Scaled molecular models can be used to show some of the steric interactions involved in these complexes.[28] In trans complexes of triethylenetetramine there is marked strain involved in the ring system in agreement with the observed instability of the trans configuration. However, the α-cis and β-cis models can be constructed with little difficulty and with seemingly little preference for either α or β configuration. In complexes containing 2,3,2-tet, the trans-*RS* (meso) configuration appears the most stable and is the isomer produced experimentally under what appear to be equilibrium conditions. The trans-*RR,SS* configuration can also be constructed with little difficulty and has also been observed experimentally. In cis complexes containing the 2,3,2-tet ligand, molecular models show that the α configuration leads to highly unfavorable steric interactions between protons on adjacent chelate rings for all conformations of the chelate rings. These interactions are very much relieved in the β configuration so that a relatively strain-free and nonsterically hindered model of the β isomer can be constructed. Proceeding to the 3,2,3-tet ligand, we find that for the β isomer the ligand either blocks the remaining coordination sites or folds into itself resulting in unfavorable proton–proton interactions. The α configuration is to be preferred although the distinctions seem less obvious in the 2,3,2-tet complex. The experimental results are in complete accord with simple, qualitative concepts of strain differences and steric hindrance among the various chelate rings in a complex.

Finally, we wish to comment on the use of infrared and nuclear magnetic resonance spectroscopy. Though Buckingham and Jones[29] correctly deduced the topology of some triethylenetetramine complexes from infrared evidence, recent reports on other systems cast doubt on the utility of these spectra.[30] We have made no effort to obtain infrared spectra. We believe that pmr spectra could be extremely useful in elucidating the configurations of these complexes; the only observable signals must come from the flexible tetramine ligand. We have not succeeded in overcoming several experimental difficulties including the low solubility of the complexes in suitable solvents and insufficient resolution at 60 MHz. Our limited observations are, however, consistent with the conclusions drawn from other spectroscopic studies.

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Competition of Chromium(II) Species Present in Aqueous Ethylenediamine Solutions in Electron-Transfer Reactions with Chloropentaamminecobalt(III) Cation[1]

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The electron-transfer reactions between $Co(NH_3)_5Cl^{2+}$ and Cr(II) in aqueous ethylenediamine solutions have been studied as a function of changing pH for constant total ethylenediamine concentration. A procedure was developed to determine the distribution of Cr(III) among the product species, $Cr(OH_2)_5Cl^{2+}$, $Cr(en)(OH_2)_3Cl^{2+}$, and $Cr(en)_2(OH_2)Cl^{2+}$, and this distribution was compared to the calculated amounts of $Cr_{aq}{}^{2+}$, $Cr(en)^{2+}$, and $Cr(en)_2{}^{2+}$ initially available for reaction. Rate constant ratios were calculated assuming that the mole fractions of the Cr(II) reactants remain constant throughout the reactions, and from these ratios and a previously reported rate constant for the $Cr_{aq}{}^{2+}$–$Co(NH_3)_5Cl^{2+}$ reaction, $k_0 = (2.2 \pm 0.5) \times 10^6\ M^{-1}\ sec^{-1}$, the rate constants for reaction of $Co(NH_3)_5Cl^{2+}$ with $Cr(en)^{2+}$, $k_1 = (4.0 \pm 2.3) \times 10^7\ M^{-1}\ sec^{-1}$, and with $Cr(en)_2{}^{2+}$, $k_2 = (1.6 \pm 0.8) \times 10^8\ M^{-1}\ sec^{-1}$, were found at 25° and an ionic strength of 1.4 *M*. The regular increases in rate as amine coordination is increased are discussed in terms of increased ligand field strength.

Introduction

Previous studies of the electron-transfer reaction between $Cr(OH_2)_6{}^{2+}$ and $Co(NH_3)_5Cl^{2+}$ [2,3] have shown the reaction occurs by a bridged mechanism with little motion of the nonbridging Co(III) ligands in the formation of the activated complex. Other work using $Co(NH_3)_5OH^{2+}$ as oxidant has indicated the rearrangement of the bridging ligand may be important in reaching the transition state.[4,5] Finally ^{18}O isotopic fractionation studies of the Cr(III) product of this reaction in strong ethylenediamine solutions (*i.e.*, $Cr(en)_2(OH_2)Cl^{2+}$) suggest that motion of nonbridging Cr(II) ligands also occurs.[6] The involvement of the nonbridging Cr(II) ligands may also be investigated by varying the ligands coordinated to Cr(II) in the activated complex. If motion of these ligands is required to form the transition state, then variation

(1) Work partly supported under Contract AT(04-3)-34, Project No. 170, between the U. S. Atomic Energy Commission and the University of California. This paper constitutes Report No. UCLA-34P170-12 to the AEC.

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of the ligand field around Cr(II) should change the amount of internal rearrangement needed and therefore the activation energy or rate of reaction.[7] For these experiments the reaction was done with excess $Co(NH_3)_5Cl^{2+}$ in aqueous ethylenediamine solutions of $CrCl_2$. The distribution of Cr(III) product species was determined as a function of changing pH using a constant total ethylenediamine concentration (*i.e.*, the fractions of $Cr(en)_n{}^{2+}$, $n = 0–2$, available for reaction were varied). Because of the low rate of amine hydrolysis for complexes such as the chromium(III)–ethylenediamine products[8] relative to the rate of electron-transfer reaction,[3] ethylenediamine appearing in the product must be included in the activated complex, presumably as ligands in the Cr(II) complex ion.

Experimental Section

Chemicals.—Solutions of complexes for testing the method used to determine the Cr(III) product distributions were prepared by aquation of the salts blue (*trans*-dichloro) $[Cr(en)(OH_2)_2Cl_2]Cl$ and *cis*- and *trans*-$[Cr(en)_2Cl_2]Cl$ previously prepared in this laboratory. Aquation studies show that aging blue $Cr(en)(OH_2)_2Cl_2{}^+$ for 90 min in 1.5 *F* $HClO_4$ at 50° gives *ca.* 95% reaction to the magenta monochloro species (probably the 1-chloro-2,3,6-triaquo isomer),[9] and nearly pure *cis*-$Cr(en)_2(OH_2)Cl^{2+}$ was obtained by aquation of *cis*-$Cr(en)_2Cl_2{}^+$ for 80 min in 0.1 *F* $HClO_4$ at 35°.[10] The *trans*-$Cr(en)_2Cl_2{}^+$ complex was aged for 30 min in 0.1 *F* $HClO_4$ at 60° and then *trans*-$Cr(en)_2(OH_2)Cl^{2+}$ was chromatographically isolated as previously described.[10] Stock solutions of Cr^{2+} were prepared by dissolving electrolytic Cr metal (99.999% pure, United Mineral & Chemical Corp., New York, N. Y.) in 1.5 *F* HCl under N_2 to give *ca.* 12.5 m*F* solutions in an apparatus[7] used for delivery into other vessels. Preparation of solutions of $Cr(OH_2)_5Cl^{2+}$ and the $[Co(NH_3)_5Cl]Cl_2$ salt have also been described.[7] Purity of all complexes was checked by their visible absorption spectra. Stock solutions of ethylenediamine in $HClO_4$ were prepared from weighed amounts of 98% Eastman White Label ethylenediamine and reagent grade $HClO_4$. Small amounts of yellow impurities from the ethylenediamine were removed by stirring with activated charcoal and filtering. Nitrogen analysis by the Kjeldahl method showed that this procedure gave the proper ethylenediamine concentration. All other chemicals were reagent grade, and all water used was distilled and demineralized (ion content <1 ppm NaCl equiv).

Reaction Procedure.—With the aid of vacuum and N_2 inlets, *ca.* 10 ml of Cr^{2+} stock solution having a known total Cr concentration was transferred to vessel C (Figure 1). After attachment of C to the rest of the apparatus of Figure 1, the apparatus was flushed with N_2 and evacuated, and the Cr^{2+} stock solution was transferred to compartment A where it was taken to dryness to remove HCl (*i.e.*, to $CrCl_2$) by distillation under vacuum for 1.5 hr at 25° (the apparatus was three-fourths submerged in a water bath thermostated at 25.0 ± 0.1°) with vigorous stirring to prevent bumping (*ca.* 45 min required to reach apparent dryness). The volume of Cr(II) stock solution used was accurately determined by weighing before and after delivery to the reaction apparatus. The ethylenediamine solutions used for each experiment was prepared by addition of NaOH to solutions of en·$2HClO_4$ and dilution to a known final volume to give a total ethylenediamine concentration of 0.47 *F* ($\mu = 1.4$ *M*). The pH of each solution was measured at 25.0 ± 0.1° using a glass electrode connected to a Radiometer TTT-1a titrator equipped with a Radiometer PHA630Ta scale expander as a pH meter, standardized against commercial buffer solutions having errors of ±0.01 unit in the stated pH values. The initial chromium(II)–ethylenediamine solutions were made by adding 25.0 ml of the ethylenediamine solution to compartment B (Figure 1) and scrubbing with N_2 for 30 min, then delivering the solution through stopcock S_2 into compartment A containing dry $CrCl_2$, and stirring continuously until after the reaction was complete. A $Co(NH_3)_5Cl^{2+}$ solution (~6.0 m*F*) was then prepared by dissolving solid $[Co(NH_3)_5Cl]Cl_2$ in 50 ml of the ethylenediamine solution in a separate vessel, then transferring 25.0 ml of this solution into compartment B (giving a ~20% excess of Co(III) over the Cr(II) in compartment A), and flushing with N_2 for 15 min. After allowing 10 min for temperature equilibration, the $Co(NH_3)_5Cl^{2+}$ was rapidly delivered (<5 sec) into compartment A containing the rapidly stirred chromium(II)–ethylenediamine solution. The reactions are essentially instantaneous, but an additional 10 sec of reaction time was allowed before adding 10 ml of $HClO_4$ (of a concentration calculated to neutralize the NaOH added to the en·$2HClO_4$ solution) through stopcock S_1 from a reservoir attached in place of vessel C.

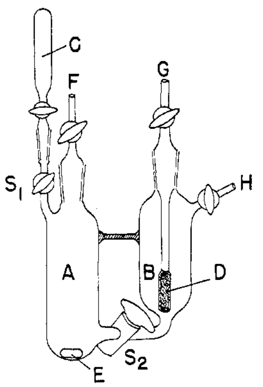

Figure 1.—Reaction apparatus (not to scale) used for preparing solutions for kinetic runs: A, 100-ml reaction compartment; B, 75-ml compartment for flushing reagents with N_2; C, 12-ml flask for weighing Cr^{2+} stock solution; D, gas dispersion tube; E, magnetic stirring bar; F, outlet to vacuum pump *via* Dry Ice trap; G, inlet for oxygen-free N_2; H, outlet to atmosphere.

Determination of Product Co(II).—A 5.00-ml aliquot of the above acidified infinite-time reaction solution was diluted to 50.00 ml and analyzed for Co(II) by the $CoCl_4{}^{2-}$ spectral method described earlier.[7] The presence of the Cr(III) species was shown not to interfere.

Determination of Cr(III) Product Distribution.—After the electron-transfer reactions are completed, the final acidified reaction solution contains the possible metal ion species $Co(OH_2)_6{}^{2+}$, $Cr(OH_2)_5Cl^{2+}$, the isomers of $Cr(en)(OH_2)_3Cl^{2+}$, and *cis*- and *trans*-$Cr(en)_2(OH_2)Cl^{2+}$ as possible reaction products,[11] in addition to excess $Co(NH_3)_5Cl^{2+}$ and the products of partial air oxidation of Cr(II) (*ca.* 10% of the total Cr, apparently resulting from leakage or incomplete removal of O_2).

It was found possible to determine the fraction of Cr(III) product present as $Cr(OH_2)_5Cl^{2+}$ by precipitation on addition of NaOH to neutralize half the acid present (giving a pH of ~7.5). About 95–100% of the $Cr(OH_2)_5Cl^{2+}$ was precipitated (probably as a "hydrous oxide") without precipitation of the other Cr(III) species, as was shown by NaOH treatment of known mixtures of $Cr(OH_2)_5Cl^{2+}$, magenta $Cr(en)(OH_2)_3Cl^{2+}$, and *cis*-$Cr(en)_2(OH_2)Cl^{2+}$ in 0.47 *F* en·$2HClO_4$. Trial determinations in such mixtures where the mole ratio of $Cr(OH_2)_5Cl^{2+}$ to total Cr was, respectively, 0.0, 0.1, 0.3, 0.4, 0.7, and 1.0 gave the correct values within a standard deviation of ±0.05. Although Cr(III) products formed by partial air oxidation of Cr(II) in the electron-transfer reaction solutions were also found to be quantitatively precipitated by the NaOH treatment, their amount could be determined (and substracted from the total Cr precipitated) by substracting from the total Cr in 50.0 ml of reaction solution the equivalents of Co(II) formed for 50.0 ml of reaction solution (equal to the equivalents of Cr(III) produced by electron-transfer reactions). Conceivably the initial Cr(III) products from air oxidation of Cr(II) could undergo an addition of en due to catalysis in the presence of Cr(II). To check this, a reaction was carried out at pH 6.6 (where nearly all Cr(II) exists as $Cr(en)^{2+}$ and $Cr(en)_2{}^{2+}$) with a 2:3 initial mixture of Cr(II) and air-oxidized Cr(III) product. There was no increase in the Cr(III) species containing ethylenediamine compared to reactions where

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[7] T. J. Williams and C. S. Garner, *Inorg. Chem.*, **9**, 2058 (1970).

[8] C. S. Garner and D. A. House, *Transition Metal Chem.*, **6**, 185 (1970).

[9] D. M. Tully-Smith, R. K. Kurimoto, D. A. House, and C. S. Garner, *Inorg. Chem.*, **6**, 1524 (1967).

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

[11] The monochloro product has been demonstrated for $Cr(OH_2)_5Cl^{2+}$ and $Cr(en)_2(OH_2)Cl^{2+}$ [6] and is therefore assumed for $Cr(en)(OH_2)_3Cl^{2+}$.

much smaller amounts of air-oxidized Cr(III) product (*ca.* 10% of the total Cr) were present.

Specifically, the procedure developed for determination of the $Cr(OH_2)_5Cl^{2+}$ content of the acidified infinite-time reaction solutions was as follows. A 50.0-ml aliquot of the solution was delivered into a fine-porosity fritted-glass filter funnel and cooled to *ca.* 5°; then 5.0 ml of 4.8 *F* NaOH was added to the solution in the filter funnel with stirring (this raised the temperature to *ca.* 10°). After the mixture was recooled to <5°, suction was applied for filtration. The precipitate was dissolved from the filter with 30 ml of 1.5 *F* $HClO_4$ and washed with H_2O into a 100-ml volumetric flask. The resulting solution was made up to 100 ml and analyzed for total Cr.[12]

An attempt was made to separate chromatographically the remaining Cr(III) products away from the Co^{2+} and excess $Co(NH_3)_5Cl^{2+}$ in the pH ~7.5 filtrate from the above precipitation and to determine the relative amounts of the mono(ethylenediamine)- and bis(ethylenediamine)chromium(III) complexes from the visible absorption spectrum of the acidified effluent. However, in the presence of the base found necessary to give a clean chromatographic separation of the Cr(III) species (apparently as hydroxo species of low charge) from the Co^{2+} and $Co(NH_3)_5Cl^{2+}$, some of the Cr(III) species partly hydrolyzed (*e.g.*, $Cr(en)(OH_2)_3Cl^{2+}$ partly hydrolyzed to $Cr(en)(OH_2)_4^{3+}$) and the spectrum of the acidified effluent was not easily interpretable. Therefore the pH ~7.5 filtrate was aged for 1.5 hr at 25° before the chromatography, since spectral scans as a function of time showed essentially no further spectral change was occurring after *ca.* 1 hr. This converted the chloromono(ethylenediamine) and chlorobis(ethylenediamine) complexes to more inert Cl-free mono-ethylenediamine and bis-ethylenediamine complexes which could survive the chromatographic separation (see below for tests of the aging procedure). The aged filtrate was added to 110 ml of cold 0.6 *F* $HClO_4$ and charged onto a 1-cm diameter × 7-cm cation-exchange column (H^+ Dowex AG50W-X8 resin, 100–200 mesh) operated at 2°. After the column was washed with 30 ml of H_2O, the Cr(III) species were moved down the column with 50 ml of 0.05 *F* NaOH–0.3 *F* $NaClO_4$; then 90 ml of 0.05 *F* NaOH–0.5 *F* $NaClO_4$ was used to elute the Cr(III) species into a 100-ml volumetric flask containing 10 ml of 6 *F* $HClO_4$. The spectrum of the resulting solution was scanned (700–340 nm) using a Cary Model 15 spectrophotometer and matched 10-cm silica cells (reference cell filled with water). An aliquot was analyzed for total Cr.[12] From the average molar extinction coefficient ϵ at 480 nm, the mole ratio of mono(ethylenediamine)- to bis(ethylenediamine)chromium(III) was calculated with the aid of an empirically determined plot (see below).

The entire procedure, including the aging procedure, was tested by running known mixtures of $Cr(en)(OH_2)_3Cl^{2+}$ and either *cis*- or *trans*-$Cr(en)_2(OH_2)Cl^{2+}$, of constant total Cr(III) concentration, as well as $Cr(en)(OH_2)_3Cl^{2+}$ and *cis*-$Cr(en)_2(OH_2)Cl^{2+}$ separately, through the whole procedure. With the *cis*-$Cr(en)_2(OH_2)Cl^{2+}$ complex alone, the acidified effluent from the chromatography had a visible absorption spectrum close to that of *cis*-$Cr(en)_2(OH_2)_2^{3+}$ (or the mainly *cis*-diaquo equilibrium mixture expected from isomerization of the labile $Cr(en)_2(OH_2)OH^{2+}$ product present at pH ~7.5). With $Cr(en)(OH_2)_3Cl^{2+}$ alone, the acidified effluent from the chromatography had a visible absorption spectrum like that of $Cr(en)(OH_2)_4^{3+}$ after it is subjected to similar basification and reacidification[13] (presumably generating a polymer). With the varying mixtures of $Cr(en)(OH_2)_3Cl^{2+}$ and *cis*- or *trans*-$Cr(en)_2(OH_2)Cl^{2+}$, the acidified chromatographic effluents exhibited isosbestic points at 428 (ϵ 22.9 ± 0.8) and 518 nm (ϵ 41.5 ± 1.3) (as do the actual processed reaction mixtures) in agreement with the isosbestic points obtained by superposition of the ϵ *vs.* λ plots for the separately processed $Cr(en)(OH_2)_3Cl^{2+}$ and *cis*-$Cr(en)_2(OH)_2Cl^{2+}$. The change in absorbance in the visible region for the processed synthetic mixtures was greatest at 480 nm ($\Delta\epsilon$ ~34–57). When a plot of ϵ at 480 nm for the known mixtures was made *vs.* the known initial mole fraction of $Cr(en)(OH_2)_3Cl^{2+}$ (defined as moles of latter divided by total moles of Cr(III)), a straight line was obtained with a standard deviation in the mole fraction of ±0.04, thus allowing the empirical determination of the Cr(III) product ratio of mono-ethylenediamine to bis-ethylenediamine product.

The efficiency of the chromatographic removal of Co^{2+} and $Co(NH_3)_5Cl^{2+}$ from the Cr(III) products, described above, was further checked by running Co^{2+} and $Co(NH_3)_5Cl^{2+}$ separately through the entire procedure, including the aging process; the amounts of the Co species not retained by the chromatographic column contributed only *ca.* 1% to the absorbance at 480 nm, and minor corrections were easily applied.

It may be noted here that the method used for determination of Cr(III) product distribution does not reveal whether $Cr(en)_2(OH_2)Cl^{2+}$ formed in the electron-transfer reaction has the cis or the trans configuration, since the method involves conversion at one point to $Cr(en)_2(OH)_2OH^{2+}$ which isomerizes relatively rapidly to an equilibrium isomeric mixture.

Results

The fraction by moles of Cr(III) products present in the electron-transfer reaction solution as $Cr(OH_2)_5Cl^{2+}$ ("mole fraction of $Cr(OH_2)_5Cl^{2+}$ product"), X_0, was determined for each reaction solution by dividing the equivalents of Cr(III) precipitated by NaOH (after correction for air oxidation of Cr(III), see Experimental Section) by the equivalents of Co(II) produced. Spectral analysis of the acidified Cr(III) effluent from the chromatographed aged filtrate from the precipitation of $Cr(OH_2)_5Cl^{2+}$ (see Experimental Section) allowed calculation of the mole fraction of mono(ethylenediamine)chromium(III) product, X_1', and mole fraction of bis(ethylenediamine)chromium(III) product, X_2', in this filtrate (X_1' and X_2' are defined as equivalents of the given product divided by total equivalents of Cr(III) in the filtrate). These mole fractions were converted to mole fractions X_1 and X_2 relative to total Cr(III) product in the electron-transfer reaction solution by multiplying by $(1 - X_0)$. The results of these determinations for mixtures from reactions at different pH values are shown in Table I.

TABLE I

MOLE FRACTIONS (X_n) OF Cr(III) PRODUCTS FROM ELECTRON-TRANSFER REACTIONS BETWEEN $Cr(en)_n^{2+}$ (n = 0–2) AND $Co(NH_3)_5Cl^{2+}$ AT 25.0 ± 0.1°[a]

No.	pH[b]	X_0[c]	X_1[c]	X_2[c]
1	5.79	0.38	0.52	0.10
2	5.80	0.36	0.50	0.14
3	5.93	0.29	0.55	0.16
4	5.96	0.26	0.58	0.16
5	6.20	0.10	0.64	0.26
6	6.20	0.11	0.65	0.24
7	6.22	0.06	0.69	0.25
8	6.28	0.00	0.68	0.32
9	6.55	0.00	0.56	0.44
10	6.58	0.00	0.58	0.42
11	6.58	0.00	0.54	0.46
12	6.76	0.00	0.31	0.69
13	6.76	0.00	0.36	0.64
14	7.25	0.00	0.00	1.00

[a] Reaction conditions: 0.47 *F* total en, μ = 1.4 *M* (controlled with $NaClO_4$), initial [Cr] ≈ 5 m*F* diluted to ~2.5 m*F* by mixing reactant solutions, *ca.* 20% excess $Co(NH_3)_5Cl^{2+}$ used over Cr(II). [b] Error in pH measurement is ±0.02 unit. [c] Error in X_n values is ±0.05; where the determined X_n values were less than 0.05 they are listed as 0.00.

Discussion

The electron-transfer reaction between $Co(NH_3)_5Cl^{2+}$ and the Cr(II) species in aqueous ethylenediamine at various pH values is given by the general equation

$$Cr(en)_n^{2+} + Co(NH_3)_5Cl^{2+} \xrightarrow{k_n} Cr(en)_n(OH_2)_{5-2n}Cl^{2+} + Co^{2+} + 5NH_3 \quad (1)$$

where n = 0–2. The reaction for each value of n

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[12] L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

[13] R. F. Childers, Jr., K. G. Vander Zyl, Jr., D. A. House, R. G. Hughes, and C. S. Garner, *ibid.*, **7**, 749 (1968).

is governed by the general rate law

$$d[\mathrm{Cr(en)}_n(\mathrm{OH_2})_{5-2n}\mathrm{Cl}^{2+}]/dt = k_n[\mathrm{Cr(en)}_n{}^{2+}][\mathrm{Co(NH_3)_5Cl}^{2+}] \quad (2)$$

If one defines by eq 3 and 4, respectively, reactant and product mole fractions relative to the total Cr concentration, $[\mathrm{Cr}]_t$ (corrected for air-oxidized Cr^{2+}),

$$f_n = [\mathrm{Cr(en)}_n{}^{2+}]/[\mathrm{Cr}]_t \quad (3)$$

$$X_n = [\mathrm{Cr(en)}_n(\mathrm{OH_2})_{5-2n}\mathrm{Cl}^{2+}]/[\mathrm{Cr}]_t \quad (4)$$

the rate law can be written as

$$dX_n/dt = k_nf_n[\mathrm{Co(NH_3)_5Cl}^{2+}] \quad (5)$$

Values for f_n were calculated for zero reaction time (*i.e.*, setting $[\mathrm{Cr}]_t$ = initial [Cr(II)]) from constants published for the equilibria

$$\mathrm{enH}_n{}^{n+} \overset{K_{an}}{\rightleftharpoons} \mathrm{enH}_{n-1}{}^{(n-1)+} + \mathrm{H}^+ \quad (6)$$

$$\mathrm{Cr(en)}_{n-1}{}^{2+} + \mathrm{en} \overset{K_{fn}}{\rightleftharpoons} \mathrm{Cr(en)}_n{}^{2+} \quad (n = 1, 2) \quad (7)$$

at 25° and $\mu = 1.4\ M$.[14] The constants used were $pK_{a1} = 10.06$, $pK_{a2} = 7.44$, $pK_{f1} = -5.15$, and $pK_{f2} = -4.04$. The initial mole fractions of the reactant species, f_n, were calculated assuming that $[\mathrm{Cr}]_t$ is much smaller than the total ethylenediamine concentration, $[\mathrm{en}]_t$, which is justified for pH values used, since $[\mathrm{Cr}]_t < 0.01[\mathrm{en}]_t$. The equations required to calculate f_n show that f_n is independent of the total [Cr(II)] and dependent only on the free ethylenediamine concentration which in turn is dependent only on $[\mathrm{H}^+]$. Calculated values for f_n at $t = 0$ under the various reaction conditions for which X_n values were determined for infinite reaction time (Table I) are shown in Table II. A qualitative comparison of the initial reactant fractions and the product fractions clearly indicates that reaction with Cr(II) species having coordinated ethylenediamine is favored. It also appears that Cr(II) species with two ethylenediamine ligands react faster than those with only one.

TABLE II

CALCULATED INITIAL REACTANT MOLE FRACTIONS (f_n) AND RATE CONSTANT RATIOS FOR ELECTRON-TRANSFER REACTIONS BETWEEN $\mathrm{Cr(en)}_n{}^{2+}$ (n = 0–2) AND $\mathrm{Co(NH_3)_5Cl}^{2+}$ AT 25.0 ± 0.1°[a]

No.	f_0	f_1	f_2	k_0/k_1	k_1/k_2
1	0.928 ± 0.007	0.072 ± 0.006	0.0004 ± 0.0001	0.038	0.030
2	0.924 ± 0.007	0.076 ± 0.007	0.0005 ± 0.0001	0.038	0.023
3	0.870 ± 0.011	0.128 ± 0.011	0.0015 ± 0.0003	0.056	0.039
4	0.854 ± 0.012	0.144 ± 0.011	0.0019 ± 0.003	0.056	0.050
5	0.654 ± 0.026	0.333 ± 0.024	0.0134 ± 0.0025	0.072	0.098
6	0.654 ± 0.026	0.333 ± 0.024	0.0134 ± 0.0025	0.077	0.11
7	0.638 ± 0.022	0.348 ± 0.020	0.0149 ± 0.0022	0.044	0.11
8	0.572 ± 0.023	0.406 ± 0.020	0.0226 ± 0.0031	...	0.12
9	0.267 ± 0.020	0.620 ± 0.008	0.1135 ± 0.0125	...	0.23
10	0.240 ± 0.021	0.630 ± 0.007	0.1300 ± 0.0140	...	0.28
11	0.240 ± 0.021	0.630 ± 0.007	0.1300 ± 0.0140	...	0.24
12	0.108 ± 0.011	0.616 ± 0.009	0.2760 ± 0.0190	...	0.20
13	0.108 ± 0.011	0.616 ± 0.009	0.2760 ± 0.0190	...	0.25
14	0.006 ± 0.001	0.240 ± 0.010	0.7539 ± 0.0190	...	...

[a] The numbered rows and reaction conditions correspond to those of Table I. The mole fractions of $\mathrm{Cr(en)}_n{}^{2+}$ species calculated for zero reaction time are denoted by f_n with the errors calculated solely from the ±0.02 pH errors. The values of the rate constant ratios, k_n/k_{n+1}, were calculated from eq 8 of the Discussion; the errors associated with these values are large because of individual errors in final X_n and initial f_n values and appear to be *ca.* ±30% for k_0/k_1 and k_1/k_2 (no. 9–13) with the possible error in k_1/k_2 increasing to at least 60–70% (no. 1–4) as pH decreased.

A quantitative treatment of the data may be possible if two conditions are approximately satisfied. The first is the approximation that the ratios f_n/f_{n+1} (n = 0, 1) remain constant as the amount of Cr(II) in solution is reduced by the reaction. Although the f_n values are independent of [Cr(II)], this assumption also requires that the rates of equilibria (eq 6 and 7) adjustment be much larger than the rates of electron transfer. That this may be approximately correct is suggested by the extremely rapid rate of Cr(II)–water exchange.[15] More convincingly, it has been found that when strong ethylenediamine solutions of $\mathrm{Co(NH_3)_5Cl}^{2+}$ (pH ~9.8) are mixed with acidic solutions of $\mathrm{Cr(OH_2)_6}^{2+}$, the products contain at least 80% of the Cr(III) formed as the bis-ethylenediamine species, apparently mainly as *trans*-$\mathrm{Cr(en)_2(OH_2)Cl}^{2+}$.[6] The second condition requires that the mixing process does not interfere with the analysis of the data. These extremely rapid reactions must occur to a significant extent during the time of mixing and therefore at the interface of the two solutions being mixed, with concentration gradients for the Cr(II) and $\mathrm{Co(NH_3)_5Cl}^{2+}$. All other experimental parameters (*i.e.*, temperature, pH, ionic strength, and total ethylenediamine concentration) should not be disturbed during the mixing since they are identical for the two solutions used in each experiment. If eq 3–5 are considered in terms of individual volume elements which are sufficiently small to make the defined concentrations $[\mathrm{Cr}]_t$ and $[\mathrm{Co(NH_3)_5Cl}^{2+}]$ uniform in each volume element during the mixing of the solutions, then for each volume element eq 5 with $n = n$ can be divided by eq 5 with $n = n + 1$, with integration of the result giving

$$k_n/k_{n+1} = (X_n/X_{n+1})/(f_n/f_{n+1}) \quad (n = 0, 1) \quad (8)$$

From the previous assumption regarding the rapid rate of equilibria adjustment, the ratio f_n/f_{n+1} will remain constant and the same for all volume elements and independent of [Cr(II)] since this ratio then depends only on the parameters (temperature, pH, ionic strength, and total ethylenediamine concentration) which remain constant and the same for all volume elements at all times. The term X_n/X_{n+1} in eq 8 is therefore constant and the same for all volume elements at any time (k_n/k_{n+1} being constant by definition) and is independent of $[\mathrm{Cr}]_t$, $[\mathrm{Co(NH_3)_5Cl}^{2+}]$, and time. The ratio X_n/X_{n+1} is therefore that measured for the bulk reaction solution at $t = \infty$.

Using the measured and calculated values for X_n and f_n in Tables I and II, respectively, one obtains the rate constant ratios k_0/k_1 and k_1/k_2 shown in Table II, which (from eq 8) should have approximately constant values as the pH is changed. Unfortunately the ratios of mole fractions involved are very sensitive to errors in the individual values, particularly when any of the mole fractions involved is out of the range 0.1–0.9. The experimental error appears to be sufficient to account for variations in the k_0/k_1 values listed in Table II, although there appears to be a regular increase in the values (except no. 7). The change in k_1/k_2, however, seems to be outside the error limits. Although there is a general increase in k_1/k_2 with increasing pH when all runs are considered,

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[14] R. L. Pecsok and J. Bjerrum, *Acta Chem. Scand.*, **11**, 1419 (1957).

[15] R. L. Connick, "Symposium on Relaxation Techniques," Buffalo, N. Y., June 1965; cited in F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 152.

reasonably constant values were found at pH >6.5 (no. 9–13), and k_1/k_2 values confined to these pH values are used below in obtaining values of k_1 and k_2. Among the possible reasons for this large change in k_1/k_2 over the entire pH range are unaccounted for errors in K_{an} or K_{tn}, which could have a greater overall effect where f_n is small, or the possibility that the amount of released NH_3 from the electron-transfer reaction is sufficiently large (~3% of the total ethylenediamine) to disturb the equilibria significantly. Certainly the errors in X_2 and especially in f_2 values at low pH used to obtain k_1/k_2 for runs 1–4 are very large and make the values of k_1/k_2 for these runs highly uncertain. Possible competition by Cr(II)–Cr(III) reactions with the Cr(II)–$Co(NH_3)_5Cl^{2+}$ reactions should have a negligible effect in altering product distributions inasmuch as rate constants at 25° for the former should be $<10^2\ M^{-1}\ sec^{-1}$ for these conditions (estimated from the $Cr(NH_3)(OH_2)_5Cl^{2+}$–Cr_{aq}^{2+} reaction[7] and allowing for additional hydroxo bridging ligands), which is very small compared to the rate constants for the Cr(II)–$Co(NH_3)_5Cl^{2+}$ reactions ($>10^6\ M^{-1}\ sec^{-1}$). Reasonably reliable estimates of the rate constant ratios and their standard errors are calculated from Table II as $k_0/k_1 = 0.055 \pm 0.015$ and $k_1/k_2 = 0.25 \pm 0.03$ (no. 9–13). Using the previously reported[3] rate constants for k_0, a value interpolated for $\mu = 1.4\ M$, namely, $k_0 = (2.2 \pm 0.5) \times 10^6\ M^{-1}\ sec^{-1}$ at 25°, yields the rate constants $k_1 = (4.0 \pm 2.3) \times 10^7\ M^{-1}\ sec^{-1}$ and $k_2 = (1.6 \pm 0.8) \times 10^8\ M^{-1}\ sec^{-1}$ at 25°.

The accepted model for the activation process in this kind of electron-transfer reaction is that electronic states in the activated complex are matched by changing bond distances and therefore the ligand fields of the reactant ions.[16] This work supports the evidence that ligand motion on the Cr(II) center probably occurs[6] since the increased rates can be related to increases in the inherent ligand field strength of the amine ligands relative to H_2O (according to the spectrochemical series). A higher initial ligand field would require less bond shortening and therefore a lower activation energy. The rate increases found (*i.e.*, an increase by a factor of *ca.* 6–8 for each amine substitution of H_2O) are similar to rate *decreases* found for analogous ligand field strength changes on Cr(III) in the $Cr(NH_3)_n(OH_2)_{5-n}Cl^{2+}$–$Cr_{aq}^{2+}$ electron-exchange reaction.[7] The observation that ligand field strength changes around Cr(III) and Cr(II) have an opposite effect on rate in these electron-transfer reactions offers some experimental support of the proposal[16] that bonds are shortened for the reductant, Cr(II), and lengthened for the oxidant, Cr(III), in the formation of activated complexes for these types of electron-transfer reactions.

This work is also directly concerned with the question of whether the rapid rates for Cr(II)–Co(III) electron-transfer reactions are governed by the rate of substitution on Cr(II) or by changes in the Cr(II) coordination sphere.[2,17] The regular increase in rate with increased ligand field strength on Cr(II) is more easily rationalized on the basis of the latter idea. The lability of water ligands on Cr(II) is certainly great enough to accommodate rates faster than the suggested upper limit, *ca.* $10^7\ M^{-1}\ sec^{-1}$,[17] for the rate constants of these reactions. Indeed the rate constant for reaction of $Cr(en)_2^{2+}$ with $Co(NH_3)_5Cl^{2+}$ is about an order of magnitude larger than this suggested upper limit. While there does not seem to be a convincing reason for proposing that the substitution of ethylenediamine on Cr(II) would favor the bridging process, the rate increase over the previously apparent upper limit can be accounted for by the suggestion of Diaz and Taube that the limiting factor is a change in the symmetry of the coordination sphere of Cr(II) from tetragonal to approximately octahedral. With ligands such as ethylenediamine having a larger ligand field potential in the Cr(II) coordination sphere less motion of the ligands would be required to reach the same state3 as for the aquo complex.

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[16] L. E. Orgel, "Report of the Tenth Solvay Conference," Brussels, 1956, p 286.

[17] H. Diaz and H. Taube, *Inorg. Chem.*, **9**, 1304 (1970); see particularly the discussion in footnote 34 of this paper.