A Hammett plot of log k/k_0 *vs.* σ for 30° is given in Fig. 3. The data, except for the 4-methylcatechol, fit a line with $\rho = -4.88$. The large negative value typifies a reaction which is aided by electron release to the aromatic ring. A Hammett plot which takes the 2-OH position as the starting point does not lead to a recognizable correlation. As a result of the correlation obtained, it seems reasonable to postulate a mechanism in which a hydronium ion attacks the oxygen of position 1 of the most loosely bound catechol. This leads to the intermediate in which hydrogen atoms are either on or close to the oxygen atoms of this catechol. This configuration is turn undergoes a rapid splitting off of a molecule of catechol and one of water. The mechanism can be described briefly as an SE2 one. This mechanism is consistent with structure I of the complex but not structure II, as the hydronium ion consumption is hardly consistent with a reaction in which two protons are needed to split out each mole of ligand.

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Kinetics and Products of Hydrolysis of *cis*- and *trans*-Chlorohydroxobis-(ethylenediamine)-chromium(III) Cations[1a]

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The kinetics and products of the aquation and base hydrolysis of *trans*- and *cis*-$Cr(en)_2(OH)Cl^+$ have been investigated in 0.1 F ethylenediamine buffer 0.1 F in $LiClO_4$ at 25 ± 1°. At pH 9.81–10.80, $k_{aq} = (4.6 \pm 0.3) \times 10^{-3}$ sec.$^{-1}$ and $k_b < 0.3$ M^{-1} sec.$^{-1}$ for the *trans* isomer; the reaction products are *trans*-$Cr(en)_2(OH)_2^+$ (87%) and *cis*-$Cr(en)_2(OH)_2^+$ (13%). For the *cis* isomer at pH 10.12–10.70, $k_{aq} = (3.3 \pm 0.3) \times 10^{-3}$ sec.$^{-1}$ and $k_b = 2.2 \pm 0.2$ M^{-1} sec.$^{-1}$, with the same reaction products (96% *cis*, 4% *trans*). For the *cis–trans* isomerization of $Cr(en)_2(OH)Cl^+$ cations ($k_c + k_t$) $< 6 \times 10^{-5}$ sec.$^{-1}$. Reaction solutions were initially 1–2 mF in reactant complex. Reaction paths consistent with the kinetic and stereochemical results are presented, and a comparison is made with the behavior of the Co(III) analogs. The visible absorption spectra of the previously unreported labile *trans*- and *cis*-$Cr(en)_2(OH)Cl^+$ cations are given.

The hydrolysis of *cis*- and *trans*-chlorohydroxobis-(ethylenediamine)-chromium(III) cations apparently has not been investigated previously, except for a qualitative observation[2] that loss of the second chloro ligand in the hydrolysis of *cis*- and *trans*-dichlorobis-(ethylenediamine)-chromium(III) in basic solution at 25° is rapid relative to the primary hydrolysis.

We report here a study of the kinetics and products of hydrolysis of the chlorohydroxo cations in aqueous ethylenediamine solution, together with considerations bearing on the rate of isomerization of these cations.

Experimental

***cis*- and *trans*-Dichlorobis-(ethylenediamine)-chromium(III) Chlorides.**—The hydrated salts were prepared and characterized as described earlier.[3,4]

***cis*- and *trans*-Diaquobis-(ethylenediamine)-chromium(III) Bromides.**—The hydrated compounds were synthesized by Woldbye's method[5] and characterized as reported previously.[6]

Lithium Perchlorate.—A stock solution of $LiClO_4$ was made by adding a stoichiometric amount of concentrated $HClO_4$ (J. T. Baker Analyzed Reagent) to reagent grade Li_2CO_3 and diluting to 2.0 F.

Ethylenediamine.—Eastman White Label ethylenediamine was distilled over NaOH. A 0.40 F aqueous solution was prepared and standardized by potentiometric titration with standard $HClO_4$.

***cis*- and *trans*-Chloroaquobis-(ethylenediamine)-chromium(III) Cations.**—Separate solutions of pure *cis*- and *trans*-$Cr(en)_2(OH_2)Cl^{+2}$ were obtained by aquating *cis*- and *trans*-$[Cr(en)_2Cl_2]Cl$, respectively, for 1 hr. in 0.1 F HNO_3 in the dark at 35°, and separating the chloroaquo complex away from other chromium species on H^+ Dowex AG50W-X8 cation-exchange columns as described earlier,[4,7] except that the columns were operated at 5°. Elution of the chloroaquo complexes was performed with 100 ml. each of 1.4 F (*trans*) or 2.0 F (*cis*) HNO_3. The HNO_3 was reduced to pH $\sim$ 2 by treatment of each solution with Dowex AG 2-X8, 50–100 mesh, in the OH^- form, at 10–25° by a technique reported earlier.[7,8] The identity and purity of the *cis*- and *trans*-chloroaquo solutions were then further established by agreement of their visible absorption spectra with those reported previously[4] for these complexes. The solutions were prepared immediately before their use in the chlorohydroxo hydrolysis measurements.

Hydrolysis Run Procedure.—The products and rates of hydrolysis of the labile *cis*- and *trans*-$Cr(en)_2(OH)Cl^+$ were determined by rapidly creating these complexes *in situ* from the corre-

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

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

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

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

(6) D. C. Olson and C. S. Garner, *Inorg. Chem.*, **2**, 415 (1963).

(7) D. J. MacDonald and C. S. Garner, *ibid.*, **1**, 20 (1962).

(8) If visible absorption spectra are to be taken of column effluents, as was done here, great care must be exercised to wash out thoroughly with distilled water a yellow resin-decompositon product formed when Dowex AG 2-X8 resin is converted from the Cl^- or NO_3^- form to the OH^- form.

sponding chloroaquo solution and following the change in visible absorption spectrum of solutions 1–2 m*F* in the reactant complex with a Cary Model 11 recording spectrophotometer. To 75.0 ml. of chloroaquo solution at pH ~ 2, 5.00 ml. of 2.0 *F* $LiClO_4$ was added, then 25.0 ml. of 0.40 *F* ethylenediamine (pH adjusted previously with $HClO_4$) quickly was ejected from a pipet into the rapidly stirred solution, which was transferred quickly into a dry 10.00-cm. quartz cell. The cell was placed in the Cary cell compartment and the spectral scan was started within 30–45 sec. from the start of injection of the ethylenediamine buffer. The region 360–640 mμ was scanned in 55 sec. (tests showed errors due to the fast scan are neglibible), then the chart paper turned back and the same region rescanned repeatedly until no further spectral changes occurred. The pH of the reaction mixture then was determined with a calibrated glass electrode and Radiometer TTT-1a pH meter. The hydrolysis rate constants were obtained from plots of $-\log (A - A_\infty)$ *vs. t*, where A and A_∞ are the observed absorbancy readings at time t and at completion, respectively, taken at 450 and 440 mμ for the *trans* complex and at 540 and 380 mμ for the *cis* complex (the ordinate is $-\log (A_\infty - A)$ at 380 mμ since $A_\infty > A$ at this wave length). Corrections were made for the different reaction times corresponding to these wave lengths. The ethylenediamine serves not only to buffer the solutions but also to repress slow hydrolytic reactions of the dihydroxo products. The added ethylenediamine does not react with the reactants or dihydroxo products inasmuch as the spectra of the latter are the same in the presence or absence of the ethylenediamine (in en, the product spectra remain unchanged over times very much longer than the chlorohydroxo hydrolysis times), and reaction of en with the reactants would give spectra greatly different from those observed (see section on spectra) in view of the great difference in crystal-field strength between en and either OH^- or Cl^-.

The final solutions were made pH ~ 2 with $HClO_4$, instantly converting the dihydroxo products to the corresponding diaquo species, and absorbancy readings were taken promptly at 486 (a *cis*-diaquo absorption maximum) and 440 mμ (an isosbestic point of the *cis*- + *trans*-diaquo system) with a Beckman DU spectrophotometer. It can be shown for any mixture of *cis*- and *trans*-diaquo that

$$\%\ trans = 100 \left[\frac{(a_c/a_i) - (A/A_i)}{(a_c/a_i) - (a_t/a_i)}\right] \qquad (1)$$

where A is the absorbancy of the mixture at an arbitrary (but non-isosbestic-point) wave length (taken here as 486 mμ) and a_c and a_t are the molar absorbancy indices of pure *cis* and pure *trans*, respectively, at this same wave length, and A_i and a_i are, respectively, the absorbancy of the mixture and the molar absorbancy index of either isomer at an isosbestic point (taken here as 440 mμ). The quantities a_c, a_t, and a_i were determined from measurements made rapidly on fresh solutions of *cis*-$[Cr(en)_2(OH_2)_2]Br_3 \cdot 2H_2O$ and *trans*-$[Cr(en)_2(OH_2)_2]Br_3 \cdot H_2O$ in the appropriate solvent. A test of the method with known mixtures of *trans*- and *cis*-diaquo gave the following results (first value, % *trans* in known; second value, % *trans* found): 80.0, 80.6; 50.0, 49.7; 31.1, 31.9; 13.1, 13.3; 10.0, 11.8.

In preliminary experiments designed to determine the extent of Cl^- released in a given time by hydrolysis of *cis*- and *trans*-$Cr(en)_2(OH)Cl^+$, separate solutions of the corresponding chloroaquo complex were made basic with NaOH to pH 11–11.5 at ~25° and 5–10 min. later put on separate Na^+ Dowex AG50W-X8 cation-exchange columns to adsorb all Cr species and the released Cl^- washed out. Titration of the Cl^- indicated ~97% of the ligand chloride was liberated by the *trans* complex and ~83% by the *cis* complex. These values are consistent with the spectrophotometrically determined accurate rate constants.

Results and Discussion

Hydrolysis Rates.—Figure 1 presents the pseudo first-order rate plots for the hydrolysis of *trans*-$Cr(en)_2(OH)Cl^+$ (solid lines) and *cis*-$Cr(en)_2(OH)Cl^+$ (dashed lines) at 25 ± 1° in 0.1 *F* ethylenediamine buffer (μ = 0.1, $LiClO_4$) at various pH values. Analysis of the six *trans* plots shows no discernible pH dependence of the rate, the hydrolysis of *trans*-$Cr(en)_2(OH)Cl^+$ therefore being nearly completely aquation in the pH range 9.81–10.80. Attempts to extend the measurements to higher pH values have been thwarted by reactions involving the dihydroxo products. Consideration of errors suggests that not more than 5% of the total hydrolysis at the higher pH can be due to base hydrolysis, allowing us to place an uper limit on the base hydrolysis rate constant, $k_b < 0.3\ M^{-1}\ sec.^{-1}$. The first-order *trans* aquation rate constant is $(4.6 \pm 0.3) \times 10^{-3}\ sec.^{-1}$ ($t_{1/2}$ = 2.5 min.). The *cis* plots, however, reveal a pH dependence, with pseudo first-order rate constants of $(3.64 \pm 0.05) \times 10^{-3}$ and $(4.71 \pm 0.08) \times 10^{-3}\ sec.^{-1}$ at pH 10.12 and 10.70, respectively. Since it is reasonable to ascribe this pH dependence to a contribution from base hydrolysis, these *cis* constants may be resolved into a first-order aquation rate constant $k_{aq} = (3.3 \pm 0.3) \times 10^{-3}\ sec.^{-1}$ and a second-order base hydrolysis rate constant $k_b = 2.2 \pm 0.2\ M^{-1}\ sec.^{-1}$, where the errors given are estimated at 10%.

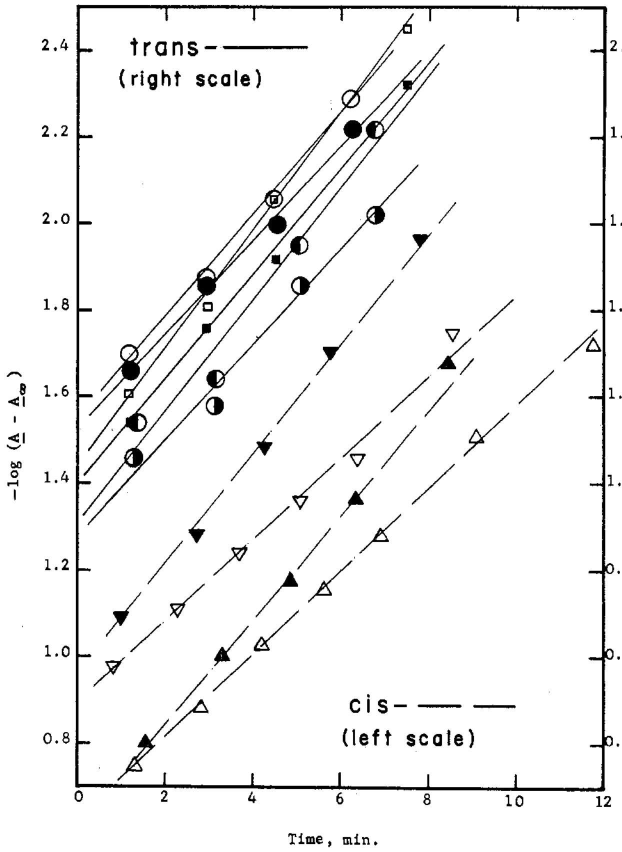

Fig. 1.—Pseudo first-order rate plots for hydrolysis of *trans*- and *cis*-$Cr(en)_2(OH)Cl^+$ in 0.1 *F* ethylenediamine, 0.1 *F* $LiClO_4$ at 25 ± 1°: ◑, pH 9.81, 440 mμ; ◐, pH 9.81, 450 mμ; ■, pH 10.50, 440 mμ; □, pH 10.50, 450 mμ; ●, pH 10.80, 440 mμ; ○, pH 10.80, 450 mμ; △, pH 10.12, 380 mμ; ▽, pH 10.12, 540 mμ; ▲, pH 10.70, 380 mμ; ▼, pH 10.70, 540 mμ; (interchange A and A_∞ for 380-mμ points).

The *trans* isomer aquates 1.4 times faster at 25° than the *cis* isomer, although similar *trans* complexes often

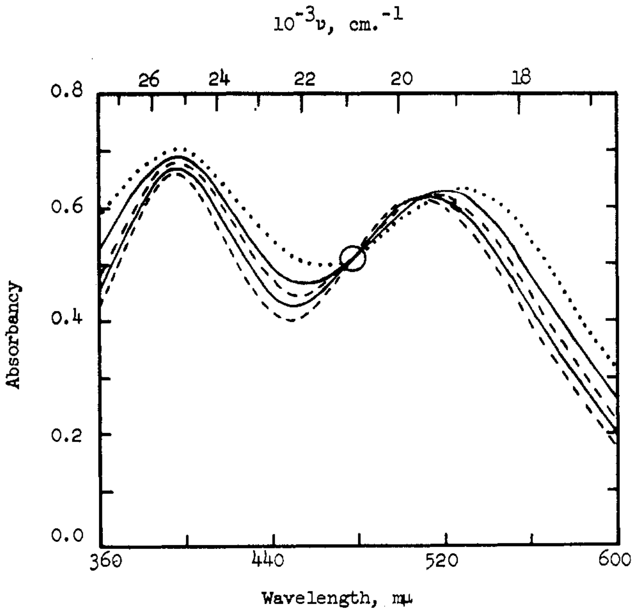

Fig. 2.—Absorption spectrum of *trans*-$Cr(en)_2(OH)Cl^+$ (dotted curve) and change in spectrum (solid and dashed curves) during hydrolysis at pH 9.81 in 0.1 *F* ethylenediamine buffer 0.1 *F* in $LiClO_4$, 25 ± 1°: reading downward at minima, reaction time is 0, 0.80, 2.62, 4.57, and 9.68 min., respectively, measured at 600 mμ; curves taken at 6.27 and 18.3 min. (latter essentially identical with 9.68-min. curve) are omitted here to clarify the spectral display.

aquate *ca.* one order of magnitude slower than the *cis* isomers. At 25° *trans*- and *cis*-$Cr(en)_2(OH)Cl^+$ aquate 3 times faster and 3.8 times slower, respectively, than their Co(III) analogs.[9,10]

At 25° *cis*-$Cr(en)_2(OH)Cl^+$ base hydrolyzes at a given pH at least 7 times faster than the *trans* isomer. For the Co(III) analogs the *cis* isomer likewise base hydrolyzes faster than the *trans* isomer, the ratio of rate constants having been found[11] to be 22 at 0°. The ratio of Co/Cr second-order rate constants at 25° is calculated[12] to be 5.5 (*cis*) and >2 (*trans*).

Thus, there appear to be no large rate differences between Cr(III) and Co(III) in either aquation or base hydrolysis of the above chlorohydroxo isomers.

Hydrolysis Products.—The existence of one isosbestic point (477 mμ) in spectra taken during the hydrolysis of *trans*-$Cr(en)_2(OH)Cl^+$ (see Fig. 2) and three isosbestic points (413, 478, 507 mμ) in the *cis*-$Cr(en)_2(OH)Cl^+$ hydrolysis (see Fig. 3) implies in each case that there is present, in addition to the reactant 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. Spectrophotometric

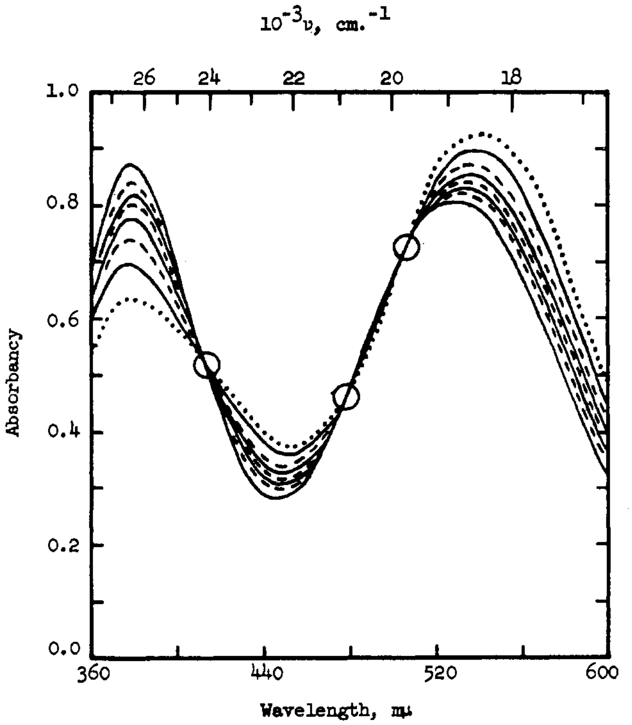

Fig. 3.—Absorption spectrum of *cis*-$Cr(en)_2(OH)Cl^+$ (dotted curve) and change in spectrum (solid and dashed curves) during hydrolysis at pH 10.12 in 0.1 *F* ethylenediamine buffer 0.1 *F* in $LiClO_4$, 25 ± 1°: reading downward at minima, reaction time is 0, 0.68, 2.11, 3.51, 4.91, 6.24, 8.37, and 25.1 min., respectively, measured at 600 mμ; curves taken at 11.0 and 15.4 min. are omitted here to clarify the spectral display.

analysis of the final reaction mixtures (see Experimental) revealed only *trans*- and *cis*-dihydroxo species as products of the hydrolysis, with the distributions shown in Table I. Within experimental error there is no pH dependence of the product distribution in the pH range shown in Table I. None would be expected for the *trans* hydrolysis since this hydrolysis has been shown above to be essentially wholly aquation, producing $Cr(en)_2(OH_2)OH^{+2}$ cations which instantly lose protons in the alkaline medium to give the observed dihydroxo species. For the *cis* hydrolysis, aquation constitutes $100(3.3/3.64) = 91\%$ and $100(3.3/4.71) = 70\%$ at pH 10.12 and 10.70, respectively; aquation of similar *cis* Cr(III) and Co(III) complexes is known to give ~100% *cis* product[13] where the product distribution

Table I

Product Distribution in Hydrolysis of *trans*- and *cis*-$Cr(en)_2(OH)Cl^+$ in 0.1 *F* Ethylenediamine ($\mu = 0.1$, $LiClO_4$) 25 ± 1°

Reactant isomer	Kinetic run pH	$Cr(en)_2(OH)_2^+$ products	
		% *trans*	% *cis*
trans	9.81	87	13
trans	10.50	84	16
trans	10.80	87	13
cis	10.12	4	96
cis	10.70	4	96

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[9] R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, **78**, 2673 (1956): $k = 1.4 \times 10^{-3}$ (*trans*) and 1.3×10^{-2} (*cis*) sec.$^{-1}$, $\mu \sim 0.004$.

[10] M. E. Baldwin, S. C. Chan, and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961): $k = 1.6 \times 10^{-3}$ (*trans*) and 1.2×10^{-2} (*cis*) sec.$^{-1}$, $\mu \sim 0.02$, by extrapolation of 0, 10.2, and 23.75° constants.

[11] S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4531 (1962).

[12] Reference 11 gives $k_b = 0.37$ (*cis*) and 0.017 (*trans*) M^{-1} sec.$^{-1}$ at 0°; using the activation energies in ref. 11, we calculate $k_b = 12$ (*cis*) and 0.58 (*trans*) M^{-1} sec.$^{-1}$ at 25°. R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Am. Chem. Soc.*, **78**, 709 (1956), report obtaining $k_b = 200$ M^{-1} sec.$^{-1}$ at 25° for the *trans* isomer by an indirect method subject to considerable error; this value, which is ~300 times greater than the 25° value calculated from the constant of Chan and Tobe, appears to be incorrect.

[13] (a) C. K. Ingold, "Theoretical Organic Chemistry," Butterworths Scientific Publications, London, 1959, pp. 84–102; (b) C. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960). These references summarize the experimental findings and give theoretical arguments for retention of configuration in cobalt *cis* aquations.

has been investigated. Although extensive configurational changes are common in base hydrolysis of the Co(III) complexes,[14] base hydrolysis of *cis*-$Co(en)_2(OH)Cl^+$ at 0° gives only 3% *trans* product[11] (and of this same order of magnitude for other Co(III) complexes where OH is the orienting ligand). Thus, the base hydrolysis of *cis*-$Cr(en)_2(OH)Cl^+$ and *cis*-$Co(en)_2(OH)Cl^+$ have in common an almost complete retention of the *cis*-configuration.

Aquation of *trans*-$Cr(en)_2(OH)Cl^+$ at 25° gives 87% *trans* and 13% *cis* product, whereas aquation of *trans*-$Co(en)_2(OH)Cl^+$ at 0° has been shown[10] to give 25% *trans* and 75% *cis* product. Although steric change is common in aquation of *trans* cobalt complexes, present theories are inadequate to allow prediction of the extent of such steric change. The differences observed here between the Cr(III) and Co(III) *trans* analogs may be associated with the known much greater affinity of chromium for oxygen in the OH ligand and its possible effect on the stereochemistry.

Rate of *cis–trans* Isomerization of $Cr(en)_2(OH)Cl^+$ Cations.—The presence of the isobestic points referred to above shows also that the product distribution in the hydrolysis is not affected by possible *cis–trans* isomerization of the $Cr(en)_2(OH)Cl^+$ reactants or $Cr(en)_2(OH)_2^+$ products. The latter isomerization is known[6] to be $\sim 10^3$ times slower than the hydrolyses at pH 11 and cannot affect the observed ratio of the hydrolysis products. Moreover, if one were to attempt to circumvent the above conclusion based on isosbestic points by assuming *cis–trans* isomerization of $Cr(en)_2(OH)Cl^+$ cations to be very rapid relative to the hydrolyses, then the product distribution in *both cis*- and *trans*-$Cr(en)_2(OH)Cl^+$ hydrolysis would be the same (namely, the *cis–trans* isomerization equilibrium ratio), in conflict with our findings. Consequently, the *cis–trans* isomerization of the chlorohydroxo cations must be at least 20 times slower than either hydrolysis reaction under our conditions; *i.e.*, $(k_c + k_t) < 2 \times 10^{-4}$ sec.$^{-1}$ at 25 ± 1°. However, we may set a still smaller lower limit by noting (see reaction scheme, Fig. 4) that the isosbestic-points argument, considered together with the experimental errors involved, implies that the isomerization rate cannot be more than 10% of the rate of the aquation path *trans*-$Cr(en)_2(OH)Cl^+ \rightarrow$ *cis*-$Cr(en)_2(OH)OH_2^{+2}$. Thus we may take $(k_c + k_t) < 6 \times 10^{-5}$ sec.$^{-1}$ at 25°.

The isomerization rate constant for the Co(III) analog apparently has not been reported. However, this isomerization is slow enough not to interfere with following the steric course[10] of aquation of *cis*- and *trans*-$Co(en)_2(OH)Cl^+$ at 25°; inasmuch as $k = 16 \times 10^{-4}$ sec.$^{-1}$ for the latter aquation, $(k_c + k_t) < 1 \times 10^{-4}$ sec.$^{-1}$ for the *cis–trans* isomerization of the $Co(en)_2(OH)Cl^+$ cations, an upper limit comparable with that deduced for the Cr(III) system. If the isomerization occurs *via* water exchange, the isomerization rates would be expected to be similar for these Cr(III) and Co(III) chlorohydroxo cations.

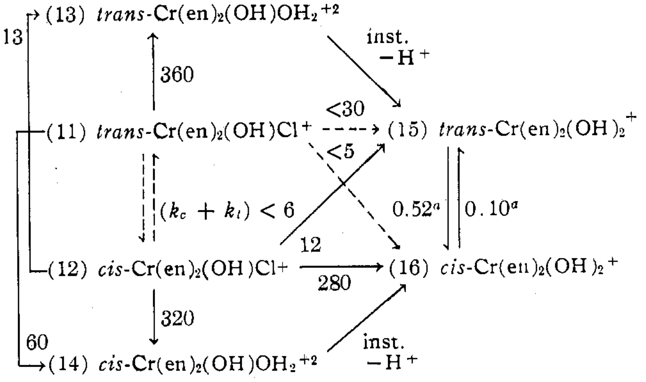

Fig. 4.—Pseudo first-order rate constants (10^5k, sec.$^{-1}$) for hydrolysis and isomerization reactions at pH 11 in 0.1 *F* ethylenediamine ($\mu = 0.1$, $LiClO_4$) at 25 ± 1°. [a] Reference 6, 25.0°.

Reaction Scheme.—At this point it is useful to construct a reaction scheme showing the possible interconversions and the rate constants found in this investigation. This has been calculated for pH 11 and is given in Fig. 4; at other pH values the base hydrolysis reactions would, of course, contribute to extents different from those shown. The dashed arrows in Fig. 4 correspond to reaction paths for which there is no direct experimental evidence either for or against the path. The *cis* hydrolysis paths were computed by noting that 4% *trans*-dihydroxo product is obtained independent of pH between 10.12 and 10.70, and using the following relations for the fraction of *trans* product at these respective pH values and solving simultaneously

$$[k_{12,13} + k_{12,15}(0.18/1.34)]/364 = 0.04 \tag{2}$$

$$[k_{12,13} + k_{12,15}(0.67/1.34)]/471 = 0.04 \tag{3}$$

for $k_{12,13}$ and $k_{12,15}$, where these are the pseudo first-order rate constants (all rate constants as 10^5k, sec.$^{-1}$) at pH 11.00 for *direct* conversion of complexes 12 to 13 and 12 to 15, respectively.[15] *E.g.*, in eq. 2 the numerator in brackets is the sum of the pseudo first-order rate constants (10^5k) for the two paths at pH 10.12 by which *cis*-chlorohydroxo ion generates *trans*-dihydroxo ion; the term $k_{12,15}$ (0.18/1.34) is $k'_{12,15}$, where the latter refers to pH 10.12, and 0.18 and 1.34 are, respectively, the millimolarities of OH^- at pH 10.12 and 11.0. The denominator in eq. 2 is the total pseudo first-order rate constant (10^5k) for disappearance of *cis*-chlorohydroxo ion by all paths, ignoring possible isomerization of *trans*-chlorohydroxo since, as shown earlier, the isomerization is too slow to perturb significantly the product distribution. Similarly, in the hydrolysis of *trans*-chlorohydroxo ion, assuming experimental errors could allow as much as 5% base hydrolysis at pH 10.80 (corresponding to 8% at pH 11.00 and 0.5% at pH 9.81)

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(14) C. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **194**, 344 (1962). This reference discusses in detail base hydrolysis of cobalt complexes.

(15) The numbering of the complexes is designed to fit in with certain other reaction schemes, such as the one in ref. 7. Molar concentrations of OH^- ion, which appear as millimolarities inside the parentheses of eq. 2–5, were computed from the relation $(OH^-) = 1.34 \times 10^{-14}$ antilog pH, valid for 0.1 *F* $LiClO_4$ and 25° and obtained by combining data in H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3d. Ed., Reinhold Publishing Corp., New York, N. Y., 1958, pp. 639–641, and in R. H. Stokes and R. A. Robinson, *J. Am. Chem. Soc.*, **70**, 1870 (1948).

and taking into account finding 87% *trans*-dihydroxo product independent of pH between 9.81 and 10.80, the analogous relations for the fraction of *trans* product produced at these respective pH values are

$$\frac{0.995(460 - k_{11,14}) + (460 \times 0.005) - k_{11,16}\left(\frac{0.086}{1.34}\right)}{460} = 0.87 \tag{4}$$

$$\frac{0.950(460 - k_{11,14}) + (460 \times 0.050) - k_{11,16}\left(\frac{0.84}{1.34}\right)}{460} = 0.87 \tag{5}$$

Spectra of *trans*- and *cis*-$Cr(en)_2(OH)Cl^+$.—Since these complexes have not been reported previously, it is of interest to give the visible absorption spectrum of each at ~25° ($\mu = 0.1$, $LiClO_4$). These spectra, given in Fig. 2 and 3 (dashed curves), were obtained by mathematical extrapolation based on the experimental rate laws. The molar absorbancy indices are 39 (398 mμ), 28 (458 mμ, min.), and 35 (532 mμ) for the *trans* absorption maxima and minimum and 51 (378 mμ), 30 (455 mμ, min.), and 74 (541 mμ) for the *cis* maxima and minimum. In comparing the *trans*-$Cr(en)_2(OH)Cl^+$ spectrum with the spectra of *trans*-dichloro[4] and *trans*-dihydroxo[5] cations it is evident that one absorption maximum remains fixed at 396–398 mμ and, as expected from crystal-field theory, the "red" peak is intermediate in wave length (532 mμ) between the dichloro (578 mμ) and dihydroxo (503 mμ) "red" peaks. The 453-mμ absorption band of the dichloro complex is reflected in the chlorohydroxo spectrum as a shallow minimum (458 mμ) and as a deep minimum (444 mμ) in the dihydroxo spectrum. The spectral comparison for the *cis* complexes is less clear-cut, probably because OH^- and Cl^- are not far apart in the spectrochemical series and the *cis* complexes have an effectively lower symmetry than the *trans* isomers. The spectra of *cis*-$Cr(en)_2(OH)_2^+$ and *cis*-$Cr(en)_2Cl_2^+$ are very similar, with only small shifts of the visible absorption maxima toward shorter wave length in going from the latter to the former. The "blue" peak of *cis*-$Cr(en)_2(OH)Cl^+$ (378 mμ) lies between the "blue" peaks of the dihydroxo (377 mμ) and dichloro (402 mμ) ions, whereas the "red" peak (541 mμ) lies at a somewhat longer wave length than either dihydroxo (526 mμ) or dichloro (528 mμ) complexes.

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CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

Exchange and Substitution Reactions of Platinum(II) Complexes. IX.[1a–h] Trichloro-(ethylene)-platinate(II)[2,3]

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The rates of isotopic exchange between free chloride ion and the chloride ligands *cis* to ethylene in equilibrium solutions of trichloro-(ethylene)-platinate(II) and *trans*-dichloroaquo-(ethylene)-platinum(II) have been determined at 15, 25, and 35°. The rate law was found to be: rate exchange = $k_c[Pt(C_2H_4)Cl_3^-] + k_c'[$*trans*-$Pt(C_2H_4)Cl_2(H_2O)] + k_2[Pt(C_2H_4)Cl_3^-] \times [$*trans*-$Pt(C_2H_4)Cl_2(H_2O)]$, where at 25°, $k_c = 2.9 \times 10^{-6}$ sec.$^{-1}$, $\Delta H^* = 21$ kcal./mole; $k_c' = 2.8 \times 10^{-5}$ sec.$^{-1}$, $\Delta H^* = 22$ kcal./mole; $k_2 = 8.6 \times 10^{-3}$ sec.$^{-1}$ M^{-1}, $\Delta H^* = 19$ kcal./mole. Acid hydrolysis accounts for the first two terms, but the third term requires that a dimer exist in the transition state.

Introduction

Previous studies in this Laboratory[1a–h] have considered the isotopic exchange of chloride ligands in the complete series of chloro–ammine complexes of platinum(II). For the exchange in these systems acid hydrolysis, in which the reversible replacement of a chloride ligand by H_2O occurs, provides an important mechanism for the exchanges. Only for $[Pt(NH_3)_3Cl]^+$ and *trans*-$[Pt(NH_3)_2Cl_2]$ does an alternative exchange process, first order in both chloride and the complex, compete to a measurable extent. Rate constants for chloride ion independent exchange processes presumably have characterized the second acid hydrolysis rates for several of the complexes. These rates could not be evaluated by other means.

The present work deals with the chloride exchange in solutions of Zeise's salt, $K[Pt(C_2H_4)Cl_3]$. With the square planar arrangement of ligands, the three chlorides in the anion are not equivalent. An analogous

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(1) Previous papers in this series: (a) L. F. Grantham, T. S. Elleman, and D. S. Martin, Jr., *J. Am. Chem. Soc.*, **77**, 2965 (1955); (b) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **80**, 536 (1958); (c) T. S. Elleman, J. W. Reishus, and D. S. Martin, Jr., *ibid.*, **81**, 10 (1959); (d) W. W. Dunning and D. S. Martin, Jr., *ibid.*, **81**, 5566 (1959); (e) C. I. Sanders and D. S. Martin, Jr., *ibid.*, **83**, 807 (1961); (f) J. W. Reishus and D. S. Martin, Jr., *ibid.*, **83**, 2457 (1961); (g) R. J. Adams and D. S. Martin, Jr., "Advances in the Chemistry of the Coordination Compounds," ed. by S. Kirschner, The Macmillan Co., New York, N. Y., 1961, p. 579; (h) F. Aprile and D. S. Martin, Jr., *Inorg. Chem.*, **1**, 551 (1962).

(2) Contribution No. 1183. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(3) The conclusions of this work were presented as part of the paper, "Ligand Exchange Reactions of Platinum(II) Complexes," symposium on "The Use of Isotopes to Study Inorganic Reaction Mechanisms," Division of Inorganic Chemistry, 143rd National Meeting of the American Chemical Society, Atlantic City, N. J., September, 1962.