The ΔH^* of 3 kcal./mole observed for reaction 5 is very small. Since it has been reported[10] that hydration effects markedly influence enthalpy changes in reactions of this type, it is dangerous to attribute this enthalpy change to differences in bonding between the starting material and activated complex. Yet it seems reasonable that this small value of ΔH^* indicates that the activated complex has a geometry more closely resembling the reactants, Cl–Pt–Br--Pt--Br^{3+}, than the products, Cl--Pt--Br–Pt–Br^{3+}.

The ratio of the average equilibrium constants reported in Table VI is 3.6. This is rather close to the ratio of 4 which is expected on statistical grounds. The values of K_1 and K_2 show that bromide is coordinated in preference to chloride; this is in line with previous equilibrium studies and thermodynamic data.[10,11] The data show that there is both an equilibrium and a kinetic "*trans* effect" in these systems, with bromide being the better *trans*-director. The equilibrium *trans* effect is very small, but the kinetic effect is quite large. It should be noted that the kinetic *trans* effect is best explained in terms of the bridging ability of the bromine atom; this explanation is quite different from those given to explain the *trans* effect as observed in platinum(II) systems.

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[10] A. J. Poë, *J. Chem. Soc.*, 1023 (1961).

[11] "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952, pp. 234, 235.

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Synthesis and Aquation Kinetics of *cis*-Chloroisothiocyanatobis(ethylenediamine)chromium(III) Cation and of *cis*- and *trans*-Isothiocyanatoaquobis(ethylenediamine)chromium(III) Cations[1]

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The new complexes *cis*-Cr(en)$_2$(NCS)Cl$^+$ and *cis*- and *trans*-Cr(en)$_2$(OH$_2$)NCS^{+2} have been synthesized and their visible absorption spectra and their aquation kinetics have been investigated in acid solution in the dark. In 0.001–1.0 *F* HClO$_4$ (μ = 0.1–1.0, NaClO$_4$) the rate constant for aquation of *cis*-Cr(en)$_2$(NCS)Cl$^+$ is $(8.1 \pm 0.4) \times 10^{-5}$ sec.$^{-1}$ at 25°, with $E_a = 20.5 \pm 1.3$ kcal. mole^{-1} and $\log PZ = 10.9 \pm 1.0$ (sec.$^{-1}$); aquation proceeds *via* Cl$^-$ release ($\leqslant 4\%$ SCN$^-$ release), the directly-formed products of Cl$^-$ release being *cis*-Cr(en)$_2$(OH$_2$)NCS^{+2} (98 ± 2%) and *trans*-Cr(en)$_2$(OH$_2$)NCS^{+2} (2 ± 2%). At 25° $k = (1.5 \pm 0.2) \times 10^{-6}$ sec.$^{-1}$ for aquation of *cis*-Cr(en)$_2$(OH$_2$)NCS^{+2} in 0.75 *F* HClO$_4$, the products apparently being Cr(en)(OH$_2$)$_3$NCS^{+2} and *cis*-Cr(en)$_2$(OH$_2$)$_2$$^{+3}$, the latter possibly formed partly or wholly *via* production of the *trans* isomer followed by relatively fast isomerization. An upper limit of $k \leqslant 2 \times 10^{-8}$ sec.$^{-1}$ was found for aquation of *trans*-Cr(en)$_2$(OH$_2$)NCS^{+2} in 0.8 *F* HClO$_4$ at 25°.

The coordination complexes *cis*-chloroisothiocyanatobis(ethylenediamine)chromium(III) and *cis*- and *trans*-isothiocyanatoaquobis(ethylenediamine)chromium(III) apparently have not been previously reported. We report here the synthesis and characterization of these new cations, their visible absorption spectra, and the results of our investigations of the aquation kinetics of these complexes in acid solution in the dark, undertaken to allow comparisons to be made with the extensively studied chloro,[2-6] bromo,[7] and fluoro[8] analogs, as well as with the Co(III) analogs to the extent that information on them is available.

Experimental

***cis*-Isothiocyanatoaquobis(ethylenediamine)chromium(III) Cation.**—This ion was prepared in solution by dissolving 0.8 g. of *cis*-[Cr(en)$_2$(NCS)$_2$]SCN·H$_2$O[9] in 500 ml. of 0.1 *F* HClO$_4$ and allowing the solution to aquate in the dark for *ca.* 8.5 hr. at 50°. The solution was cooled and passed through a 10-cm. × 1-cm. diameter column of H$^+$ Dowex AG50W-X8 (100–200 mesh) cation-exchange resin to adsorb all Cr cationic species, then 900

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[1] (a) Work partly supported under Contract AT(11-1)-34, Project No. 12, between the U. S. Atomic Energy Commission and the University. (b) Based upon the Ph.D. dissertation of Jon M. Veigel, UCLA, Jan. 1965. (c) Presented before the Division of Inorganic Chemistry at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965.

[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., The Macmillan Co., New York, N. Y., 1961, pp. 266–275.

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

[6] D. C. Olson and C. S. Garner, *ibid.*, **2**, 414 (1963).

[7] L. P. Quinn and C. S. Garner, *ibid.*, **3**, 1348 (1964).

[8] K. R. A. Fehrmann and C. S. Garner, *J. Am. Chem. Soc.*, **83**, 1276 (1961).

[9] Prepared by a modification of the method of P. Pfeiffer, *Chem. Ber.*, **37**, 4268 (1904).

ml. of 1 *F* $HClO_4$ eluent was used to remove unreacted *cis*-$Cr(en)_2(NCS)_2^+$ and at least two unidentified complexes. The desired *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ was eluted with *ca.* 250 ml. of 1.5 *F* $HClO_4$, giving an orange solution *ca.* 3 m*F* in the complex (~33% yield).

The complex was characterized as *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ by its visible absorption spectrum (Figure 1; this spectrum was identical with that of the product complex separated chromatographically from *cis*-$Cr(en)_2(NCS)Cl^+$ aquated at 25° for *ca.* six half-lives), by a SCN^-/Cr mole ratio of 1.02, and by the elution behavior from H^+ Dowex AG50W-X8 resin.[10]

***trans*-Isothiocyanatoaquobis(ethylenediamine)chromium(III) Cation.**—Crude *trans*-$[Cr(en)_2(NCS)_2]SCN \cdot H_2O$ was prepared[11] and purified by recrystallization from 60° water. One gram of this salt was dissolved in 500 ml. of 0.1 *F* $HClO_4$ and allowed to aquate in the dark for *ca.* 2.5 days at 50°. The solution was cooled and passed through a 10-cm. × 1-cm. diameter column of H^+ Dowex AG50W-X8 resin to adsorb all Cr cationic species, then unreacted *trans*-$Cr(en)_2(NCS)_2^+$ was eluted with 250 ml. of 0.2 *F* $HClO_4$, followed by 250 ml. of 0.8 *F* $HClO_4$ to elute *trans*-$Cr(en)_2(OH_2)NCS^{+2}$ as a violet solution *ca.* 3 m*F* in this complex (~30% yield).

Characterization of the complex as *trans*-$Cr(en)_2(OH_2)NCS^{+2}$ was based upon its visible absorption spectrum (Figure 1), upon a SCN^-/Cr mole ratio of 1.01, and by the elution behavior from H^+ Dowex AG50W-X8 resin.[10] In particular, assignment of this complex as the *trans* isomer and that described in the preceding section as the *cis* isomer was made on the basis of their absorption spectra (see Discussion) and the presumed greater ease of elution of the *trans* isomer off the resin as reflected in the lower acid concentration needed to elute the *trans* isomer.

Unsuccessful Attempts to Synthesize *cis*-Chloroisothiocyanatobis(ethylenediamine)chromium(III) Cation.—Considerable difficulty was experienced with the synthesis of this cation. We found the following approaches inadequate either because of no reaction or reaction producing at least one other singly charged complex cation, usually *cis*-$Cr(en)_2(NCS)_2^+$, which additional products prevented isolation of the desired complex in adequate purity by ion-exchange chromatographic or precipitation techniques: (1) *cis*-$Cr(en)_2(OH_2)Cl^{+2}$ treated with KSCN in 0.1 *F* HCl at 25 or 60° apparently gave only *cis*-$Cr(en)_2(NCS)_2^+$, even with the use of absolute ethanol to try to repress substitution by the second SCN^- (*cis*-$Cr(en)_2(NCS)_2^+$ is rapidly formed when a solution of *cis*-$[Cr(en)_2Cl_2]Cl$ and KSCN is heated); (2) *trans*-$Cr(en)_2Cl_2^+$ heated with KSCN in 1 m*F* $HClO_4$ at 65° gave a complex mixture of many products; (3) solid *trans*-$[Cr(en)_2Cl_2]SCN$ heated at 178° (higher temperatures gave charring) changed from green to a purple color in *ca.* 6 days, the products being *cis*-$Cr(en)_2(NCS)_2^+$, *cis*-$Cr(en)_2(NCS)Cl^+$, and unreacted parent; (4) the same products plus two others were obtained on photolysis with visible light of *trans*-$[Cr(en)_2Cl_2]SCN$ suspended in benzene; (5) solid *cis*- or *trans*-$[Cr(en)_2(NCS)_2]Cl$ gave no evidence of reaction on heating until charring set in at *ca.* 180°.

Successful Synthesis of *cis*-Chloroisothiocyanatobis(ethylenediamine)chromium(III) Cation.—This ion was synthesized by Cl^- anation of *cis*-$Cr(en)_2(OH_2)NCS^{+2}$. In order to concentrate the 3 m*F* solutions of this latter complex prepared as described earlier we diluted them with at least an equal volume of water to reduce the original 1.5 *F* $HClO_4$ concentration, thus allowing adsorption of the complex on H^+ Dowex AG50W-X8 cation-exchange resin that was then added. The mixture was stirred vigorously for 10 min., after which the resin was separated by decanting and the now colorless supernatant solution was discarded. The complex (*ca.* 2.3 mfwt.) was eluted from the resin with *ca.* 110 ml. of 6 *F* HCl and allowed to Cl^- anate in the dark at 25° for *ca.* 8.5 hr.

In order to permit chromatographic separation of the *cis*-$Cr(en)_2(NCS)Cl^+$ formed from unreacted *cis*-$Cr(en)_2(OH_2)NCS^{+2}$, the above 6 *F* HCl anation solution was placed in an ice bath and titrated to a pH of 2 with *ca.* 1.2 kg. of OH^- Dowex AG1-X8 resin.[12] After removal of the resin the solution was put on a 5-cm. × 1-cm. diameter column of H^+ Dowex AG50W-X8 resin, the column was then washed with 50 ml. of 1 m*F* $HClO_4$, then the *cis*-$Cr(en)_2(NCS)Cl^+$ was easily eluted from the much more strongly bound *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ with 85 ml. of 0.5 *F* $HClO_4$, giving a red-violet solution *ca.* 1 m*F* in the desired complex (~4% yield from *cis*-$Cr(en)_2(OH_2)NCS^{+2}$).

The complex was characterized as *cis*-$Cr(en)_2(NCS)Cl^+$ by SCN^-/Cr mole ratios of 0.96–1.05 and Cl/Cr atom ratios of 1.01–1.04 (different preparations), by its elution behavior in cation-exchange chromatography,[10] and by its visible absorption spectrum (see Figure 1 and Discussion). Subsequent to this research, pure solid Br^- and ClO_4^- salts of *cis*-$Cr(en)_2(NCS)Cl^+$ were prepared[13] and found to exhibit a visible absorption spectrum identical with that of our *cis*-$Cr(en)_2(NCS)Cl^+$.

Isothiocyanatotriaquomono(ethylenediamine)chromium(III) Cation.—Aquation of *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ in 0.8 *F* $HClO_4$ at 25 and 50° produces at least two products, one of which has a red color the amount of which increases with reaction time and which can be chromatographed nonquantitatively but in a state of reasonable purity from a H^+ Dowex AG50W-X8 column with 2 *F* $HClO_4$ eluent after prior elution of its parent (plus some of the red cation) with 1.5 *F* $HClO_4$. This elution behavior suggests the red cation is doubly charged. Values of 0.95 and 1.00 were found for the SCN^-/Cr mole ratio. On the basis of these facts, together with spectral evidence (see Discussion), the red species is tentatively characterized as $Cr(en)(OH_2)_3NCS^{+2}$ (unknown configuration).

Attempted Preparation of *trans*-Chloroisothiocyanatobis(ethylenediamine)chromium(III) Cation.—Unsuccessful attempts to synthesize this complex were made as follows: (1) *trans*-$Cr(en)_2(OH_2)Cl^{+2}$ solution 0.01 *F* in $HClO_4$ and 1 *F* in NaSCN was heated at 35° for 12 hr., but visible spectral scans taken at various times showed only changes opposite to those expected for conversion to *trans*-$Cr(en)_2(NCS)Cl^+$, and cation-exchange chromatography of the final reaction mixture (after 40-fold dilution with water) showed no singly charged cationic species were present; (2) *trans*-$Cr(en)_2(OH_2)NCS^{+2}$ was heated at various temperatures for various times in several different concentrations of HCl, the most favorable spectral change apparently corresponding to 6 hr. at 50° in 9 *F* HCl; after treatment with OH^- Dowex AG1-X8 and adsorption of the resulting solution on H^+ Dowex AG50W-X8, elution with 0.6 *F* $HClO_4$ (which should elute any singly charged Cr(III) cationic species) gave only a violet solution with a SCN^-/Cr mole ratio *ca.* one-seventh that expected for *trans*-$Cr(en)_2(NCS)Cl^+$; (3) similar chromatographic behavior was obtained with a solid isolated by slow evaporation at 30° of solvent from a 6 *F* HCl solution of *trans*-$Cr(en)_2(OH_2)NCS^{+2}$; (4) *cis*-$Cr(en)_2(NCS)Cl^+$ was heated in methanol at 40° for several days in an attempt to isomerize the complex, but with little evidence of reaction; (5) *trans*-$Cr(en)_2(NCS)_2^+$ was treated with H_2O_2 in 6–12 *F* HCl at 0° in the presence of $(NH_4)_2MoO_4$ catalyst, but only *trans*-$Cr(en)_2Cl_2^+$ was isolated.

Other Chemicals.—All other chemicals were reagent grade or C.P. The water was house-distilled water which was either passed through a mixed-bed anion–cation-exchange resin or redistilled from alkaline $KMnO_4$ and then redistilled without $KMnO_4$.

Analytical Methods.—Chromium was determined by treating the complexes with hot alkaline peroxide and spectrophotometrically determining the resulting chromate at 372 mμ. Thiocyanate in solution was determined by mixing, in the order given, 5.00 ml. of the unknown solution (20–200 μ*M* SCN^-) with 50.00 ml.

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[10] Based on analogies with the behavior of the chloro and bromo analogs; see ref. 3–5, 7.

[11] C. L. Rollinson and J. C. Bailar, Jr., *Inorg. Syn.*, **2**, 201 (1946).

[12] The preparation of the resin and the procedure was similar to that of ref. 5. The OH^- resin exchanges with the Cl^- of the reaction solution, releasing OH^- which reacts with the H^+ of the reaction solution, thus reducing the ionic strength to the point where the Cr(III) cationic species can be adsorbed efficiently by the resin in the following step.

[13] D. A. House and C. S. Garner, unpublished research of this laboratory.

of ethanol–dioxane solution (10 vol. % absolute ethanol, 90 vol. % Eastman Kodak White Label *p*-dioxane[14]) and 10.00 ml. of $Fe(NH_4)(SO_4)_2$–$HClO_4$ solution (80 g. of 12-hydrate per 1000 ml. of 4 *F* $HClO_4$), and allowing to cool in a stoppered flask for 10 min. in the dark, then spectrophotometrically determining the resulting $FeSCN^{+2}$ at 460 mμ *vs.* a reference solution prepared in the same way except with 5.00 ml. of water in place of the SCN^- solution. All spectrophotometric analyses were made in matched 10.00-cm. quartz cells with a Beckman DU spectrophotometer. Chloride was determined potentiometrically,[2] after destroying any SCN^- present by a modification of the method of Hart and Meyrowitz[15] (1 ml. of 2.1 *F* $NaNO_2$ and 2 ml. of 2.8 *F* HNO_3 were added to 25 ml. of solution being analyzed and kept at 80° for 0.5 hr.).

Kinetic Measurements.—Hydrolysis of some of the complexes was studied in the acid used to elute the complex, sometimes after *ca.* 2-fold dilution with water. For *cis*-$Cr(en)_2(NCS)Cl^+$ the solutions obtained by elution were used directly or titrated at 0° with OH^- AG1-X8 resin[12] to a pH of 1.04. Solid $NaHCO_3$ was added to some of these pH 1.04 solutions until the pH was 3.05, giving run solutions which were 0.001 *F* in $HClO_4$ and 0.1 *F* in $NaClO_4$. In additional runs the acidity and ionic strength were varied by addition of $HClO_4$ and $NaClO_4$. Immediately after their preparation all run solutions were put in glass-stoppered Pyrex flasks, covered with Al foil to exclude light, and placed in thermostated baths at 24.65 ± 0.05° (spectrophotometric runs on *cis*-$Cr(en)_2(NCS)Cl^+$), 15.00 ± 0.05, 25.00 ± 0.03, or 35.00 ± 0.03° (all other runs). Aliquots were removed at known times and the extent of reaction followed by several methods.

Spectrophotometric scans were made in matched 10.00-cm. quartz cells with a Cary Model 11 or Model 15 recording spectrophotometer to search for isosbestic points as well as to follow the change in absorbancy with time. Light was excluded from the run solutions except during actual scanning.

Release of ligand chloride by *cis*-$Cr(en)_2(NCS)Cl^+$ was followed by delivering each 5.00-ml. aliquot into 20 ml. of 0° water to quench the reaction and dilute the solution for adsorption of Cr cationic species onto a 2-cm. × 1-cm. diameter column of H^+ Dowex AG50W-X8 resin; the effluent was collected in a 50.00-ml. volumetric flask and the column was washed with *ca.* 25 ml. of 0° 1 m*F* $HClO_4$ into the same flask to collect all free anions. Chloride in this solution was determined potentiometrically after destroying any SCN^-, as described above. Tests showed no Cr species were present in these effluents.

Disappearance of *cis*-$Cr(en)_2(NCS)Cl^+$ was followed by quantitatively eluting it from the above column with 100 ml. of 1 *F* $HClO_4$, which was found not to elute other Cr species present, and determining Cr as described earlier.

Release of ligand isothiocyanate from the complexes was followed by the $FeSCN^{+2}$ spectrophotometric method given above after removal of cationic Cr species by the same chromatographic procedure used above to separate Cl^- from Cr species.

To prevent photolysis of the complexes all cation-exchange chromatography was carried out with columns shielded with Al foil in a dimly lighted room.

Results

Spectra of New Complexes.—Figure 1 exhibits the visible and near-ultraviolet absorption spectra of the new Cr(III) complexes *cis*-$Cr(en)_2(NCS)Cl^+$, *cis*- and *trans*-$Cr(en)_2(OH_2)NCS^{+2}$, and the species tentatively identified as $Cr(en)(OH_2)_3NCS^{+2}$ (unknown configuration). Spectra[16] of *cis*- and *trans*-$Cr(en)_2(OH_2)_2{}^{+3}$ are included to permit understanding the spectrophotometric evidence presented for the products of the *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ hydrolysis.

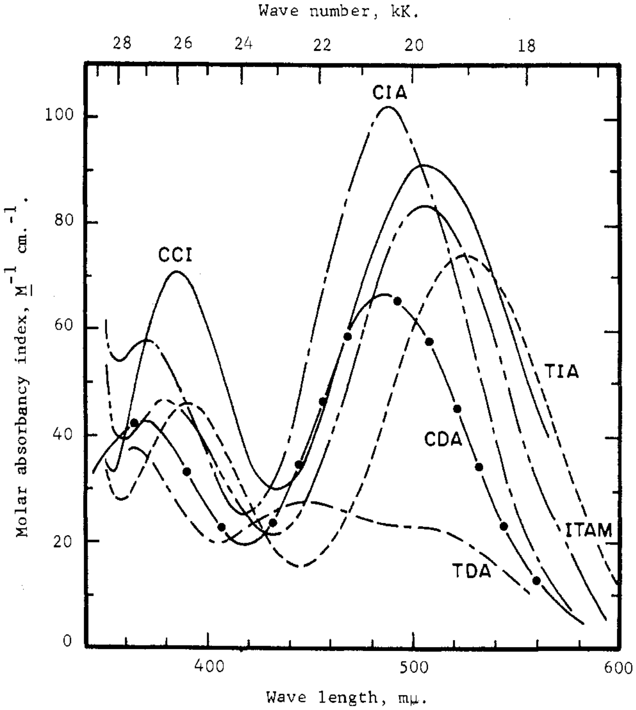

Figure 1.—Visible absorption spectra of chromium(III) complexes at 25°: CCI, *cis*-$Cr(en)_2(NCS)Cl^+$, 1 *F* $HClO_4$; CIA, *cis*-$Cr(en)_2(OH_2)NCS^{+2}$, 1.5 *F* $HClO_4$; TIA, *trans*-$Cr(en)_2(OH_2)NCS^{+2}$, 1 *F* $HClO_4$; ITAM, $Cr(en)(OH_2)_3NCS^{+2}$(?), 2 *F* $HClO_4$; CDA, *cis*-$Cr(en)_2(OH_2)_2{}^{+3}$, 0.1 *F* HNO_3 + 1 *F* $NaNO_3$; TDA, *trans*-$Cr(en)_2(OH_2)_2{}^{+3}$, 0.02 *F* HNO_3 + 1 *F* $NaNO_3$; the molar absorbancy index a_M (extinction coefficient ε) is defined by the relation $\log (I_0/I) = a_M cd$.

Aquation of *cis*-$Cr(en)_2(NCS)Cl^+$.—Determinations of the molar concentration *C* of unreacted *cis*-$Cr(en)_2(NCS)Cl^+$ chromatographically separated from reaction solutions at time *t* allowed construction of $\ln (C/C_0)$ *vs.* *t* plots; these were linear to 50–70% reaction. A typical plot is shown in Figure 2.

A similar plot, linear to 70% Cl^- release, was made for one run in which released Cl^- was titrimetrically determined; *C* was taken as $C_0 - (Cl^-)$.

The rate was also followed spectrophotometrically. Figure 3 displays the spectral changes during a typical *cis*-$Cr(en)_2(NCS)Cl^+$ hydrolysis run. In terms of the optical absorbancies A_0, A, and A_∞ (at a given wave length) at time zero, time *t*, and at 100% hydrolysis of the chloro ligand, respectively, the first-order rate equation is

$$\ln [(A_0 - A_\infty)/(A - A_\infty)] = kt \qquad (1)$$

With A_∞ calculated assuming aquation to 100% *cis*-$Cr(en)_2(OH_2)NCS^{+2}$, plots of this logarithmic function of the absorbancies at 385, 400, 480, 490, 540, and 560 mμ *vs.* *t* generally have good straight lines up to at least 50% reaction, with *k* values obtained from the slopes exhibiting a ±8% range around their average.

A summary of values of *k* for the rate law

$$-\frac{d(cis\text{-}Cr(en)_2(NCS)Cl^+)}{dt} = k(cis\text{-}Cr(en)_2(NCS)Cl^+) \qquad (2)$$

is given in Table I.

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[14] Dioxane containing peroxide inhibitors should not be used because they bleach the color from $FeSCN^{+2}$.

[15] D. Hart and R. Meyrowitz, *Ind. Eng. Chem.*, **13**, 237 (1941).

[16] F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958).

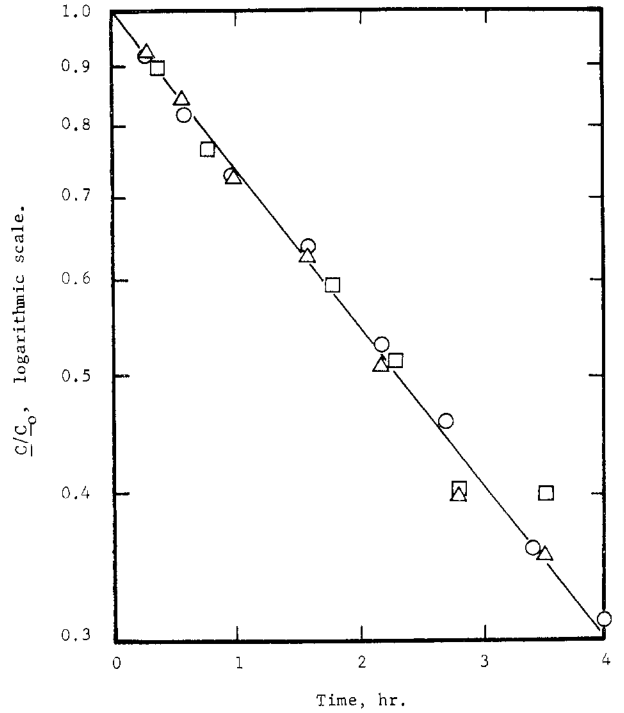

Figure 2.—Typical kinetic plot illustrating first-order dependence of $-d(cis\text{-}Cr(en)_2(NCS)Cl^+)/dt$ on $(cis\text{-}Cr(en)_2(NCS)Cl^+)$ and zero-order dependence on (H^+) at 25.0°, C_0 = 1.0–1.3 m*M*: ○, pH 0.10 (μ = 0.79); △, pH 1.04 (μ = 0.10); □, pH 3.04 (μ = 0.10).

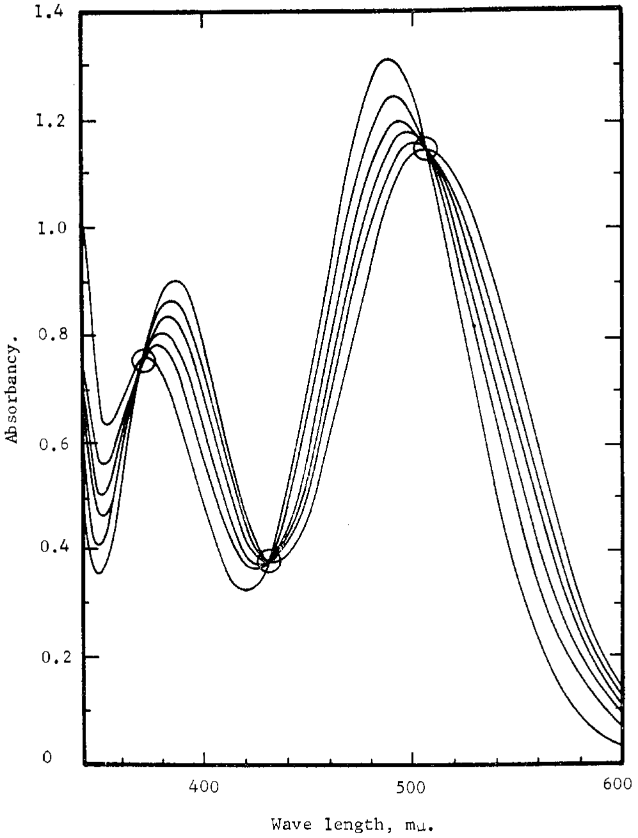

Figure 3.—Change in absorption spectrum of $cis\text{-}Cr(en)_2(NCS)Cl^+$ reaction solution during aquation in 0.79 *F* $HClO_4$ at 24.65°: reading upward at 480 mμ, reaction time is 0.09, 0.70, 1.40, 2.20, 3.70, and 14.40 hr., respectively.

TABLE I

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR AQUATION OF $cis\text{-}Cr(en)_2(NCS)Cl^+$ IN THE DARK

Method[a]	Temp., °C.	$(HClO_4)$, *F*	C_0, m*F*	μ, *M*[b]	10^6k, sec.$^{-1}$
Spectro.	24.65	1.0	0.76	1.0	8.7 ± 0.9^c
Spectro.	24.65	0.8	1.80	0.8	9.2 ± 0.9^c
Chrom.	25.00	0.79	1.29	0.79	8.1 ± 0.4^d
Cl^-	25.00	0.79	1.29	0.79	8.4 ± 0.3^d
Spectro.	24.65	0.79	1.29	0.79	8.6 ± 0.9^c
Spectro.	24.65	0.10	0.52	0.78	8.6 ± 0.9^c
Chrom.	25.00	0.10	1.21	0.10	8.1 ± 0.4^d
Chrom.	25.00	0.001	1.04	0.10	7.9 ± 0.4^d
Chrom.	15.00	0.10	1.07	0.10	2.6 ± 0.2^d
Chrom.	35.00	0.10	0.66	0.10	26.3 ± 1.8^d

[a] Spectro. = spectrophotometric analysis at several wave lengths; chrom. = determination of chromatographically separated unreacted $cis\text{-}Cr(en)_2(NCS)Cl^+$; Cl^- = titration of released Cl^-. [b] Ionic strength controlled with $NaClO_4$. [c] Estimated standard error. [d] Standard error obtained from least-squares treatment.

Aquation of $cis\text{-}Cr(en)_2(OH)_2NCS^{+2}$.—The rate of disappearance of the isothiocyanatoaquo complex was followed spectrophotometrically at 25.00 ± 0.03° in 0.75 *F* $HClO_4$ in the absence of light (except from the spectrophotometer during actual scans). The data were analyzed with eq. 1 at 480 mμ, which is in the region of greatest observed absorbancy change, and with A_∞ calculated from the molar absorbancy index of the 480-mμ isosbestic point of the apparent aquation products $cis\text{-}Cr(en)_2(OH_2)_2^{+3}$ and $Cr(en)(OH_2)_3NCS^{+2}$ (see Figure 1 and Discussion). The first-order rate plots were linear to *ca.* 50% reaction, giving pseudo-first-order rate constants of 1.49×10^{-6} and 1.43×10^{-6} sec.$^{-1}$ for C_0 values of 0.75 and 1.23 m*F*, respectively; we take $(1.5 \pm 0.2) \times 10^{-6}$ sec.$^{-1}$ ($t_{1/2}$ = 5.3 days) for the total aquation rate constant.

The rate of thiocyanate release was also followed under the above conditions. Plots of log $[1 - (SCN^-)/(SCN^-)_\infty]$ *vs.* *t*, where $(SCN^-)_\infty$ was taken as the initial molarity of $cis\text{-}Cr(en)_2(OH_2)NCS^{+2}$, exhibited curvatures (corresponding to a reduced rate of SCN^- release) after only 10–20% SCN^- release, and there was evidence of slow decomposition of free SCN^- in such solutions, perhaps catalyzed by Cr(III) species. We therefore take the average value of the pseudo-first-order rate constant calculated from the initial slopes of these rate plots, namely $(1.0 \pm 0.3) \times 10^{-6}$ sec.$^{-1}$, as a lower limit for SCN^- release at 25°.

Aquation of $trans\text{-}Cr(en)_2(OH)_2NCS^{+2}$.—Two experiments were made on the rate of disappearance of the *trans*-isothiocyanatoaquo complex in 0.8 *F* $HClO_4$ at 25.00° in the dark, primarily to facilitate the consideration of various reaction pathways in aquation of $cis\text{-}Cr(en)_2(NCS)Cl^+$ and $cis\text{-}Cr(en)_2(OH_2)NCS^{+2}$. With C_0 = 1.5 m*F*, periodic observations of the absorption spectrum in the range 340–640 mμ for 34 days showed a maximum change in absorbancy of only 3% at any given wave length. Inasmuch as the spectra of such probable reaction products as $cis\text{-}Cr(en)_2(OH_2)NCS^{+2}$, *trans*- or $cis\text{-}Cr(en)_2(OH_2)_2^{+3}$, and $Cr(en)(OH_2)_3NCS^{+2}$ are substantially different from the spectrum of *trans*-

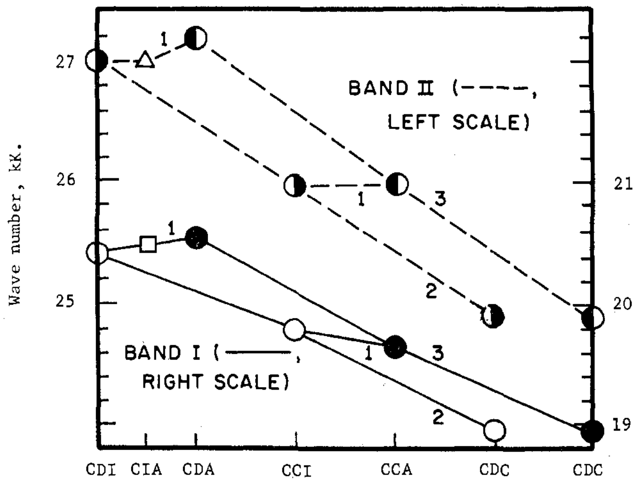

Figure 4.—Effect of ligand substitution on wave number of absorption maxima of *cis*-$Cr(en)_2AX^{+n}$ at 25°: substitution of NCS for H_2O (curves 1), of NCS for Cl (curves 2), of H_2O for Cl (curves 3); CDI, *cis*-$Cr(en)_2(NCS)_2^+$, 0.1 *F* $HClO_4$ (K. G. Poulsen and C. S. Garner, unpublished research); CIA, *cis*-$Cr(en)_2(OH_2)NCS^{+2}$, 1.5 *F* $HClO_4$; CDA, *cis*-$Cr(en)_2(OH_2)_2^{+3}$, 0.1 *F* HNO_3 + 1 *F* $NaNO_3$; CCI, *cis*-$Cr(en)_2(NCS)Cl^+$, 1 *F* $HClO_4$; CCA, *cis*-$Cr(en)_2(OH_2)Cl^{+2}$, 2 *F* HCl (ref. 3, 4); CDC, *cis*-$Cr(en)_2Cl_2^+$, 0.1 *F* HCl (ref. 3, 4).

$Cr(en)_2(OH_2)NCS^{+2}$ (see Figure 1), we infer that no more than 5% reaction of the latter complex occurred, corresponding to an upper limit of $k < 2 \times 10^{-8}$ sec.$^{-1}$ ($t_{1/2} > 450$ days), assuming

$$-\frac{d(trans\text{-}Cr(en)_2(OH_2)NCS^{+2})}{dt} = k(trans\text{-}Cr(en)_2(OH_2)NCS^{+2}) \quad (3)$$

Discussion

Spectra.—The two main visible absorption bands of Cr(III) complexes arise from d–d transitions, and since ligand isothiocyanate and ligand water are near to each other in the spectrochemical series, little change in wave number of bands I and II is expected on substitution of isothiocyanate for water in the first coordination sphere. Figure 4 (curves 1) shows this expectation is justified for both bands I and II for the sequences *cis*-$Cr(en)_2(OH_2)_2^{+3}$ → *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ → *cis*-$Cr(en)_2(NCS)_2^+$ and *cis*-$Cr(en)_2(OH_2)Cl^{+2}$ → *cis*-$Cr(en)_2(NCS)Cl^+$. An increase in molar absorbancy indices of the absorption maxima and of total integrated intensity along these same two sequences presumably reflects the effect of additional vibronic mixing in excited states and increased participation of d–π bonding in the Cr–NCS bond. Figure 4 also shows the changes in wave number of bands I and II as ligand isothiocyanate (curves 2) or ligand water (curves 3) is substituted for ligand chloride in the respective series *cis*-$Cr(en)_2Cl_2^+$ → *cis*-$Cr(en)_2(NCS)Cl^+$ → *cis*-$Cr(en)_2(NCS)_2^+$ and *cis*-$Cr(en)_2Cl_2^+$ → *cis*-$Cr(en)_2(OH_2)Cl^{+2}$ → *cis*-$Cr(en)_2(OH_2)_2^{+3}$; the similarity of these changes is in agreement with the rule of average environment[17] and lends strong support to our assignment of the *cis*-configuration to the species we have described as *cis*-$Cr(en)_2(NCS)Cl^+$ and *cis*-$Cr(en)_2(OH_2)NCS^{+2}$.

The spectroscopic relations among the *trans* complexes are complicated by the splitting of band I, which is normally twice as great for the *trans* as for the *cis* isomer, and which leads for some *trans* complexes (*e.g.*, *trans*-$Cr(en)_2(OH_2)_2^{+3}$) to a shoulder on the high wave-length side of band I or to an actual split absorption peak, whereas in the *cis* and other *trans* isomers (*e.g.*, *trans*-$Cr(en)_2(NCS)_2^+$) this band is merely broadened. The total intensity of the *trans* species is expected to be less than for the *cis* isomer because the latter lacks a center of symmetry and more interactions are allowed; our characterizations of the *trans* and *cis* isomers of $Cr(en)_2(OH_2)NCS^{+2}$ are in accord with this rule (see Figure 1). Although one might think from the spectrochemical series that *trans*-$M(en)_2(OH_2)NCS^{+2}$ and *trans*-$M(en)_2(NCS)_2^+$ would qualitatively have the same spectra, for M = Cr or for M = Co, such is not observed, although band I shows no splitting for these complexes. Bands I and II for *trans*-$Cr(en)_2(OH_2)NCS^{+2}$ and band II (band I appears not to have been reported) for the Co analog[18,19] lie at substantially longer wave lengths than for their diisothiocyanato analogs; Jørgensen[20] has suggested this may be due to an asymmetry more frequently known in *cis* complexes such that the doubly degenerate component of cubic triply degenerate bands tends to determine the position of the band observed.

The spectrum of the species tentatively characterized as $Cr(en)(OH_2)_3NCS^+$ (unknown configuration) has its two absorption maxima and the minimum at the same wave lengths within experimental error as the species identified by Schläfer and Kollrack[21] as $Cr(en)(OH_2)_4^{+3}$, in accord with predictions based on the spectrochemical series. The molar absorbancy indices at the absorption peaks of the former complex are roughly twice those for the latter complex.

Aquation Reactions and Related Isomerizations.—At 25° the values of *k* found for aquation of *cis*-$Cr(en)_2(NCS)Cl^+$ by the three methods (Table I) are in satisfactory agreement considering the relatively large errors inherent in the spectrophotometric method. This suggests that aquation by paths involving release of SCN^- or ethylenediamine is unimportant; the former conclusion is supported additionally by finding only 2 ± 2% of the ligand thiocyanate as free SCN^- in an aquation reaction solution processed after 2.4 half-lives for Cl^- release. Cation-exchange chromatography of a reaction solution after *ca.* 5 half-lives showed, after removal of unreacted parent, the presence of only *cis*-$Cr(en)_2(OH_2)NCS^{+2}$. Moreover, Figure 3 and related runs showed over six half-lives good isosbestic points at 370 ± 1 mμ (a_M = 57 ± 2 M^{-1} cm.$^{-1}$), 430 ±

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[17] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1962, p. 109.

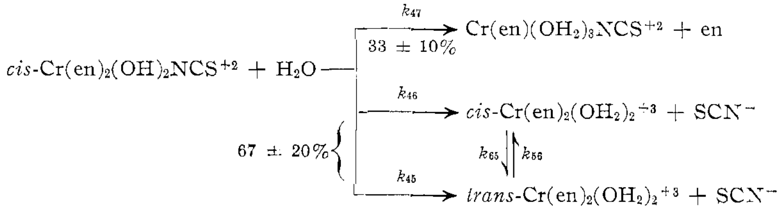
[18] F. Basolo, B. D. Stone, and R. G. Pearson, *J. Am. Chem. Soc.*, **75**, 819 (1953).

[19] C. K. Ingold, R. S. Nyholm, and M. L. Tobe, *J. Chem. Soc.*, 1691 (1956).

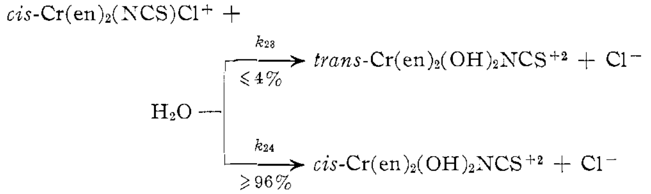
[20] C. K. Jørgensen, private communication.

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

Scheme I



2 mμ ($a_M = 29.0 \pm 0.5\ M^{-1}$ cm.$^{-1}$), and 507 ± 1 mμ ($a_M = 87 \pm 2\ M^{-1}$ cm.$^{-1}$), in excellent agreement with values expected for the *cis*-$Cr(en)_2(NCS)Cl^+$–*cis*-$Cr(en)_2(OH_2)NCS^{+2}$ system (see Figure 1), namely, 370 mμ ($a_M = 57.6\ M^{-1}$ cm.$^{-1}$), 431 mμ ($a_M = 29.5\ M^{-1}$ cm.$^{-1}$), and 507 mμ ($a_M = 89.9\ M^{-1}$ cm.$^{-1}$). Construction of spectral curves involving production of various ratios of *cis* and *trans*-$Cr(en)_2(OH_2)NCS^{+2}$ showed that up to 4% of the $Cr(en)_2(OH_2)NCS^{+2}$ formed could be the *trans* isomer without causing the computed isosbestic points to deviate from the experimental values by more than their experimental errors. Calculations of spectrophotometric values of *k* with A_∞ values based on up to 4% *trans* product were still in acceptable agreement with *k* values determined chromatographically. Thus, the stereochemical result of the aquation of this complex at 25° is



Perturbations caused by aquation or isomerization of the isothiocyanatoaquo complexes are negligible, as shown by the above isosbestic-point data and by arguments presented below. In the absence of aquation data on *trans*-$Cr(en)_2(NCS)Cl^+$, which complex we have been unable to synthesize, we cannot completely exclude the possibility that the observed products form *via* a rate-controlling *cis*-to-*trans* isomerization of the reactant, followed by a much faster (*i.e.*, $k >> 8 \times 10^{-5}$ sec.$^{-1}$ at 25°) aquation of the *trans*-$Cr(en)_2(NCS)Cl^+$. However, the first-order rate constants[22] for aquation of *cis*- and *trans*-$Co(en)_2(NCS)Cl^+$ at 25°, namely, 1.1×10^{-5} and 0.005×10^{-5} sec.$^{-1}$, respectively, strongly imply that our assignment of the value 8×10^{-5} sec.$^{-1}$ to *cis*-$Cr(en)_2(NCS)Cl^+$ *aquation* is correct in view of the generally found close similarity in $M(en)_2AX^{+n}$ aquation rates at 25° of Cr(III) and Co(III) analogs of given configuration. Elimination of the reactant isomerization path as a significant contribution to the aquation mechanism is further supported by evidence based on the rates found in this research for *cis*- and *trans*-$Cr(en)_2(OH_2)NCS^{+2}$ aquation; we would infer from the latter, in particular, that *trans*-$Cr(en)_2(NCS)Cl^+$ would probably have a pseudo-first-order rate constant less than 1×10^{-6} sec.$^{-1}$ at 25°, based on analogies with the Co(III) complexes.

Taking the average of the chromatographic values of the *cis*-$Cr(en)_2(NCS)Cl^+$ *k* ($k = k_{23} + k_{24}$) as most reliable, namely $(8.1 \pm 0.4) \times 10^{-5}$ sec.$^{-1}$ ($t_{1/2}$ = 2.4 hr.), we obtain $k_{23} \leq 3 \times 10^{-6}$ sec.$^{-1}$ and $k_{24} = (8.0 \pm 0.5) \times 10^{-5}$ sec.$^{-1}$ in 0.001–1.0*F* $HClO_4$ (μ = 0.1–1.0, $NaClO_4$) at 25°. From the temperature variation of *k* (Table I) we obtain a good linear Arrhenius plot from which $E_a = 20.5 \pm 1.3$ kcal. mole^{-1} and log *PZ* (sec.$^{-1}$) = 10.9 ± 1.0 ($\Delta S^* = -10.5 \pm 4.4$ cal. deg.$^{-1}$) at 25°. These values of E_a and log *PZ* are approximately the same as found[22] for aquation of the Co(III) analog (to a reported 100% *cis*-$Co(en)_2(OH_2)NCS^{+2}$) at 25°, namely, 20.8 kcal. mole^{-1} and 10.3, respectively; *k* for *cis*-$Cr(en)_2(NCS)Cl^+$ aquation is 7.4 times *k* for the Co analog and 1/4.1 (1/8.2, if the statistical factor is included) times *k* for *cis*-$Cr(en)_2Cl_2^+$.[3,4] These activation energies are lower than usually encountered in $M(en)_2AX^{+n}$ aquation; Baldwin and Tobe[22] have suggested that the low activation energies may be associated with the isothiocyanato ligand orienting a solvating water molecule, which could then hydrogen bond with the *cis*-chloro ligand, assisting its dissociation.

Aquation of *cis*-$Cr(en)_2(OH_2)NCS^{+2}$, according to chromatographic and spectrophotometric evidence, appears to give mainly a mixture of *cis*-$Cr(en)_2(OH_2)_2^{+3}$ and $Cr(en)(OH_2)_3NCS^{+2}$; evidence for aquation resulting in replacement of one ethylenediamine ligand by two molecules of H_2O in related Cr(III) complexes has been presented earlier.[3–5,7] The one isosbestic point observed during the aquation occurred at 520–560 mμ, with the large error arising from the steep slopes of the curves in this region. Construction of trial theoretical spectral curves for the aquation, assuming various proportions of the above products, gave fairly good agreement with the observed spectral changes, including the one isosbestic point, when the products were assumed to be formed in the fixed ratio 70 ± 5% *cis*-$Cr(en)_2(OH_2)_2^{+3}$ (or 65% *cis*-diaquo, 5% *trans*-diaquo, which is the equilibrium diaquo isomer ratio) to 30 ± 5% $Cr(en)(OH_2)_3NCS^{+2}$. It was for this reason that the 480-mμ predicted isosbestic point for the *cis*-$Cr(en)_2(OH_2)_2^{+3}$–$Cr(en)(OH_2)_3NCS^{+2}$ system was used in analyzing the 25° rate data in *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ aquation to get the total rate constant, $(1.5 \pm 0.2) \times 10^{-6}$ sec.$^{-1}$. If we now subtract off $(k_{45} + k_{46}) = (1.0 \pm 0.3) \times 10^{-6}$ sec.$^{-1}$ for the SCN^- release, we obtain $(0.5 \pm 0.4) \times 10^{-6}$ sec.$^{-1}$ for k_{47} in the proposed scheme (Scheme I) which is consistent within the rather large errors with the above spectral-change evidence. Attempts to

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[22] M. E. Baldwin and M. L. Tobe, *J. Chem. Soc.*, 4275 (1960).

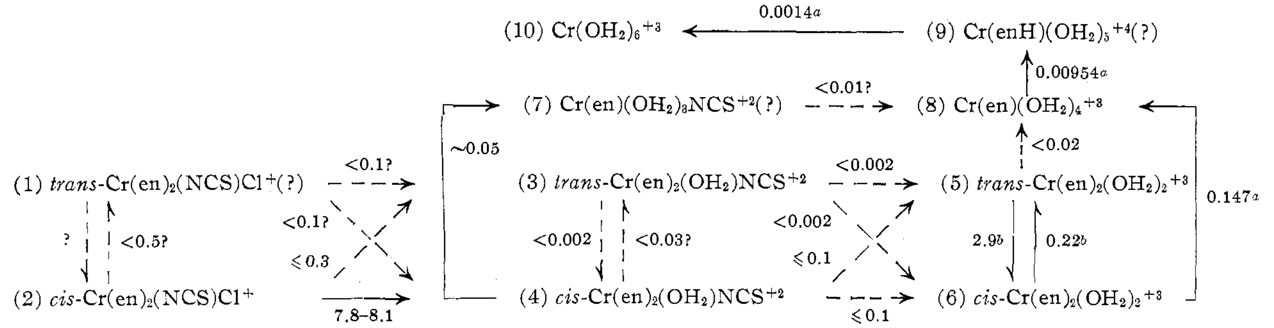

Figure 5.—First-order rate constants (10^5k, sec.$^{-1}$) for aquation and isomerization reactions in 0.1–0.8 F $HClO_4$ at 25° in the absence of light (k values followed by ? are estimates based on limited experimental data, or on analogies with relative k values in related systems). [a] Calcd. from data in ref. 21. [b] Ref. 23, 0.01 F HCl.

throw more light on the product ratio of $Cr(en)_2(OH_2)_2^{+3}$ to $Cr(en)(OH_2)_3NCS^{+2}$ by quantitative chromatographic separations were unsuccessful. Recently Adamson[23] has found $k_{65} = 2.9 \times 10^{-5}$ sec.$^{-1}$ and $k_{56} = 0.22 \times 10^{-5}$ sec.$^{-1}$ in 0.01 F HCl at 25°, so the diaquo isomers essentially attain their 93% *cis*, 7% *trans* equilibrium ratio rapidly relative to the *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ aquation, thus removing any possibility of examining the stereochemical course of the aquation. Inasmuch as Cr(III) and Co(III) *cis* reactants normally give ~100% *cis* products stereochemically in $M(en)_2AX^{+n}$ aquation, *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ probably generates its diaquo product directly in the *cis* configuration, followed by isomerization to the equilibrium *cis–trans* mixture. A reaction path involving isomerization of *cis*-$Cr(en)_2(OH_2)NCS^{+2}$, followed by aquation reactions of the *trans* isomer, can be eliminated because the rate of aquation of *trans*-$Cr(en)_2(OH_2)NCS^{+2}$ is too slow (see Results) to account for the observed rate of aquation of the *cis* isomer; moreover, no *trans* isomer was chromatographically observed in aquation solutions of the *cis* isomer. These and other considerations allow us to place upper limits of $k_{43} < 3 \times 10^{-7}$ sec.$^{-1}$ and $k_{34} < 2 \times 10^{-8}$ sec.$^{-1}$ on the *cis*-to-*trans* and *trans*-to-*cis* first-order rate constants, respectively, for isomerization of the isothiocyanatoaquo ions in these acid solutions at 25°; thus, these isomerizations are too slow to affect significantly the product distribution in *cis*-$Cr(en)_2(NCS)Cl^+$ or *cis*-$Cr(en)_2(OH_2)NCS^{+2}$ aquation. Comparisons with aquation rates of *cis*- and *trans*-$Co(en)_2(OH_2)NCS^{+2}$ are not possible since their aquation rates apparently have not been published.

It is useful to construct a reaction scheme (Figure 5) showing all possible interconversions and associated rate constants determined in this study; the dashed arrows correspond to reaction paths for which there is no direct experimental evidence (*e.g.*, *cis*-diaquo is a product of *cis*-isothiocyanatoaquo aquation, but it is not known whether it is formed directly or *via* isomerization of a *trans*-diaquo intermediate). Comparisons can then readily be made with similar reaction schemes for related Cr(III) complexes presented in earlier papers[4–7] from this laboratory and with related Co(III) complexes by adding the rate results from this study to Table IV of ref. 7. The same general order of orienting ligands for labilizing of the outgoing ligand is found among the Cr(III) complexes of the $M(en)_2AX^{+n}$ type as for their Co(III) analogs among the complexes investigated so far. As in the present and some earlier studies, the Cr(III) complexes may exhibit an observable tendency to aquate with replacement of an ethylenediamine ligand by two water molecules in competition with the usual replacement of X and A by H_2O, which aquation mode is apparently the only one observed to date with the Co(III) analogs. This tendency for Cr(III) appears to be related to the relative ease of formation of Cr–O bonds of considerable stability.

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(23) A. W. Adamson, Preprint of "Mechanisms of Inorganic Reactions," University of Kansas, June 1964, p. 220. We have resolved his total k with the aid of the *cis*-to-*trans* equilibrium quotient of 13 (in 0.02 F HNO_3–1 F $NaNO_3$) given by Woldbye (ref. 16). These k values are ten times those estimated earlier (ref. 4, 5, 7) from qualitative remarks made in Woldbye's paper; conclusions drawn by us in earlier papers (ref. 4, 5, 7) based on those estimated k values are not materially affected.