−79° and the evacuated tubes were stored at this temperature until ready to run.

Hydrolysis of the Reaction Intermediate. (A) Anaerobic Conditions.—To the orange diamagnetic powder obtained on warming a sample of dichlorobis(triethylamine)copper(II) to a temperature just above 0° was added an excess of water. The mixture was stirred for 10 min., and the more volatile materials so liberated were removed by distillation in the vacuum system. In addition to a little water, the distillate was found to contain large amounts of acetaldehyde, diethylamine, and triethylamine. Acetaldehyde was characterized by precipitation of its 2,4-dinitrophenylhydrazone from a solution of the distillate in dilute hydrochloric acid (m.p. 142–143°, authentic sample m.p. 146°, m.m.p. 145°). The distillate was evaporated to dryness and the amine hydrochlorides were taken up in the minimum amount of water. Concentrated sodium hydroxide was added to the solution, and the amine fraction was obtained by distillation. Using an F. and M. flame ionization gauge vapor phase chromatograph with a helium carrier gas flow rate of 50 ml./min. and a 2-ft. column packed with silicone rubber at 35°, the amine fraction was separated into two peaks having retention times of 2.48 and 5.45 min., respectively. These peaks were identical with those shown by a 50:50 synthetic mixture of di- and triethylamines, and the second peak was identical with that of authentic triethylamine. Separation of the amine fraction by the Hinsberg method also permitted characterization of diethylamine as the benzenesulfonamide, m.p. 41–42°, authentic sample m.p. 42°, m.m.p. 42°.

(B) Aerobic Conditions.—A similar sample was hydrolyzed at 0° over a period of 2 hr. in a system open to the air. The mixture was made acidic, distillation of the water was commenced, and the aldehyde portion was found to be concentrated in the forerun. It gave the 2,4-dinitrophenylhydrazone of glyoxal (m.p. 326°, authentic sample m.p. 324°, m.m.p. 323°) and was in fact glycolaldehyde (the glyoxal derivative being formed by an osazone reaction). Thus, the aldehyde gave a negative test for glyoxal with *o*-phenylenediamine, and gave positive tests for glycolaldehyde with orcinol and phloroglucinol.[11] Formation of glycolaldehyde from the originally liberated acetaldehyde under aerobic conditions is attributed to air reoxidation of some copper(I) to copper(II) chloride, which is known[12] to convert carbonyl compounds to the α-chloro derivatives. Hydrolysis of chloroacetaldehyde would then yield glycolaldehyde.

After distillation of the aldehyde portion, the hydrolyzed reaction mixture was made alkaline and the amine portion was then obtained by distillation. In addition to triethylamine, it contained diethylamine which was separated and identified by the Hinsberg method, *p*-benzenesulfonamide m.p. 36°, authentic sample m.p. 42°, m.m.p. 38°.

N.m.r. and Infrared Spectra.—In the previous work,[1] the postulate was made that product B of eq. 2 corresponds to triethylammonium dichlorocuprate(I) (except that the alkylammonium moiety is about 85% triethylammonium ion and about 15% the conjugate acid of the polymeric amine derived from repeated steps of oxidative deprotonation of triethylamine). To obtain further evidence on this point, a sample of B was prepared in the manner previously given. The n.m.r. spectrum of this reaction product was compared with that of authentic triethylammonium dichlorocuprate(I), prepared as previously described,[1] using a Varian A-60 spectrometer. The sample tubes were loaded in a nitrogen-filled drybox and closed with plastic caps sealed with wax. The results are shown in Fig. 3. Carbon tetrachloride and carbon disulfide extracts of the dark liquid product were only slightly yellow, indicating fairly low solubility. A Perkin-Elmer Infracord was used to obtain infrared spectra of these solutions, but the results showed poor definition and differed from triethylamine and triethylammonium chloride spectra only by absorption in the 1250–1275 cm.$^{-1}$ region.

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[11] E. Tommila, *Acta Chem. Fennica*, **7B**, 85 (1934); *Chem. Abstr.*, **28**, 4008 (1934).

[12] C. E. Castro, *J. Org. Chem.*, **26**, 4183 (1961); J. K. Kochi, *J. Am. Chem. Soc.*, **77**, 5274 (1955).

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Kinetics of Aquation of Dibromo- and Bromoaquobis(ethylenediamine)chromium(III) Cations[1]

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The kinetics and products of aquation of *cis*- and *trans*-$Cr(en)_2Br_2^+$ and *cis*- and *trans*-$Cr(en)_2(OH_2)Br^{+2}$ have been investigated in acid solution at 24.8 ± 0.2°. In 0.01–0.1 F $HClO_4$ (μ = 0.1, $LiClO_4$) k_{aq} is (2.8 ± 0.3) × 10^{-3} sec.$^{-1}$ for *cis*-$Cr(en)_2Br_2^+$ and (3.2 ± 0.2) × 10^{-4} sec.$^{-1}$ for *trans*-$Cr(en)_2Br_2^+$. The directly-formed products of *cis*-$Cr(en)_2Br_2^+$ aquation are *cis*-$Cr(en)_2(OH_2)Br^{+2}$ (97 ± 3%) and *trans*-$Cr(en)_2(OH_2)Br^{+2}$ (3 ± 3%). In *trans*-$Cr(en)_2Br_2^+$ aquation 96% of the first-formed product is *trans*-$Cr(en)_2(OH_2)Br^{+2}$; the other 4% of first-formed product is either *cis*-$Cr(en)_2(OH_2)Br^{+2}$ (aquation) or *cis*-$Cr(en)_2Br_2^+$ (isomerization). In 0.06–0.14 F $HClO_4$ or HNO_3 *cis*-$Cr(en)_2(OH_2)Br^{+2}$ has k_{aq} = (1.8 ± 0.2). × 10^{-4} sec.$^{-1}$, the directly-formed products being *cis*-$Cr(en)_2(OH_2)_2^{+3}$ (95 ± 5%) and *trans*-$Cr(en)_2(OH_2)_2^{+3}$ (5 ± 5%) In 1.4 F HNO_3 *trans*-$Cr(en)_2(OH_2)Br^{+2}$ releases Br^- at an initial rate corresponding to k = (3.0 ± 0.2) × 10^{-6} sec.$^{-1}$; there is evidence for a faster competing reaction, probably involving loss of ligand ethylenediamine. Upper limits for the *cis–trans* isomerization rates have been estimated. Reaction paths consistent with the kinetic and stereochemical results are presented, and a comparison is made with the aquation behavior of the chloro analogs and the Co(III) analogs. The previously unreported visible absorption spectra of these Cr(III) species are given.

The hydrolysis of *cis*- and *trans*-dibromobis(ethylenediamine)chromium(III) cations and the related bromoaquo complexes apparently has not been investigated previously. We report here a study of the kinetics and products of aquation of these species in acid solution, undertaken to allow comparisons to be

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made with the extensively studied chloro analogs[2–6] and with *cis*-difluorobis(ethylenediamine)chromium(III) cation,[7] as well as with the Co(III) analogs to the extent that information on them is available. Considerations bearing on the rates of the *cis–trans* isomerization of these bromo complexes are presented.

Experimental

cis-**Dibromobis(ethylenediamine)chromium(III) Bromide.**—A modification of the methods of Pfeiffer[8,9] was used. Five grams of *cis*-$[Cr(en)_2Cl_2]Cl$, the preparation of which is described elsewhere,[3] was dissolved in the minimum amount (*ca.* 30 ml.) of 60° water and kept at 60° for 20 min. to allow for aquation to *cis*-$Cr(en)_2(OH_2)_2^{+3}$. After the solution was filtered, 15 ml. of 9 *F* HBr was added and the filtrate was evaporated to dryness on a steam bath in *ca.* 20 min. Another 15 ml. of 9 *F* HBr was added, the undissolved crystals were crushed, and the mixture was taken to dryness again. The deep pink material obtained was purified by slurrying it with *ca.* 150 ml. of 95% ethanol, filtering, then washing the solid twice with ethanol. The solid was dried at 105° for 15 hr.; yield 5.1 g. (69%).

Anal. Calcd. for *cis*-$[Cr(en)_2Br_2]Br$: C, 11.7; H, 3.9; Br, 58.2; Cr, 12.6; N, 13.6. Found: C, 12.2; H, 4.2; Br, 58.4; Cr, 12.5; N, 13.5.

cis-**Dibromobis(ethylenediamine)chromium(III) Perchlorate.**—*Ca.* 11 g. of *cis*-$[Cr(en)_2Br_2]Br$ was triturated with 20 ml. of 10 *F* $HClO_4$ to convert the bromide salt to the perchlorate. The slurry was filtered and the process repeated. The solid was crushed with 95% ethanol and then with ether; then 7 g. of the dry solid was slurried with 700 ml. of absolute ethanol at 60° for 5 min., and the solution was allowed to cool for 5 min., then filtered. This procedure was repeated twice and the final solid was dried for 15 hr. at 130°. *Anal.* Calcd. for *cis*-$[Cr(en)_2Br_2]ClO_4$: C, 11.1; H, 3.7; Br, 37.0; Cr, 12.0; N, 13.0. Found: C, 11.2; H, 3.5; Br, 37.0; Cr, 12.3; N, 13.4.

This compound was used in certain spectral studies, but its use was discontinued upon our learning that the dichloro Co(III) analog can apparently be detonated[10] under certain conditions.

cis-**Bromoaquobis(ethylenediamine)chromium(III) Cation.**—This ion was prepared in solution by dissolving 63 mg. of *cis*-$[Cr(en)_2Br_2]Br$ in 100 ml. of 0.1 *F* $HClO_4$ and allowing the solution to aquate in the dark for 19 min. (*ca.* 4.8 half-lives). The Cr species from the entire solution were then adsorbed on a 40 × 9 mm. diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh). Unreacted parent was removed by eluting with 100 ml. of 0.6 *F* HNO_3. The desired *cis*-$Cr(en)_2(OH_2)Br^{+2}$ was removed with 50 ml. of 2 *F* HNO_3. In order to reduce the HNO_3 concentration of some of these effluents to be used in kinetic runs they were titrated with Dowex AG 2-X8 anion-exchange resin (100–200 mesh) in the OH^- form[5] to the desired acidity using a Beckman pH meter; final H^+ concentrations were determined by passing an aliquot of the solution through a H^+ Dowex AG50W-X8 column and titrating the H^+ with standard NaOH (correcting for H^+ displaced by the Cr species adsorbed).

The complex was characterized as *cis*-$Cr(en)_2(OH_2)Br^{+2}$ by its visible absorption spectrum (*vide infra*), by a Br/Cr atom ratio of 0.966, and by its elution behavior from H^+ Dowex AG50W-X8 resin.[11] Solutions of the complex were used for kinetic measurements immediately after their synthesis.

Attempted Preparation of *cis*-**Bromoaquobis(ethylenediamine)chromium(III) Bromide.**—Pfeiffer[8] prepared a compound to which he ascribed the formula $[Cr(en)_2(O_2H_4)Br]Br_2$. Schläfer and Kollrack[12] apparently considered this substance to be *cis*-$[Cr(en)_2(OH_2)Br]Br_2 \cdot H_2O$ and prepared for use as a synthesis intermediate what they assumed to be the anhydrous form of this compound by a modification of Pfeiffer's method. In an attempt to prepare this compound we used the procedure of Schläfer and Kollrack. Two batches were prepared. *Anal.* Calcd. for $[Cr(en)_2(OH_2)Br]Br_2 \cdot H_2O$: C, 10.7; H, 4.5; Br, 53.6; Cr, 11.6; N, 12.5. Found (batch 1): C, 11.5; H, 4.8; Br, 54.4; Cr, 11.8; N, 12.9. Found (batch 2): C, 11.7; H, 4.8; Br, 53.3; Cr, 11.6; N, 12.8. Both lots were dried by suction and vacuum desiccation at 25° (drying the compound at 100° is stated[9] to produce *cis*-$[Cr(en)_2Br_2]Br$).

Although these analytical results are in reasonably good agreement with the hypothesized formula, rate measurements made on the hydrolysis of the material in acid solution gave data which, when plotted according to a first-order rate law, gave curved rate plots which were resolvable into a short-lived component and a longer-lived component. The former ($t_{1/2} \sim 40$ min.) constituted 25% and the latter ($t_{1/2} \sim 420$ min.) constituted 75% of the mixture. Attempts to separate the two materials on a cation-exchange resin failed. The short-lived component may be *cis*-$[Cr(en)_2(OH_2)Br]Br_2$; the composition of the long-lived component is completely unknown. Thus, the material is a mixture. Since rate experiments repeated at a later date on the material gave somewhat different results, there is a possibility the mixture arises from a decomposition process. In any event, the purported *cis*-$[Cr(en)_2(OH_2)Br]Br_2 \cdot H_2O$ has different properties from the *cis*-$Cr(en)_2(OH_2)Br^{+2}$ prepared (*vide ante*) by chromatographic isolation from *cis*-$[Cr(en)_2Br_2]Br$ aquation mixtures, and we abandoned further attempts to synthesize a solid salt of the *cis*-bromoaquo complex.

trans-**Dibromobis(ethylenediamine)chromium(III) Bromide.**—A modification of the method of Pfeiffer[8] was used. A mixture of 8 g. of 9 *F* HBr, 16 g. of $HgBr_2$, 16 ml. of 50° H_2O, and 8 g. of the material described by Pfeiffer[8] as $[Cr(en)_2(O_2H_4)Br]Br_2$ (*vide ante*) was evaporated to dryness on a steam bath. The product, the green double salt, *trans*-$[Cr(en)_2Br_2]Br \cdot HgBr_2$, was washed with 0.6 *F* HBr until the washings (*ca.* 50 ml.) were clear. The double salt is not appreciably water-soluble; yield 9.0 g. (52%).

A slurry of 5 g. of the double salt in 30 ml. of H_2O was treated with H_2S for 10 min. with occasional shaking. After filtering off the HgS precipitate, the green *trans*-$Cr(en)_2Br_2^+$ solution was cooled to 0° and gaseous HBr bubbled in for 30 min. A green precipitate formed which was filtered on sintered glass and washed with 1 bed volume of 9 *F* HBr and rinsed with 3 bed volumes of absolute ethanol. Purification was accomplished by dissolving 6.3 g. of the salt in the minimum volume (*ca.* 85 ml.) of 25° H_2O, filtering, and reprecipitating the green compound with HBr as before. The product was dried 15 hr. under vacuum at 103°; yield 19%. *Anal.* Calcd. for *trans*-$[Cr(en)_2Br_2]Br$: C, 11.7; H, 3.91; Br, 58.2; Cr, 12.6; N, 13.6. Found: C, 11.8; H, 3.93; Br, 58.4; Cr, 12.4; N, 13.7.

trans-**Bromoaquobis(ethylenediamine)chromium(III) Cation.**—This cation has apparently not been previously reported. *trans*-$[Cr(en)_2Br_2]Br$ (0.1 g.) was dissolved in 90 ml. of H_2O and 10 ml. of 1 *F* $HClO_4$ added immediately. The solution was allowed to aquate in the dark for 105 min. (*ca.* 3 half-lives). Adsorption of the entire sample on a 40 × 9 mm. diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) was followed by elution of the unreacted *trans*-$Cr(en)_2Br_2^+$ with 100 ml. of 0.6 *F* $HClO_4$ or HNO_3. The *trans*-$Cr(en)_2(OH_2)Br^{+2}$ ion

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[2] D. J. MacDonald and C. S. Garner, *J. Inorg. Nucl. Chem.*, **18**, 219 (1961).

[3] D. J. MacDonald and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 4152 (1961).

[4] C. S. Garner and D. J. MacDonald in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan Co., New York, N. Y., 1961, pp. 266–275.

[5] D. J. MacDonald and C. S. Garner, *Inorg. Chem.*, **1**, 20 (1962).

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[8] P. Pfeiffer, *Z. anorg. Chem.*, **56**, 279 (1908).

[9] P. Pfeiffer, *Chem. Ber.*, **40**, 3828 (1907).

[10] W. R. Tomlinson, K. G. Ottoson, and L. F. Audrieth, *J. Am. Chem. Soc.*, **71**, 375 (1949).

[11] Based on analogies with the behavior of the chloro analogs; see ref. 3–5.

[12] H. L. Schläfer and R. Kollrack *Z. physik. Chem.* (Frankfurt) **18**, 348 (1958).

was then eluted with 35 ml. of 2.0 *F* $HClO_4$ or HNO_3. Since our chromatographic procedure did not cleanly separate *trans*- and *cis*-$Cr(en)_2(OH_2)Br^{+2}$, and since there was evidence of the presence of *ca.* 4% of the *cis* isomer in the *trans* solution, the solution was aged for 3 *cis* aquation half-lives (reducing the *cis* content to <0.5%), then rechromatographed to remove the *cis*-$Cr(en)_2(OH_2)_2^{+3}$ formed and to give essentially pure *trans*-$Cr(en)_2(OH_2)Br^{+2}$ in solution. Analysis of the solutions so obtained gave a Br/Cr atom ratio of 1.00. The complex was further characterized by its elution behavior in cation-exchange chromatography[11] and by its visible absorption spectrum (*vide infra*). Solutions of the complex were used immediately in kinetic runs.

Lithium Perchlorate.—A weighed amount of reagent grade Li_2CO_3 was titrated to pH 7 with concentrated $HClO_4$ (J. T. Baker Analyzed Reagent). The solution was boiled to remove CO_2 and the procedure repeated after cooling until there was no further change in pH observed on boiling and cooling. All other chemicals were either reagent grade or C.P.

Analytical Methods.—Visible absorption spectra were obtained with a Cary Model 11 recording spectrophotometer, using matched 10-cm. quartz cells and a temperature-controlled cell compartment. Bromide analyses were performed by digesting the complex with excess NaOH at 85°, then reacidifying after cooling and titrating to a potentiometric end point with standard $AgNO_3$ in the presence of a nonionic detergent–acetone mixture. Chromium was determined by treatment of the complex with hot alkaline peroxide and spectrophotometrically determining the resulting chromate at 3725 Å. with a Beckman DU spectrophotometer.

Kinetic Measurements.—Separate freshly prepared solutions of *cis*- and *trans*-$Cr(en)_2Br_2^+$ and *cis*- and *trans*-$Cr(en)_2(OH_2)Br^{+2}$ (usually *ca.* 0.15 m*F* in complex) in $HClO_4$ or HNO_3 of the desired concentration were allowed to react in a quartz spectrophotometer cell in the absence of light. Scans were made at appropriate intervals to search for isosbestic points and to obtain the change in absorbancy as a function of reaction time *t*. The data were plotted as log $(A_\infty - A_0)/(A_\infty - A)$ *vs.* *t*, where A_0 and A are the absorbancies (at a given wave length) initially and at time *t*, and A_∞ is the absorbancy calculated for the reaction products, except in the case of *trans*-$Cr(en)_2Br_2^+$ where A_∞ is the observed absorbancy at equilibrium. Values of the rate constants were calculated from 2.30 times the slopes of these linear rate plots.

Reaction mixtures prepared in an analogous manner were analyzed at known reaction times for released Br^- by adsorbing an aliquot of the solution on a 40 × 9 mm. diameter column of H^+ Dowex AG50W-X8 cation-exchange resin (100–200 mesh) and washing out the released Br^- from the column with several bed volumes of 0.001 *F* $HClO_4$; these effluents were titrated potentiometrically with $AgNO_3$. Experiments showed the resin did not catalyze the release of Br^-. The method was not suitable for use in following the aquation of *cis*-$Cr(en)_2Br_2^+$ inasmuch as significant decomposition of that complex occurred on the resin because of its short half-life and the fairly long contact time on the resin.

In the *trans*-dibromo aquation studies it was possible to follow the reaction by the above chromatographic procedure by eluting out the unreacted *trans*-$Cr(en)_2Br_2^+$ with 100 ml. of 0.3 *F* $HClO_4$ (after the Br^- was washed out of the column) and determining the Cr in this effluent. This eluting agent cleanly separates *trans*-$Cr(en)_2Br_2^+$ from the *cis* isomer (which requires 100 ml. of 0.6 *F* $HClO_4$ for its elution) and from the *cis*- and *trans*-bromoaquo reaction products (which require 100 ml. of 2 *F* $HClO_4$ for their elution).

Light Sensitivity.—All of the coordination compounds prepared during this research were found to be light sensitive. Hence the characterized compounds were stored in sealed vials in the dark. Kinetic runs were made in the absence of light (except for exposure to the spectrophotometer light during spectral scans).

Spectra.—Absorption spectra of the complexes were obtained from spectral kinetic runs by extrapolating the spectra back to zero time.

Results and Discussion

Aquation of *cis*-$Cr(en)_2Br_2^+$; Related Isomerizations.—Table I presents the first-order rate constants for aquation of *cis*-$Cr(en)_2Br_2^+$ in $HClO_4$ solution at 24.8° determined by a spectrophotometric method (see Experimental section), with A_∞ calculated from the spectrum of *cis*-$Cr(en)_2(OH_2)Br^{+2}$; *i.e.*, for the reaction

$$cis\text{-}Cr(en)_2Br_2^+ + H_2O \longrightarrow cis\text{-}Cr(en)_2(OH_2)Br^{+2} + Br^- \quad (1)$$

Good first-order rate plots were obtained over 50–80% reaction, except for the 400 mμ data at the two lower acid concentrations. Over the thousandfold range of acid concentration the aquation rate constant may be taken as $(2.8 \pm 0.3) \times 10^{-3}$ sec.$^{-1}$ ($t_{1/2}$ = 4.1 min.). The apparent increase in *k* calculated from the 400 mμ data with decreasing acidity below 0.00985 *F* $HClO_4$ is presumably not associated with a contribution from base hydrolysis of *cis*-$Cr(en)_2Br_2^+$ inasmuch as base hydrolysis is known[13] to contribute negligibly in the case of the analogous dichloro complex at such pH values, and our *k* values calculated from the 600 mμ data do not show this trend. Rather the effect appears to be related to increased proportions of the bromohydroxo species (presumably present in small amounts as a result of acid dissociation of bromoaquo species even at $t = 0$ because of the slow dissolution of solid *cis*-$[Cr(en)_2Br_2]Br$ reactant in the reaction solvent requiring *ca.* 1.6 half-times before the first spectral scan could be made); *cis*-$Cr(en)_2(OH)Br^+$ would be expected to aquate somewhat faster than the chlorohydroxo analog, which has been shown[14] to aquate at 25° with a 3-min. half-time, and the *cis*-diaquo known to form as principal product has a spectrum (see Fig. 2) such that *k* calculated at 400 mμ would be greater than at 600 mμ. Further resolution of this question will be left for a possible future study of the hydrolysis in basic solution.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF *cis*-$Cr(en)_2Br_2^+$ AT 24.8 ± 0.2°, C_0 = 1.5 m*F*, μ = 0.103 ($LiClO_4$)

$HClO_4$, *F*	10^3k, sec.$^{-1}$
0.0985	2.5,[a] 2.7,[b] 2.8[c]
0.00985	2.8,[a] 2.8[c]
0.000985	2.7,[a] 5.8[d]
0.0000976	2.9,[a] 9.6[d]

[a] 600 mμ. [b] 530 mμ. [c] 400 mμ. [d] 400 mμ; estimated from initial slope of curved rate plot.

At least at the higher acidities (0.0985–0.00985 *F* $HClO_4$) the *directly-formed* aquation product is essentially all *cis*-$Cr(en)_2(OH_2)Br^{+2}$. This has been shown from the following facts. First, three sharp isosbestic points were observed at 387 (a_M = 57.4 M^{-1} cm.$^{-1}$), 457 (a_M = 29.2 M^{-1} cm.$^{-1}$), and 515 mμ (a_M = 70.1 M^{-1} cm.$^{-1}$), in agreement within experimental error with the isosbestic points predicted for the *cis*-$Cr(en)_2Br_2^+$–*cis*-$Cr(en)_2(OH_2)Br^{+2}$ system (see Fig. 2),

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[13] R. G. Pearson, R. A. Munson, and F. Basolo, *J. Am. Chem. Soc.*, **80**, 504 (1958).

[14] D. C. Olson and C. S. Garner *Inorg. Chem.*, **2**, 558 (1963).

namely, 390 ($a_M = 60.2\ M^{-1}$ cm.$^{-1}$), 462 ($a_M = 30.6\ M^{-1}$ cm.$^{-1}$), and 519 mμ ($a_M = 72.1\ M^{-1}$ cm.$^{-1}$). Construction of spectral curves for *cis*-$Cr(en)_2Br_2^+$ aquating to fixed ratios of *cis*- and *trans*-$Cr(en)_2(OH_2)Br^{+2}$ showed, however, that as much as 5% of the *trans* isomer could be directly formed and still give these same isosbestic points within the experimental errors.[15] Thus an upper limit of 1.5×10^{-4} sec.$^{-1}$ may be taken for the first-order rate constant at 24.8° associated with the reaction

$$cis\text{-}Cr(en)_2Br_2^+ + H_2O \longrightarrow trans\text{-}Cr(en)_2(OH_2)Br^{+2} + Br^- \qquad (2)$$

Second, there is no positive evidence for the production of any *trans*-$Cr(en)_2(OH_2)Br^{+2}$ inasmuch as the rate constants were calculated with A_∞ evaluated from the spectrum of *cis*-$Cr(en)_2(OH_2)Br^{+2}$ and the k values calculated from the 400 and 530 mμ data agree within experimental error (the absorbancies of *cis*- and *trans*-$Cr(en)_2(OH_2)Br^{+2}$ differ considerably at these two wave lengths), as they do with the 600 mμ k at the higher acidities. Attempts to search for possible *trans*-$Cr(en)_2(OH_2)Br^{+2}$ in the reaction mixture by cation-exchange chromatographic procedures used successfully in studying the chloro analogs[3-5] were thwarted because the separation of *trans*-$Cr(en)_2(OH_2)Br^{+2}$ from the *cis* isomer was found in control experiments to be grossly incomplete (probably because the bromo complexes presumably exhibit a much smaller difference in electric dipole moment between the *cis* and *trans* isomers). Third, evidence from our study of *trans*-$Cr(en)_2Br_2^+$ and *trans*-$Cr(en)_2(OH_2)Br^{+2}$ aquation (*vide infra*) indicates that the observed *cis*-$Cr(en)_2(OH_2)Br^{+2}$ product of *cis*-$Cr(en)_2Br_2^+$ aquation does not form as a result of isomerization of a possible first-formed *trans*-$Cr(en)_2(OH_2)Br^{+2}$ product, since the *trans*-to-*cis* isomerization of $Cr(en)_2(OH_2)Br^{+2}$ is too slow at 25°. Lastly, isomerization of the *cis*-$Cr(en)_2Br_2^+$ reactant is too slow to affect the product distribution. This is known from analysis of the rate data on *cis*-$Cr(en)_2Br_2^+$ aquation at 600 mμ (the approximate wave length where *trans*-$Cr(en)_2Br_2^+$ has its main visible absorption peak and where the molar absorbancy index of the *cis* isomer is not greatly larger, whereas that of the product *cis*-bromoaquo is small), which gives an aquation rate constant essentially the same as that obtained from the 400 and 530 mμ data. If we allow for experimental errors (without vitiating any of the earlier conclusions based on the isosbestic points) there could possibly be a small proportion of *trans*-$Cr(en)_2Br_2^+$ formed by isomerization of the *cis* reactant; a conservative upper limit of 1×10^{-4} sec.$^{-1}$ may be taken for the *cis*-to-*trans* isomerization rate constant of *cis*-$Cr(en)_2Br_2^+$ at 25°, which thus isomerizes at least 30 times slower than it aquates.

Since *cis*-$Cr(en)_2(OH_2)Br^{+2}$ isomerizes at 25° to the *trans* isomer at a rate much lower than the *cis*-$Cr(en)_2Br_2^+$ aquation rate (fast isomerization is incompatible with the *cis*- and *trans*-$Cr(en)_2(OH_2)Br^{+2}$ aquation observations), the existence of *sharp* isosbestic points over 2–3 half-times in *cis*-$Cr(en)_2Br_2^+$ aquation implies that *trans*-$Cr(en)_2(OH_2)Br^{+2}$ could not be formed to an extent greater than *ca.* 1% by isomerization of the directly-formed *cis*-$Cr(en)_2(OH_2)Br^{+2}$ aquation product in a 12-min. reaction time (longest investigated). This allows setting an upper limit of 3×10^{-5} sec.$^{-1}$ for the *cis*-to-*trans* isomerization rate constant of $Cr(en)_2(OH_2)Br^{+2}$ at 25° (the back reaction of *trans*-to-*cis* isomerization need not be considered in the consecutive-reaction scheme since that isomerization is too slow).

Aquation of *cis*-$Cr(en)_2(OH_2)Br^{+2}$; Related Isomerizations.—The first-order rate constants for aquation of *cis*-$Cr(en)_2(OH_2)Br^{+2}$ in $HClO_4$ or HNO_3 solution at 24.8° are given in Table II. The first-order rate plots from the spectrophotometric data were linear over 45–65% reaction; Br^- release was followed over only 30–50% reaction, giving linear first-order rate plots. Within the relatively large experimental errors,[16] there appears to be no effect of the changed acid concentration (HNO_3 or $HClO_4$) on k, and no meaningful distinction between the k values determined by the two methods; thus the reaction is aquation over the indicated acid range. We may take as a weighted average $(1.8 \pm 0.2) \times 10^{-4}$ sec.$^{-1}$ ($t_{1/2}$ = 64 min.) for the aquation rate constant of *cis*-$Cr(en)_2(OH_2)Br^{+2}$ in 0.06–0.14 F HNO_3 or $HClO_4$ at 24.8°.

TABLE II

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF *cis*-$Cr(en)_2(OH_2)Br^{+2}$ AT 24.8 ± 0.2°, C_0 = 1.1–1.5 mF

Method	(H^+), F[a]	10^4k, sec.$^{-1}$
Spectro.	0.0591[b]	2.1[d]
	0.0725[c]	1.9,[d] 2.0[e], 1.6[f]
Br^- release	0.103[c]	1.7
	0.115[b]	1.5
Spectro.	0.116[b]	1.9[d]
	0.142[b]	1.9[d]

[a] Ionic strength *ca.* same as (H^+). [b] HNO_3. [c] $HClO_4$. [d] 387 mμ. [e] 520 mμ. [f] 560 mμ.

The spectrophotometrically determined values of this aquation rate constant were obtained with A_∞ calculated from the spectrum of *cis*-$Cr(en)_2(OH_2)_2^{+3}$. This ion must be the main reaction product because the k values agree within experimental error when calculated from data at several wave lengths (see Table II) where contributions to the absorbancy from *cis*-diaquo, *trans*-diaquo, and *trans*-bromoaquo possible reaction products bear widely differing relationships to the absorbancy of the unreacted parent *cis*-bromoaquo complex.

Sharp isosbestic points were observed at 368 ($a_M = 41.5\ M^{-1}$ cm.$^{-1}$), 436 ($a_M = 24.2\ M^{-1}$ cm.$^{-1}$), and 496 mμ ($a_M = 61.4\ M^{-1}$ cm.$^{-1}$) over 1.3 half-times, in good

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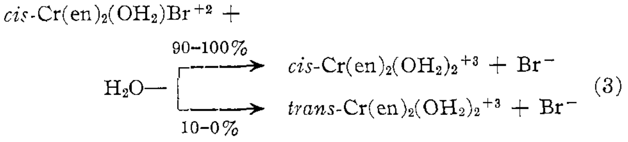
(15) The existence of isosbestic points implies that there is present, in addition to the parent complex, either only one other species absorbing significantly in this wave length region or two or more such species produced *in a constant ratio* to each other.

(16) The errors are partly associated with chromatographic isolation of the *cis*-bromoaquo complex from *cis*-$Cr(en)_2Br_2^+$ reaction mixtures and adjustment of acidity and ionic strength of the *cis*-bromoaquo solutions with OH^- anion resin.

agreement with the values 367 ($a_M = 42.2\ M^{-1}\ \text{cm.}^{-1}$), 435 ($a_M = 25.3\ M^{-1}\ \text{cm.}^{-1}$), and 496 mμ ($a_M = 62.6\ M^{-1}\ \text{cm.}^{-1}$) predicted from Fig. 2 for the system *cis*-$\text{Cr(en)}_2(\text{OH}_2)\text{Br}^{+2}$ aquating to *cis*-$\text{Cr(en)}_2(\text{OH}_2)_2{}^{+3}$. However, construction of spectral curves for various fixed ratios of *cis*-diaquo and *trans*-diaquo on the one hand and *cis*-diaquo and *trans*-bromoaquo on the other hand shows that there could be up to 10% of *trans*-diaquo or *trans*-bromoaquo produced in the reaction mixture without affecting the isosbestic points beyond their experimental errors. Because of the slowness of hydrolysis of *trans*-$\text{Cr(en)}_2(\text{OH}_2)\text{Br}^{+2}$ and the relevant *cis–trans* isomerizations (*vide infra*), we can state that the stereochemical result of *cis*-$\text{Cr(en)}_2(\text{OH}_2)\text{Br}^{+2}$ aquation at 25° is



$$\textit{cis}\text{-Cr(en)}_2(\text{OH}_2)\text{Br}^{+2} + \text{H}_2\text{O} \begin{cases} \xrightarrow{90\text{–}100\%} \textit{cis}\text{-Cr(en)}_2(\text{OH}_2)_2{}^{+3} + \text{Br}^- \\ \xrightarrow[10\text{–}0\%]{} \textit{trans}\text{-Cr(en)}_2(\text{OH}_2)_2{}^{+3} + \text{Br}^- \end{cases} \quad (3)$$

We may also take as upper limit for the rate constants $2 \times 10^{-5}\ \text{sec.}^{-1}$ for both the aquation of *cis*-$\text{Cr(en)}_2(\text{OH}_2)\text{Br}^{+2}$ to *trans*-$\text{Cr(en)}_2(\text{OH}_2)_2{}^{+3}$ and the *cis*-to-*trans* isomerization[17] of *cis*-$\text{Cr(en)}_2(\text{OH}_2)\text{Br}^{+2}$. The isomerization of the diaquo ions is known[18] to be too slow at 25° to affect significantly the product distribution between the diaquo isomers, as is also true of the possible isomerization of the *cis*-$\text{Cr(en)}_2(\text{OH}_2)\text{Br}^{+2}$ reactant.

Aquation of *trans*-$\text{Cr(en)}_2\text{Br}_2{}^+$; Related Isomerizations.—Table III gives the first-order rate constants found for aquation of *trans*-$\text{Cr(en)}_2\text{Br}_2{}^+$ at 24.8° determined by three independent methods (see Experimental section). In the spectrophotometric method the data were analyzed at 606 and 390 mμ (*k* values agreed within experimental error), using A_∞ values found experimentally at 6 half-times, after the system came to an apparent equilibrium; first-order rate plots were linear to at least 85% reaction. Bromide release was followed titrimetrically, with first-order rate plots linear over 30% reaction. The reaction was also followed by separating the unreacted *trans*-dibromo reactant chromatographically from the reaction products and determining its amount as a function of reaction time; first-order rate plots were linear over at least 75% reaction. In 0.01–0.1 *F* HClO_4 the reaction is aquation since the rate constant is independent of hydrogen ion concentration in this range, and a value of $(3.2 \pm 0.2) \times 10^{-4}\ \text{sec.}^{-1}$ may be taken for the aquation rate constant at 24.8°.

Sharp isosbestic points were found at 342 ($a_M = 13.1\ M^{-1}\ \text{cm.}^{-1}$), 415 ($a_M = 30.6\ M^{-1}\ \text{cm.}^{-1}$), 451 ($a_M = 24.8\ M^{-1}\ \text{cm.}^{-1}$), and 572 mμ ($a_M = 21.3\ M^{-1}\ \text{cm.}^{-1}$) over 4 half-times. In addition there was a broad region in the vicinity of 480 mμ (a_M = 19–20 $M^{-1}\ \text{cm.}^{-1}$) where the spectral curves nearly give an isosbestic point. These isosbestic points are in fair agreement with those predicted from the spectra (see Fig. 2) of *trans*-$\text{Cr(en)}_2\text{Br}_2{}^+$ and *trans*-$\text{Cr(en)}_2(\text{OH}_2)\text{Br}^{+2}$. However, the experimental isosbestic points are in excellent agreement with those predicted for *trans*-dibromo ion reacting to form a product which is 96% *trans*-bromoaquo and 4% *cis*-diaquo, namely, 342 ($a_M = 13.3\ M^{-1}\ \text{cm.}^{-1}$), 418 ($a_M = 30.0\ M^{-1}\ \text{cm.}^{-1}$), 451 ($a_M = 25.4\ M^{-1}\ \text{cm.}^{-1}$), and 573 mμ ($a_M = 21.3\ M^{-1}\ \text{cm.}^{-1}$). The spectrum of the reaction mixture found experimentally after 6 half-times is in good accord with that predicted for the 96% *trans*-bromoaquo, 4% *cis*-diaquo mixture.

TABLE III

FIRST-ORDER RATE CONSTANTS FOR AQUATION OF *trans*-$\text{Cr(en)}_2\text{Br}_2{}^+$ AT 24.8 ± 0.2°, C_0 = 1.5 m*F*, μ = 0.10–0.11 (LiClO_4)

Method	HClO_4, *F*	10^4k, sec.$^{-1}$
Spectro.	0.0100	3.2
	0.0976	3.2
Br^- release	0.107	3.3
Chromatog.		3.0

These observations are compatible with aquation of *trans*-dibromo 96% to *trans*-bromoaquo and 4% to *cis*-bromoaquo as first-formed products. Alternatively, the 4% path may correspond to isomerization of the *trans*-dibromo reactant to *cis*-dibromo (rate-determining step for this path), followed by aquation of the *cis*-dibromo to *cis*-bromoaquo at a rate which is known (*vide ante*) to be so much faster that the intermediate *cis*-dibromo would not be detectable by our methods. In either of these 4% paths the *cis*-bromoaquo formed would be removed by aquation to the observed *cis*-diaquo product at a rate so great that the *cis*-bromoaquo concentration would remain very low. Isomerization of either the product *trans*-bromoaquo or the intermediate *cis*-bromoaquo is too slow to alter detectably the ratio of *trans* to *cis* product found.

As an additional check on the per cent of reaction producing *cis*-diaquo product, a value for the per cent *cis*-bromoaquo plus *cis*-diaquo product can be calculated from the spectrum of the reaction mixture at 6 half-times of the *trans*-dibromo reaction. At this time only 1.6% of the *trans*-dibromo is left, and if we analyze the data at 497 mμ, where *cis*-bromoaquo and *cis*-diaquo have an isosbestic point and the molar absorbancy index of *trans*-dibromo is very small, we can compute the fraction x of chromium species present as *cis*-bromoaquo plus *cis*-diaquo product from the relationship

$$xa_M + (1 - x)a_M' = A/cd \qquad (4)$$

where a_M and a_M' are the molar absorbancy indices of *cis*-diaquo and *trans*-bromoaquo, respectively, and A is the observed absorbancy (all at 497 mμ), c is the formal concentration of chromium species, and d the optical path length in cm. Solution of eq. 4 gives $100x = 4.2$, in excellent agreement with the 4% *cis* product found by the isosbestic-point procedure. Consequently, we may take $1.3 \times 10^{-5}\ \text{sec.}^{-1}$ as an upper

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[17] The *k* upper limit value given here is in reasonable agreement with the upper limit of $3 \times 10^{-5}\ \text{sec.}^{-1}$ calculated (*vide ante*) from *cis*-$\text{Cr(en)}_2\text{Br}_2{}^+$ aquation data.

[18] Rate constants in 0.02 *F* HNO_3, 2 *F* NaNO_3, estimated from the data of F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958), and of Schläfer and Kollrack, ref. 12.

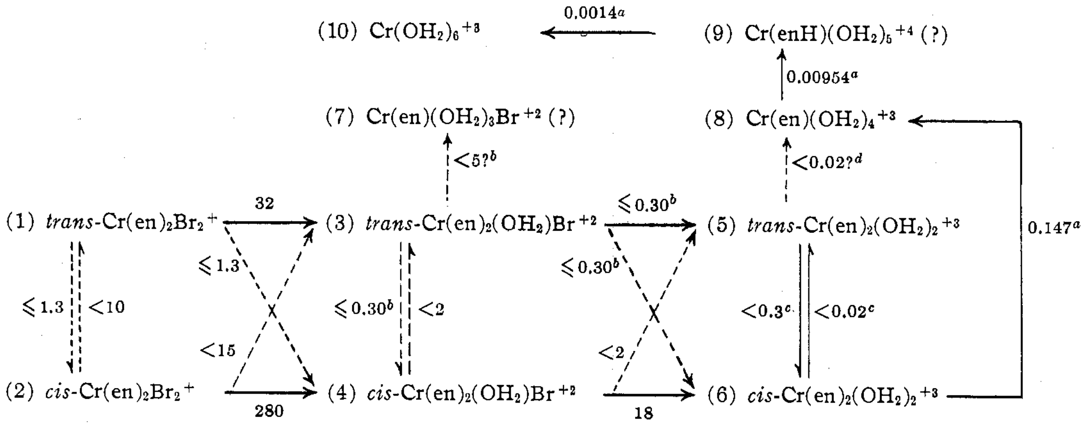

Fig. 1.—First-order rate constants (10^6k, sec.$^{-1}$) for aquation and isomerization reactions in 0.1 *F* $HClO_4$ at 24.8° in the absence of light. ^{a} Calcd. from data in ref. 12. ^{b} 1.4 *F* HNO_3 or $HClO_4$. ^{c} 0.02 *F* HNO_3, 2 *F* $NaNO_3$; calcd. from data of Woldbye (see ref. 18). ^{d} An estimate.

limit for the rate constant for *trans*-$Cr(en)_2Br_2^+$ either aquating *directly* to *cis*-bromoaquo or isomerizing to *cis*-dibromo at 24.8°.

From Table III it is seen that Br^- release is not slower than either the disappearance of *trans*-dibromo reactant by all paths (chromatographic k) or the spectrophotometrically found rate. This implies that loss of one ethylenediamine ligand by a reaction such as

$$trans\text{-}Cr(en)_2Br_2^+ + 2H_2O \longrightarrow Cr(en)(OH_2)_2Br_2^+ + en \quad (5)$$

is apparently not important in the aquation of *trans*-$Cr(en)_2Br_2^+$ under the experimental conditions. In aquation of the *trans*-dichloro analog at 35° such aquation with loss of ethylenediamine ligand apparently competes to the extent of *ca.* 10% with aquation accompanied by Cl^- release.[3-5] The seemingly negligible (or at least lower) rate of ethylenediamine release for the dibromo system may simply be a result of the fact that Br^- release from *trans*-dibromo is much faster than Cl^- release from *trans*-dichloro at 25°.

Hydrolysis of *trans*-$Cr(en)_2(OH_2)Br^{+2}$.—In 1.4 *F* HNO_3 *trans*-$Cr(en)_2(OH_2)Br^{+2}$ was found to release Br^- at an initial rate corresponding to $k = (3.0 \pm 0.2) \times 10^{-6}$ sec.$^{-1}$ ($t_{1/2} = 3800$ min.). Attempts to follow the rate spectrophotometrically were unsuccessful because an equilibrium state apparently could not be attained and the spectral changes could not be unambiguously assigned to any given set of plausible products whose spectra are known. Three isosbestic points, not fully sharp, were obtained over a 150-min. reaction period, at average values 371 ($a_M = 38.6\ M^{-1}$ cm.$^{-1}$), 433 ($a_M = 24.8\ M^{-1}$ cm.$^{-1}$), and 548 mμ ($a_M = 22.1\ M^{-1}$ cm.$^{-1}$), in only rough agreement with those expected for *trans*-bromoaquo hydrolyzing to either *cis*- or *trans*-diaquo ion. Plots of the rate data over this reaction time at different wave lengths indicated that an A_∞ corresponding to 100% *trans*-diaquo product could not account for the data, whereas an A_∞ corresponding to 100% *cis*-diaquo product gave reasonably good first-order plots at 500, 510, and 580 mμ, and complex plots with a fair linear first portion at 475, 498, and 537 mμ, all corresponding to half-times of *ca.* 800 min. Since this half-time appears to be incompatible with that for Br^- release, we conclude that the product is not mainly either *cis*- or *trans*-diaquo ion, nor a mixture of them. Indeed, the evidence on the Br^- release suggests that the hydrolysis is slow enough so that *cis–trans* isomerization of any diaquo products would appreciably alter the ratio of *cis*- to *trans*-diaquo product during the hydrolysis, with consequent loss of the isosbestic points. At reaction times greater than about 150 min. there are no isosbestic points, and the nature of the spectra strongly suggests that at least one absorbing chromium(III) reaction product is present other than the plausible *cis*- and *trans*-diaquo and *cis*-bromoaquo possible products (the data cannot be interpreted in terms of *trans*-to-*cis* isomerization of the *trans*-bromoaquo parent either). Attempts to separate out *cis* and/or *trans*-diaquo from the hydrolysis reaction mixtures (or from *trans*-bromoaquo in control experiments) chromatographically were not successful. Considering the fact that analysis of the spectral rate data with A_∞ values corresponding to the above-mentioned possible products or presumably any other likely products (which would be expected to have A_∞ values at least of the same general order of magnitude) consistently gives rate "constants" much larger than that found for the initial rate of Br^- release, we are inclined to interpret all these findings as strong circumstantial evidence for a hydrolytic reaction in which one important path is the loss of an ethylenediamine ligand, presumably with replacement by two molecules of H_2O, *e.g.*

$$trans\text{-}Cr(en)_2(OH_2)Br^{+2} + 2H_2O \xrightarrow{k'} Cr(en)(OH_2)_3Br^{+2} + en \quad (6)$$

Such a reaction was postulated in the aquation of *trans*-$Cr(en)_2(OH_2)Cl^{+2}$ and supporting kinetic and other evidence presented.[4,5] If we assume that the spectrophotometric rate data may be analyzed in terms of reaction 6, we may estimate $k' < 5 \times 10^{-5}$ sec.$^{-1}$ as a conservative upper limit at 25°. In view of our present inability to separate *cis*- and *trans*-$Cr(en)_2(OH_2)Br^{+2}$ from each other chromatographically or from *cis*- and *trans*-$Cr(en)_2(OH_2)_2^{+3}$, we feel that further work on the hydrolysis of *trans*-$Cr(en)_2(OH_2)Br^{+2}$ in an attempt to

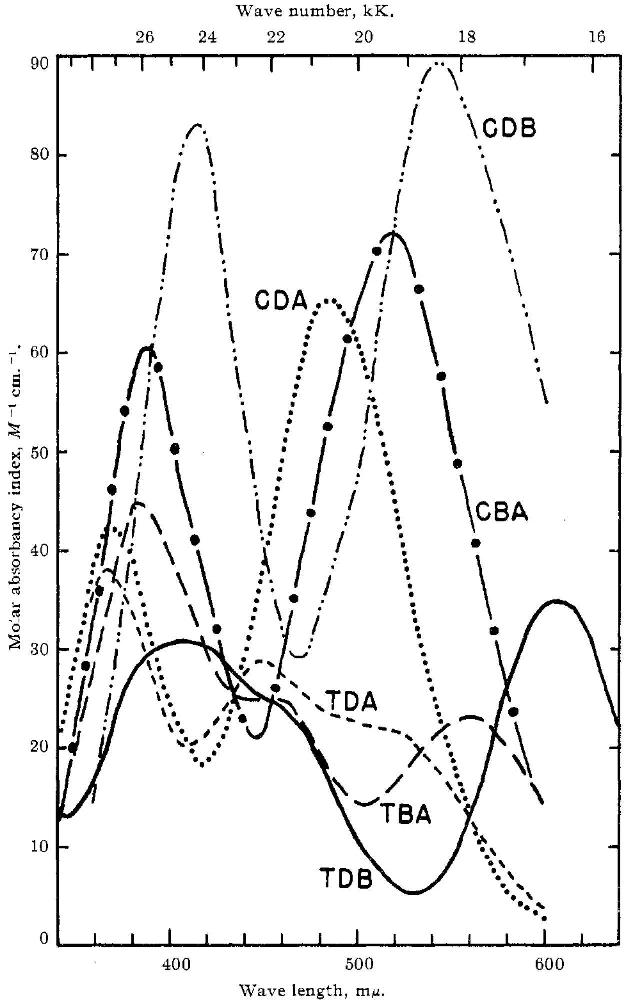

Fig. 2.—Visible absorption spectra of chromium(III) complexes at 25°: CDB, *cis*-$Cr(en)_2Br_2^+$, 0.1 *F* $HClO_4$; TDB, *trans*-$Cr(en)_2Br_2^+$, 0.1 *F* $HClO_4$; CBA, *cis*-$Cr(en)_2(OH_2)Br^{+2}$, 0.04 *F* HNO_3; TBA, *trans*-$Cr(en)_2(OH_2)Br^{+2}$, 1.4 *F* HNO_3; CDA, *cis*-$Cr(en)_2(OH_2)_2^{+3}$, 0.1 *F* $HClO_4$; TDA, *trans*-$Cr(en)_2(OH_2)_2^{+3}$, 1.4 *F* HNO_3; the molar absorbancy index a_M (extinction coefficient ϵ) is defined by the relation $\log (I_0/I) = a_M cd$.

learn more of the nature of the reaction products is not warranted. Hence, at present the rate constant associated with Br^- release from the *trans*-bromoaquo ion can only be taken as an upper limit for either of two possible reaction paths: (1) *trans*-bromoaquo → *cis*- and/or *trans*-diaquo, and (2) *trans*-bromoaquo → *cis*-bromoaquo (the latter followed by the known relatively fast release of Br^- to form predominantly *cis*-diaquo ion).

Reaction Scheme.—At this point it is useful to construct a reaction scheme showing all possible interconversions and associated rate constants determined in this study (Fig. 1). The dashed arrows in Fig. 1 correspond to reaction paths for which there is no direct experimental evidence either for or against the path.

Comparison with Chloro and Co(III) Analogs.—A full comparison of the rates and products of aquation and isomerization of the bromo complexes with their chloro analogs is best made by comparing Fig. 1 of this paper with Fig. 1 of ref. 5 (the latter reaction scheme is given at 35° but may be corrected to 25° with the aid of activation energies where they are known, or approximately by division of the 35° rate constants by 3.5). Table IV gives a less detailed intercomparison with the chloro and fluoro analogs and with the Co(III) bromo analogs.

Table IV

Rate Constants and Percentages of First-Formed Products Having a *trans* Configuration in Aquation of $M^{III}(en)_2AX^{+n}$ in 0.1*F* $HClO_4$ or HNO_3 at 25°

M	Complex	Config.	10^5k, sec.$^{-1}$	% *trans* product
Cr	Dibromo	*cis*	280[a]	0–5[a]
		trans	33[a]	≥96[a,b]
Co		*trans*	14[c,d]	68–72[d]
Cr	Dichloro	*cis*	33.0[e]	~0[f]
		trans	2.25[g]	≥86[b,f]
	Difluoro	*cis*	0.53[h]	~0[h]
	Bromoaquo	*cis*	18[a]	0–10[a]
		trans	<0.30[a,i]	
Co		*cis*	<4[j]	
		trans	<4[j]	
Cr	Chloroaquo	*cis*	2.8[e]	~0[f]
		trans	~0.3[k]	

[a] This research. [b] The *cis* product could arise from aquation or possible reactant isomerization. [c] Ref. 19. [d] Ref. 20, 0.01 *F* HNO_3. [e] J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **79,** 4285 (1957). [f] 35° data of ref. 3 and 4. [g] Ref. 2; *k* for Cl^- release, although loss of one en ligand apparently contributes significantly to aquation. [h] Ref. 7, 0.1 *F* $HClO_4$ value; 10^5k = 1.4 in 0.1 *F* HNO_3—reaction is acid-catalyzed. [i] *k* for Br^- release in 1.4 *F* HNO_3, which could arise from aquation or partly or wholly from possible reactant isomerization. [j] Estimated from data in ref. 20. [k] *k* for Cl^- release, estimated from 35° data of ref. 3 and 4; loss of one en ligand apparently contributes significantly to aquation.

Analogous Cr(III) and Co(III) complexes generally exhibit no striking differences in aquation rates in acid solution at room temperature. Among the Co(III) dibromo and bromoaquo analogs apparently the only complex which has been studied kinetically is *trans*-$Co(en)_2Br_2^+$ ion.[19,20] The aquation rates of this ion and *trans*-$Cr(en)_2Br_2^+$ are seen to differ by a factor of only *ca.* 2 at 25°.

Chan and Tobe[20] have pointed out that the rate of aquation is increased, often by a factor of 5 to 6, for $Co(en)_2AX^{+n}$ complexes when the leaving ligand X is changed from Cl to Br. Examination of Table IV shows that this increase in rate also occurs for the Cr(III) complexes investigated here, the factor of increase being 6 to 15. Aquation of *cis* isomers of these Cr(III) complexes gives within experimental error only the *cis* product, as has been found for related Co(III) complexes. The *trans* isomers of these Cr(III) complexes, which aquate roughly one order of magnitude more slowly than the *cis* analogs, give predominantly and possibly wholly *trans* product (the uncertainty arises because the small percentage of *cis* product observed could arise at least partly from isomerization of the *trans* reactant). Unlike the chloro case, *trans*-$Cr(en)_2Br_2^+$ apparently does not aquate

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(19) F. Basolo, W. R. Matoush, and R. G. Pearson, *J. Am. Chem. Soc.*, **78**, 4883 (1956).

(20) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).

appreciably with loss of one ethylenediamine ligand, although *trans*-$Cr(en)_2(OH_2)Br^{+2}$ probably does so. For many $Co(en)_2AX^{+n}$ complexes the *trans* isomer tends to aquate with pronounced steric change and the *cis* isomer with retention of configuration. This behavior has recently been rationalized[20] in terms of an SN1 dissociation mechanism producing a trigonal bipyramidal intermediate which retains the leaving X group in close proximity; derivation of this intermediate from the *trans* isomer would probably tend to leave A and X on opposite sides of the central metal atom, whereas derivation from the *cis* isomer could tend to leave A and X on adjacent sides. A and X would then compete in the former case and reinforce each other in the latter case for orienting the incoming water molecule. From our earlier and present work on these Cr(III) complexes it would seem that, since the *trans* isomers show much less steric change on aquation than their Co(III) analogs, the tendency of A and X to be opposite each other in the reaction intermediate is less for Cr(III) than for Co(III), although why this happens (if it does) is not clear.

TABLE V

ABSORPTION MAXIMA AND MINIMA OF $Cr(en)_2AX^{+n}$ AT 25°

A	X	Config.	Solvent	λ, mμ	a_M, M^{-1} cm.$^{-1}$
Br	Br[a]	*cis*	0.1 *F* $HClO_4$	415 (max.)	83.0
				468 (min.)	29.2
				544 (max.)	89.4
		trans		406 (max.)	30.7
				~460 (sh.)	~24
				530 (min.)	5.2
				607 (max.)	34.9
Cl	Cl[b]	*cis*	0.1 *F* HCl	402 (max.)	68.5
				456 (min.)	20.7
				528 (max.)	70.6
		trans	0.1 *F* HNO_3	396 (max.)	34.0
				439 (min.)	22.3
				453 (max.)	22.8
				514 (min.)	8.1
				578 (max.)	24.5
H_2O	Br[a]	*cis*	0.04 *F* HNO_3	387 (max.)	60.5
				446 (min.)	21.0
				519 (max.)	72.2
		trans	1.4 *F* HNO_3	384 (max.)	44.8
				444 (min.)	24.7
				455 (max.)	24.9
				504 (min.)	14.2
				561 (max.)	23.2
	Cl[b]	*cis*	2 *F* HCl	385 (max.)	55.7
				438 (min.)	20.3
				510 (max.)	71.4
		trans	0.2 *F* HNO_3	380 (max.)	45.4
			or	428 (min.)	23.7
			1.2 *F* HCl	448 (max.)	24.4
				500 (min.)	15.4
				546 (max.)	20.5

[a] This research. [b] Ref. 3 and 4.

Comparison between *cis*-$Cr(en)_2Br_2^+$ and *cis*-$Cr(en)_2F_2^+$ aquation rates (Table IV) is not directly meaningful, since the latter aquation is acid-catalyzed and the empirical rate constant for it presumably includes an unknown equilibrium constant associated with protonation of the difluoro reactant in a rapid pre-equilibrium step.

Spectra.—The previously unreported visible absorption spectra of *cis*- and *trans*-$Cr(en)_2Br_2^+$ and *cis*- and *trans*-$Cr(en)_2(OH_2)Br^{+2}$ are given in Fig. 2. Comparison with the chloro analogs is presented in Table V. In general these spectra are similar to those reported earlier[3,4] for their chloro analogs, except that the absorption bands are shifted an average of *ca.* 12 mμ toward longer wave lengths for the bromo complexes, as would be expected from the relative crystal-field strengths of Br and Cl. The intensity relationships of the bands are approximately the same for these bromo and chloro complexes except for the *trans*-dihalo complexes.