en complexes of the type *cis*-Cr(AA)₂-XBrⁿ⁺, where X = Br⁻ or H₂O. Similar results have been reported previously for the *cis*-dichloro systems.^{2,13} On the other hand, for the *trans* isomers, the rates of aquation differ by a factor of 1.2 for X = Br⁻ and a factor of 8 for X = H₂O, in both instances the pn complex reacting faster. It should be noted that neither of the two *trans*-bromoquo aquation reactions have been completely characterized and the ratio is for bromide release. The previously reported pn/en ratio for the *trans*-dichloro system is 1.4.³

All Cr(III) complexes above (where products have been characterized) react with essentially complete retention of configuration except the *trans*-dichloro systems. It should be noted that these two complexes are also the only cases where Cr-N bond breaking plays a significant role in aquation. Two recent studies would tend to indicate that *cis*-chloroquo is not a directly formed product in the aquation of these *trans*-dichloro cations. First, Pyke and Linck¹⁴ found that *trans*-Cr(en)₂F₂⁺ aquates to give solely Cr(en)(enH)(OH₂)F₂²⁺. This monodentate ethylenediamine complex aquates in turn to give 30% *cis*-Cr(en)₂-

(12) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 4.

(13) See footnote e, Table II.

(14) S. C. Pyke and R. G. Linck, *Inorg. Chem.*, **10**, 2445 (1971).

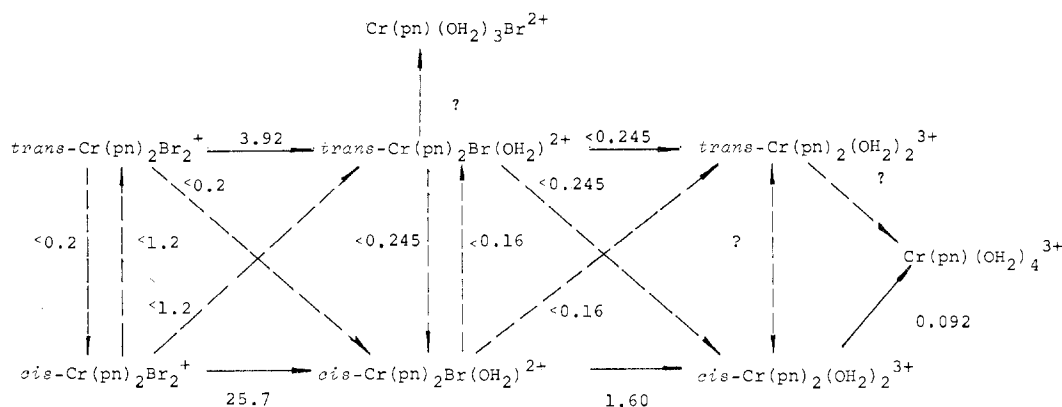


Figure 3. First-order rate constants ($10^4 k$, sec^{-1}) for aquation and isomerization in acidic medium at 25° in the absence of light. The dashed lines correspond to reaction paths for which there is no direct experimental evidence either for or against the path.

Table IV. Rates of Aquation of $\text{Co}(\text{AA})_2\text{XY}^+$ at 25°

Config	AA	X	Y	k , sec^{-1}	pn/en
Trans ^a	en	NCS	Cl	5.0×10^{-8}	36
Trans ^a	pn	NCS	Cl	1.8×10^{-6}	
Trans ^a	en	NCS	Br	5.0×10^{-7}	32
Trans ^a	pn	NCS	Br	1.6×10^{-5}	
Trans ^b	en	Cl	Cl	3.5×10^{-5}	1.8
Trans ^c	pn	Cl	Cl	6.2×10^{-5}	
Cis ^b	en	Cl	Cl	2.4×10^{-4}	1.7
Cis ^d	pn	Cl	Cl	4.1×10^{-4}	

^a Reference 10. ^b M. E. Baldwin, S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961). ^c R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, 78, 2673 (1956). ^d Reference 2.

$(\text{OH}_2)\text{F}^{2+}$ by rechelation and 70% $\text{Cr}(\text{en})(\text{OH}_2)_2\text{F}_2^+$ by further Cr-N bond rupture. Second, the Hg^{2+} -catalyzed aquation of $\text{trans-Cr}(\text{en})_2\text{Cl}_2^+$ is stereorententive.¹⁵ These observations could be interpreted to mean that Cr(III) complexes are generally stereorententive and the isomeric products found in spontaneous aquation are due to rechelation of a monodentate diamine ligand subsequent to Cr-N bond breaking.

Studies of linear free energy relationships suggest that the aquation mechanisms of Co(III) and Cr(III) are different. Langford¹⁶ has shown that a plot of $\log k_{\text{aq}}$ vs. $-\log K$ (equilibrium constant) for the aquation of $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ complexes gives a straight line whose slope

is 1.0. These results indicate that X is a solvated ion in both the transition state and the product and are consistent with a dissociative (D) mechanism. A similar plot of $\log k_{\text{aq}}$ vs. $-\log Q$ (the stability quotient) for the aquation of $\text{Cr}(\text{OH}_2)_5\text{X}^{2+}$ gives a straight line whose slope is 0.59.¹⁷ This was interpreted to mean that the separation of X in the transition state is only 60% complete.

The results of the present study are consistent with an interchange mechanism which is more dissociative than associative in character. In Cr(III)-pn complexes the steric crowding of the C-methyl group will have a smaller effect on k_{aq} than in corresponding Co(III)-pn complexes which are largely dissociative. Similarly, E_a is expected to be lower for pn than en in Co(III) complexes but the associative character of the dissociative mechanism of Cr(III) complexes compensates for this difference. Finally, this mechanism also accounts for the stereochemical behavior of trans Cr(III) complexes which are stereorententive whereas extensive rearrangement is observed for Co(III) analogs.

Registry No. *cis*- $[\text{Cr}(\text{en})_2\text{Br}_2]\text{Br}$, 14263-07-1; *cis*- $[\text{Cr}(\text{en})_2(\text{OH}_2)\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$, 30172-32-8; *cis*- $[\text{Cr}(\text{pn})_2\text{Br}_2]\text{Br}$, 17968-01-3; *trans*- $[\text{Cr}(\text{pn})_2\text{Br}_2]\text{Br}$, 31144-86-2; *trans*- $\text{Cr}(\text{pn})_2(\text{OH}_2)\text{Br}^{2+}$, 38217-30-0; *cis*- $\text{Cr}(\text{pn})_2(\text{OH}_2)\text{Br}^{2+}$, 38136-21-9; *cis*- $\text{Cr}(\text{en})_2(\text{OH}_2)_2^{3+}$, 22432-36-6; *cis*- $[\text{Cr}(\text{en})_2\text{OH}(\text{OH}_2)] \cdot \text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$, 34076-61-4; $[\text{Cr}(\text{pn})_2(\text{OH})(\text{OH}_2)] \text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$, 38136-15-1.

(15) W. G. Jackson, private communication.

(16) C. H. Langford, *Inorg. Chem.*, 4, 265 (1965).

(17) T. W. Swaddle and G. Guastalla, *Inorg. Chem.*, 7, 1915 (1968).