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Chromium(II)-Catalyzed Aquation of the Fluoroisothiocyanatotetraaquochromium(III) Ion[1]

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The kinetics of the chromium(II)-catalyzed aquation of the fluoroisothiocyanatotetraaquochromium(III) ion have been investigated. The reaction proceeds to about 80% completion forming predominantly fluoropentaaquochromium(III) ion. An unusual rate law for Cr(III)–Cr(II) reactions of the form $d(\ln [Cr(\mathit{N}CS)F^+])/dt = a[Cr^{2+}]/(1 + b[Cr^{2+}])$ has been observed in the temperature range 15–35 °C and $\sum[ClO_4^-] = 1.0$ M, where $a = 5.38\ (\pm 0.04) \times 10^{-2}\ M^{-1}\ s^{-1}$ and $b = 1.9 \pm 0.3\ M^{-1}$ at 25 °C. The rate law has been interpreted in terms of a mechanism involving the equilibrium formation of an unproductive intermediate $FCr(NCS)Cr^{3+}$ followed by a fluoride ion bridged, rate-determining reaction between $Cr(\mathit{N}CS)F^+$ and Cr^{2+}. Alternate mechanisms are also discussed.

Introduction

The chemistry of disubstituted tetraaquochromium(III) ions has been rather well documented in the literature for those species involving identically substituted groups, i.e., $Cr(H_2O)_4X_2^{2+}$.[2] By contrast, however, progress in the study of the chemistry for mixed disubstituted species, $CrXY^{n+}$, has been limited due largely to difficulties in their preparation. Taube[3] prepared the first such complex in noting the effect of added pyrophosphate ion on the $Co(NH_3)_5Cl^{2+}$–Cr^{2+} reaction. A chromium(III) complex containing both chloride and pyrophosphate ions was isolated. Earley and Gorbitz[4] repeated this work and formulated its composition as $Cr(H_2O)_n(P_2O_7H_2)Cl$, where $n \leq 4$. Subsequently, Manning and Jarnagin[5] reported that in the presence of chloride ion the $Co(NH_3)_5FumH^{2+}$–Cr^{2+} reaction yielded a substantial fraction of a complex containing both fumarate and chloride ions. More recently, Brown and Pennington[6] reported the preparation, aquation, and linkage isomerization of $Cr(H_2O)_4(\mathit{S}CN)(\mathit{N}CS)^+$, and Pennington[7] reported some general strategies for the preparation of mixed-ligand complexes. Vanderheiden and King[8] have since isolated a complex, $Cr(DMSO)I^{2+}$, from aqueous dimethyl sulfoxide and separated the geometric isomers by ion-exchange chromatography. Finally, Schilt and Schaap[9] reported that the anation of $Cr\mathit{C}N^{2+}$ by thiocyanate ion produces $Cr(\mathit{N}CS)(\mathit{C}N)^+$.

In addition to the above direct observations of mixed disubstituted tetraaquochromium(III) ions there have been numerous studies in which such species have been postulated as reaction intermediates. Thus the spontaneous[10,11] and chromium(II)-catalyzed[12,13] aquations, as well as the formation reactions,[14] of monosubstituted pentaaquochromium(III) ions exhibit kinetic terms (inverse first order in hydrogen ion) which are interpreted in terms of $Cr(OH)X^+$ species. Ardon[15] observed the formation of ~15% $CrCl^{2+}$ or $CrBr^{2+}$ among the products of aquation of CrI^{2+} in HCl or HBr media, assuming that the replacement occurs only by the acid-dependent path. Whereas Ardon interpreted his results in terms of an SN1 mechanism, Moore, Basolo, and Pearson[16] suggested that the substitution products arose from intermediates of the type $CrIX^+$. Carey, Jones, and Swaddle[17] extended Ardon's observations to the $CrBr^{2+}$ and $Cr\mathit{O}NO_2^{2+}$ complexes. Their results, taken together with the results of Haim and Sutin[18] for $Cr\mathit{S}CN^{2+}$, rule out the sole operation of an SN1 (or dissociative) mechanism for the aquation/anation reactions since the yields of $CrCl^{2+}$ vary with the substituent on chromium(III). Moreover they noted a rough linear free energy relationship of slope >0.9 for a plot of log k_{-1} vs. log Q (where k_{-1} and Q are the rate constant for the inverse acid path and the concentration quotient) for the aquations of CrX^{2+}, a result implying a dissociative interchange mechanism for aquations of $Cr(OH)X^+$ species. The observed slope is markedly greater than the value of 0.56 observed by Swaddle and Guastalla[19] for the acid-independent path, where an associative interchange mechanism is postulated. Pennington and Haim[13] also postulated the formation of $CrIX^+$ species in the chromium(II)-catalyzed substitutions of iodide ion in CrI^{2+} by fluoride, chloride, and bromide ions.

Anet and Leblanc[20] and Kochi and Buchanan[21] have postulated the formation of several benzylchromium(III) intermediates of the type $Cr(Bzl)X^+$. More recently, Matts and Moore[22] postulated the formation of some mixed-ligand O-bonded nitrito complexes in the nitrogen(IV)-catalyzed aquations of aquochromium(III) species. Similarly Carlyle and King[23] examined the sulfur(IV)-catalyzed aquations of a variety of chromium(III) complexes but they, like Matts and Moore,[22] were unable to detect the analogous labile intermediates. Scott, Weeks, Bracken, and King[24] postulated the existence of $Cr(DMSO)I^{2+}$ in a study of the aquation of CrI^{2+} in aqueous dimethyl sulfoxide, and the complex was subsequently isolated.[8] In the present work we wish to report our results on the preparation and chromium(II)-catalyzed aquation of the $Cr(\mathit{N}CS)F^+$ ion.

Experimental Section

Materials. Chromium(II) perchlorate solutions were prepared, stored, and analyzed as described previously.[12] Solutions of the air-sensitive material were transfered by means of hypodermic syringe techniques.

Sodium perchlorate solutions were prepared by neutralization of standard perchloric acid solutions with anhydrous sodium carbonate. Solutions of sodium thiocyanate were prepared from the reagent grade

Table I. Stoichiometry of the $Cr(\mathit{N}CS)F^+$–Cr^{2+} Reaction[a]

Initial mmol of $Cr(\mathit{N}CS)F^+$	mmol of CrF^{2+}	Final mmol of $Cr(\mathit{N}CS)F^+$	mmol of $Cr\mathit{N}CS^{2+}$	mmol of Cr^{2+}	mmol of Cr blank	mmol of NCS^- blank	Oxidant
0.110	0.086 (2) 78%	0.020[b] 18%	0.0048 (3) 4%	0.182	0.0114 (14)[c]	0.0045 (5)[c]	$Co(NH_3)_5OxH^{2+}$
0.100	0.0805 (15) 81%	0.012[b] 12%	0.0073 (4) 7%	0.165	0.0109 (18)[c]	0.0016 (4)[c]	$FeOx^+$
0.110	0.0804[b] 79%	0.0206 (2) 21%		0.182	0.0025 (5)[d]		O_2 (air)

[a] Each entry is the average of duplicate experiments with average deviations in parentheses on measured quantities only. [b] Obtained by difference of initial mmol of $Cr(\mathit{N}CS)F^+$ and mmol of CrF^{2+} and $Cr\mathit{N}CS^{2+}$. [c] Correction for 2+ fraction for Cr^{2+} quenching. [d] Correction for 1+ fraction for Cr^{2+} quenching.

salt and analyzed as $FeNCS^{2+}$ according to the method of Haim and Sutin.[18]

Triply distilled water was used to prepare all solutions involved in the kinetic and stoichiometric studies.

The ion-exchange resin, Dowex 50W-X8 (50–100 mesh, H^+ form), was treated as described earlier[12] to remove impurities.

$[Co(NH_3)_5F](NO_3)_2$ was prepared by the method of Basolo and Murmann[25] except that $[Co(NH_3)_5H_2O](ClO_4)_3$ was used in place of $[Co(NH_3)_5CO_3]NO_3$. The nitrate salt was converted to the perchlorate salt by dissolving the former in a minimum of water and adding a saturated sodium perchlorate solution until no further precipitate formed. The precipitate was filtered and washed successively with ice-cold water, 95% alcohol, and ether and then dried for 1 h at 90 °C.

Solutions of $Cr(\mathit{N}CS)F^+$ ion were prepared by treating an equimolar solution of chromium(II) perchlorate and sodium thiocyanate with a saturated solution of $[Co(NH_3)_5F](ClO_4)_2$ containing a 10–20% excess of the salt and sufficient acid to neutralize the ammonia released and to leave the solution about 0.1 M in acid. The reaction was carried out with rapid stirring at 0 °C under an atmosphere of argon. The resulting mixture was diluted tenfold and ion exchanged by Dowex 50W-X8 resin. The resin was washed with water until the effluent was free of thiocyanate ion (by $FeNCS^{2+}$ test), and the complex was eluted with either 0.1 M $HClO_4$ or 0.1 M $NaClO_4$ containing 0.01 M $HClO_4$. After the identity of the complex ion was established, it was eluted with $HClO_4$–$NaClO_4$ solutions containing 1.3 M total perchlorate ion to yield more concentrated solutions of the complex ion. Extensive, though unsuccessful, efforts were made to effect separation of the anticiptated cis and trans isomers by cation-exchange chromatography.

Analyses. The total chromium concentration of complex ion solutions was determined spectrophotometrically after oxidation of an aliquot to CrO_4^{2-} in alkaline peroxide by the method of Haupt.[26] Thiocyanate ion concentrations were determined as described above after treatment of an aliquot of the complex ion solution with base (to release both fluoride and thiocyanate ions) followed by reacidification. For a second aliquot of the above solution fluoride ion was determined potentiometrically using a Coleman Model 3-803 fluoride ion electrode in a 1 M sodium acetate–acetic acid system. A calibration curve was prepared with standard sodium fluoride solutions and the method of analysis was verified by treatment of a standard CrF^{2+} solution in the same manner as the $Cr(\mathit{N}CS)F^+$.

Stoichiometry. Experiments performed to establish the stoichiometry of the $Cr(\mathit{N}CS)F^+$–Cr^{2+} reaction were carried out in serum bottles containing the desired volumes of $Cr(\mathit{N}CS)F^+$, perchloric acid, and sodium perchlorate solutions. The bottles were stoppered with self-sealing rubber septa and deaerated with prepurified argon. An aliquot of chromium(II) solution was then injected via a hypodermic syringe. After the time necessary for complete reaction, usually several hours at the concentrations of chromium(II) used, the chromium(II) was oxidized to chromium(III) by molecular oxygen (in air) or by $Co(NH_3)_5C_2O_4H^{2+}$ or $FeC_2O_4^+$ for the identification of the 1+ or 2+ charged reaction products, respectively. (See Discussion.) The resulting solutions were then diluted fivefold and percolated through Dowex 50W-X8 ion-exchange columns. The columns were rinsed with 0.1 M perchloric acid to remove any species of 1+ charge held by the resin. The original effluent and the rinse solutions were combined for analysis. The 2+ fraction was then eluted with 1 M perchloric acid and retained for analysis. Products of charge greater than 2+ were oxidized directly from the resin as CrO_4^{2-} and analyzed spectrophotometrically. All solutions were analyzed by visible and ultraviolet spectra and for total chromium content. The 2+ fractions were also analyzed for thiocyanate ion. Appropriate blank experiments were run for each type of quenching reaction.

Kinetics. Reaction vessels were 5-cm cylindrical spectrophotometric cells capped with self-sealing septa. Solutions of $Cr(\mathit{N}CS)F^+$, perchloric acid, sodium perchlorate, and triply distilled water were pipetted into the cell which was then capped and deaerated. Following the temperature equilibration of the cell contents, the requisite volume of chromium(II) was injected and the absorbance change followed at 415 nm employing a Cary 14 recording spectrophotometer. All kinetic runs were carried out at constant (0.598 M) acidity at 15, 25, and 35 °C and $\sum[ClO_4^-] = 1.0$ M. Semilogarithmic plots of $A_t - A_\infty$ were linear for greater than 2 half-lives, where A_t and A_∞ are the absorbances at time t and after 8–10 half-lives, respectively. Data plots were not extended beyond 2–3 half-lives due to the small values of $A_t - A_\infty$.

Results

Preparation and Analysis of the $Cr(\mathit{N}CS)F^+$ Ion. The reaction of excess $Co(NH_3)_5F^{2+}$ with a 1:1 mole ratio of Cr^{2+}:NCS^- yields 40 ± 10% $Cr(\mathit{N}CS)F^+$ and 60 ∓ 10% CrF^{2+} based upon the amount of chromium(II) consumed. Maximum yields of $Cr(\mathit{N}CS)F^+$ were obtained by the dropwise addition of the chromium(II) thiocyanate solution to a rapidly stirred, saturated solution of $Co(NH_3)_5F^{2+}$ near 0 °C. Duplicate analyses of the $Cr(\mathit{N}CS)F^+$ species yielded a Cr:NCS:F ratio of 1.00:0.98 (±0.03):0.99 (±0.03). The complex exhibited absorption maxima (ϵ, $M^{-1}\ cm^{-1}$) at 587 (29.0), 415 (25.7), 261 ($2.6_2 \times 10^3$), and 211 nm ($8.7_3 \times 10^3$).

In Table I are presented the results of experiments performed to establish the stoichiometry of the $Cr(\mathit{N}CS)F^+$–Cr^{2+} reaction. The major features of the stoichiometry are these. First, CrF^{2+} is formed in approximately 80% yield and, second, there is about 20% $Cr(\mathit{N}CS)F^+$ remaining at the conclusion of the reaction. A small amount (4–7%) of $Cr\mathit{N}CS^{2+}$ is also formed. The stoichiometry is thus adequately represented by the equation

$$Cr(\mathit{N}CS)F^+\ (20\%) \overset{Cr^{2+}}{\rightleftharpoons} CrF^{2+}\ (80\%) + NCS^- \tag{I}$$

Substantial difficulty was encountered in the stoichiometric experiments due to the necessity of oxidizing the chromium(II) in the presence of free thiocyanate ion. No single oxidant was found which would allow direct analyses of both 1+ and 2+ charged products. Therefore, when the 2+ fraction was to be analyzed, either of two oxidants, $Co(NH_3)_5OxH^{2+}$ or $FeOx^+$, was used to quench Cr^{2+}. Principally $CrOx^+$ (or $CrOx(\mathit{N}CS)$) is formed so that ion exchange of the product solution allows for analysis of the 2+ products with only minor chromium and thiocyanate ion corrections from the quenching process (cf. columns 6 and 7). When $FeOx^+$ was used, iron(II) was reoxidized to iron(III) with peroxydisulfate prior to the ion-exchange procedure. When the 1+ product fraction was to be analyzed, air was used as the quenching agent. Only the 1+ product was recovered in the ion-exchange procedure since substantial amounts of $Cr\mathit{N}CS^{2+}$ were formed upon air quenching Cr^{2+}. The blank corrections never amounted to

Table II. Kinetic Experiments at $\Sigma[ClO_4^-] = 1.0$ M^a for the Reaction $Cr(NCS)F^+ + Cr^{2+} \rightleftharpoons CrF^{2+} + NCS^- + Cr^{2+}$

Expt no.	Temp, °C	$10^2[Cr^{2+}]$, M	10^3k_{obsd}, s^{-1}	10^2k^{2d}, M^{-1} s^{-1}
1	15.0	1.35	0.313	2.32
2	15.1	1.35	0.313	2.32
3	15.0	2.02	0.434	2.15
4	15.0	3.31	0.695	2.10
5	15.0	5.64	1.10	1.95
6	15.1	9.94	2.05	2.06
7	15.1	11.3	2.23	1.97
8	25.0	1.35	0.720	5.33
9	25.0	2.02	1.06	5.25
10	24.9	3.31	1.70	5.13
11	25.0	4.04	1.98	4.90
12	25.1	5.64	2.81	4.63
13	25.2	9.94	4.60	4.63
14	25.1	9.94	4.67	4.70
15	25.0	11.3	5.15	4.55
16	35.1	1.35	1.60	11.8
17	35.1	3.31	3.68	11.1
18	35.1	5.64	6.00	10.6
19	35.1	9.94	10.3	10.4
20	34.9	11.3	11.7	10.4

[a] $[Cr(NCS)F^+] = 9.05 \times 10^{-3}$ M; $[H^+] = 5.98 \times 10^{-1}$ M.

more than 12% of the initial amounts of $Cr(NCS)F^+$ even though the amounts of Cr^{2+} quenched were in nearly twofold molar excess.

Since the individual kinetic runs were clearly pseudo first order for greater than 2 half-lives, the second-order rate constants were calculated for each experiment from the relation $k_{obsd} = k^{2d}[Cr^{2+}]$. In Table II are presented the results of these experiments. An examination of columns 3 and 5 for entries 8–15 indicate that k^{2d} decreases with increasing chromium(II) concentration, suggesting that $k_{obsd} = a\cdot[Cr^{2+}]/(1 + b[Cr^{2+}])$. Rearranging the latter expression for k_{obsd} yields a linear equation

$$1/k_{obsd} = 1/a[Cr^{2+}] + b/a \tag{II}$$

A plot of $1/k_{obsd}$ vs. $1/[Cr^{2+}]$ for the data at 25 °C is excellently linear, confirming the proposed dependence on the chromium(II) concentration. Similar graphs for the data at 15 and 35 °C are also linear except for the points represented by the lowest chromium(II) concentration. From a linear least-squares fit of the data the values of a and b were determined from the slopes and intercepts to be $(5.46 \pm 0.03) \times 10^{-2}$ M^{-1} s^{-1} and 2.0 ± 0.3 M^{-1}, respectively, at 25 °C, $(2.20 \pm 0.05) \times 10^{-2}$ M^{-1} s^{-1} and 1.2 ± 0.6 M^{-1} at 15 °C, and $(1.22 \pm 0.02) \times 10^{-1}$ M^{-1} s^{-1} and 2.1 ± 0.5 M^{-1} at 35 °C. The errors given are standard errors as defined by Squires,[27] and it is noteworthy that there are substantial errors in the intercepts.

It may be noted that the function $k_{obsd} = k_0 + k[Cr^{2+}]$ also fits our data fairly well. Several experiments were performed to detect the k_0 path, implying spontaneous aquation, without success. Thus, spectral scans of reaction solutions at the same acidity, but less the catalyst, exhibit *no* changes in absorbance at 35 °C for periods in excess of 7 half-lives for the catalyzed reaction at the lowest $[Cr^{2+}]$ nor upon standing overnight at room temperature. We therefore reject the binomial-type rate law.

Activation parameters for the rate constants were derived from the slopes of Arrhenius plots and the equations $E_a = \Delta H^\ddagger + RT$ and $k = (\kappa RT/N_0h)\exp(-\Delta H^\ddagger/RT)\exp(\Delta S^\ddagger R)$,[28] assuming $\kappa = 1$ and taking $T = 298$ K. Values of ΔH and ΔS for the concentration quotients were derived graphically from the relation $2.30 \log Q = -\Delta H/RT + \Delta S/R$. Individual rate constants and concentration quotients were weighted according to the inverse square of their fractional standard error (FSE)[27] and normalized to the least precise point.

Table III. Summary of Kinetic and Thermodynamic Parameters for Mechanisms A and B in the Reaction of $Cr(H_2O)_4(NCS)F^+$ with Cr^{2+}

	Constant (25 °C, $\Sigma[ClO_4^-] = 1.0$ M)	$\Delta H^\ddagger$ (ΔH),^{a} kcal/mol	$\Delta S^\ddagger$ (ΔS),^{a} eu
Q_1	1.9 (3) M^{-1}	3.0 (5)	+11 (2)
k_2	5.38 (4) × 10^{-2} M^{-1} s^{-1}	14.6 (2)	−15.4 (8)
Q_3	1.9 (3) M^{-1}	2.9 (3)	+11 (1)
k_4	2.9 (4) × 10^{-2} s^{-1}	11.6 (5)	−27 (2)

[a] $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for kinetic entries; ΔH and ΔS for equilibrium entries.

Standard errors in the slopes and intercepts of the various linear plots were calculated employing the same weighting factors used in making the given plot. In order to minimize the errors in Q_1 and Q_3 (obtained from b and a), the values of k_2 and k_4 were reevaluated at each temperature from the least-squares fit of the Arrhenius plot. In Table III is presented a summary of the various rate constants, equilibrium quotients, and their associated activation and thermodynamic parameters.

Discussion

From the Results it is clear that major features of the stoichiometry are as follows: (1) only about 80% of the original complex reacts; (2) the dominant chromium(III) product is CrF^{2+}. A small (4–7%) amount of $CrNCS^{2+}$ is also formed. At least two plausible hypotheses could account for observation 1. First, since the complex ion was produced in an unspecified isomeric composition, one of the isomers in ~20% abundance could be unreactive toward the chromium(II) on the time scale of the more reactive one. If the statistical isomeric distribution resulted from the reaction used to prepare $Cr(NCS)F^+$, the trans isomer would be implicated as the unreactive species. DeChant and Hunt[29] have presented definitive evidence to support the contention[30] that stretching of a Cr–O bond is associated with a special rate-enhancing effect of water trans to the bridging group in chromium(II)–chromium(III) electron-transfer reactions. In the present case assignment of *cis*-$Cr(NCS)F^+$ (with water trans to fluoride ion) as the more reactive isomer is not inconsistent with the above arguments.

Alternatively it is possible that the $Cr(NCS)F^+$ species possesses some thermodynamic stability *relative to aquochromium(III) and the free ions*. Both CrF_2^+ and $Cr(NCS)_2^+$ are known[31-33] to possess some stability with formation quotients of 3.8×10^7 M^{-2} (25 °C, $\mu = 0.5$ M)[31] and 9.6×10^2 M^{-2} (25 °C, $\mu = 1$ M),[32] respectively. An approximate formation constant Q_{form} can be obtained for the mixed-ligand complex using the formation quotient of CrF^{2+} (from Cr^{3+} and HF),[31] K_{HF},[31] and the stoichiometric results (assuming that the system reaches equilibrium). The product distribution of 80% CrF^{2+} (and NCS^-)–20% $Cr(NCS)F^+$ for the equilibrium $CrF^{2+} + NCS^- = Cr(NCS)F^+$ gives a value of $Q = 0.31$ M^{-1} which when combined with the above-noted quotients yields $Q_{form} = 6.2 \times 10^3$ M^2 (25 °C, $\sum[ClO_4^-] = 1.0$ M). The value lies between Q_{form}'s for $Cr(NCS)_2^+$ and CrF_2^+ and is therefore entirely reasonable. It is noteworthy, however, that the kinetics of approach to such an equilibrium state are strictly pseudo first order with no hint of deviation due to the reverse reaction. Similar results were observed by Chia and King[34] in the reaction of *cis*-CrF_2^+ with chromium(II), *but not with trans*-CrF_2^+. Thus, either interpretation of the results would appear to implicate the cis isomer of $Cr(NCS)F^+$ as the reactive species; the two interpretations are not mutually exclusive. Thus, the kinetics are interpreted in terms of the reaction of *cis*-$Cr(NCS)F^+$ with chromium(II). The origin of the $CrNCS^{2+}$ product will be considered in the discussion of mechanisms to follow.

There are at least three mechanisms which are consistent with the experimental rate law—all involving formation of

Scheme I

mechanism A

$$\mathrm{Cr}(N\mathrm{CS})\mathrm{F}^{+} + \mathrm{Cr}^{2+} \overset{Q_1}{\rightleftharpoons} \mathrm{FCr(NCS)Cr}^{3+} \qquad (1)$$

$$\mathrm{Cr}(N\mathrm{CS})\mathrm{F}^{+} + \mathrm{Cr}^{2+} \xrightarrow[\text{slow}]{k_2} \mathrm{CrF}^{2+} + \mathrm{Cr}^{2+} + \mathrm{NCS}^{-} \qquad (2)$$

mechanism B

$$\mathrm{Cr}(N\mathrm{CS})\mathrm{F}^{+} + \mathrm{Cr}^{2+} \overset{Q_3}{\rightleftharpoons} \mathrm{SCNCrFCr}^{3+} \qquad (3)$$

$$\mathrm{SC}N\mathrm{CrFCr}^{3+} \xrightarrow[\text{slow}]{k_4} \mathrm{CrF}^{2+} + \mathrm{Cr}^{2+} + \mathrm{NCS}^{-} \qquad (4)$$

mechanism C[35]

$$\mathrm{Cr}(N\mathrm{CS})\mathrm{F}^{+} \overset{Q_5}{\rightleftharpoons} {}^{*}\mathrm{Cr(NCS)F}^{+} \qquad (5)$$

$$^{*}\mathrm{Cr(NCS)F}^{+} + \mathrm{Cr}^{2+} \xrightarrow[\text{slow}]{k_6} \mathrm{CrF}^{2+} + \mathrm{Cr}^{2+} + \mathrm{NCS}^{-} \qquad (6)$$

stoichiometrically significant amounts of an intermediate prior to the rate-determing step. (See Scheme I.)

Interpretations of the empirical parameters *a* and *b* differ for the various mechanisms as follows: mechanism A, $a = k_2$, $b = Q_1$; mechanism B, $a = Q_3k_4$, $b/a = 1/k_4$; mechanism C, $a = Q_5k_6$, $b/a = 1/k_{-5}$. For mechanism C it is not possible to obtain the temperature dependencies of Q_5 or k_6 separately. Since values of k_2, k_4, and k_{-5} are obtained directly from the empirical parameters, the activation parameters are more precise than the concentration quotients Q_1 and Q_3 which reflect errors in both *a* and *b*.

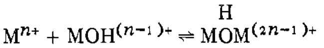
Mechanism A involves the reversible formation of an unproductive or "dead-end" intermediate (which is thiocyanate ion bridged) followed by a fluoride ion bridged electron-transfer reaction. The mode of bonding between the thiocyanate ion and the two metal ions is not completely specified in step 1. The chromium(II) may be attached either remotely to sulfur or adjacently to nitrogen. Ball and King[36] considered a similar situation in discussing a mechanism for the $\mathrm{Cr}N\mathrm{CS}^{2+}$–$^{*}\mathrm{Cr}^{2+}$ exchange reaction. It was noted, however, that in order for both metal ions to be bonded at nitrogen, chromium(II) would (for steric reasons) be required to lose at least two water molecules. Although the question of adjacent vs. remote attack involving thiocyanate ion has been explored in redox reactions,[37,38] there has been no conclusive evidence to support adjacent attack at nitrogen. Nevertheless, it is noteworthy that ΔS for Q_1 is +11 eu, an unusual value for an association reaction unless there is substantial disordering accompanying the process. King and Gallagher[39] have presented an entropy correlation supporting a change in coordination number for the reaction

$$\mathrm{Hg(H_2O)_3Cl_3}^{-} + \mathrm{Cl}^{-} \rightleftharpoons \mathrm{HgCl_4}^{2-} + 3\mathrm{H_2O}$$

Here three water molecules are lost. The values of $\Delta S^{\circ}_{\text{exptl}}$ and $\Delta S^{\circ}_{\text{cor}}$ (corrected for symmetry number factors, σ values) are +5.1 and +12.3 eu, respectively. These values compare with values in the present work of +11 and <+11 eu. [$\Delta S_{\text{cor}} = \Delta S_{\text{exptl}} + R \ln (\sigma_{\text{prod}}/\sigma_{\text{react}})$, and the reactants are more symmetric than the products.] Thus it would appear that the positive entropy change for Q_1 is certainly a reasonable value for loss of two water molecules, the minimum number suggested by Ball and King.[36] However, because of the difference in charge types in the two systems being compared, the agreement may be fortuitous. Moreover the low value of 3.03 kcal/mol for ΔH is consistent with substitution on labile chromium(II).

The origin of the small amounts of $\mathrm{Cr}N\mathrm{CS}^{2+}$ among the following reaction products may lie in the "dead-end" intermediate. If a small amount of this complex were to undergo electron transfer, $\mathrm{Cr}N\mathrm{CS}^{2+}$ would result. On the other hand, a small amount of chromium(II)-catalyzed substitution of thiocyanate ion for fluoride ion in the CrF^{2+} product could also account for small amounts of $\mathrm{Cr}N\mathrm{CS}^{2+}$. In mechanism B to follow, the latter pathway would, of necessity, be operative. Analogous reactions have been observed for the substitution of iodide ion in CrI^{2+} by fluoride, chloride, and bromide ions.[12]

Mechanism B features the formation of a fluoride ion bridged intermediate which then decays to products. Now the intermediate may be formulated as either $\mathrm{SC}N\mathrm{Cr^{III}}$–F–$\mathrm{Cr^{II}}$ or $\mathrm{SC}N\mathrm{Cr^{II}}$–F–$\mathrm{Cr^{III}}$. The former is preferred since substitution on chromium(II) is rapid,[40] whereas electron transfer between chromium(II) and -(III) is usually slow when fluoride ion is the bridging ligand. For either formulation the value of $Q_3 = 1.9\ \mathrm{M}^{-1}$ for the fluoride-bridged intermediate lies within the range 10^{-1}–10^{1} established by Cannon and Earley[41] for similar reactions of the type



$$\mathrm{M}^{n+} + \mathrm{MOH}^{(n-1)+} \rightleftharpoons \mathrm{M}\overset{\mathrm{H}}{\mathrm{O}}\mathrm{M}^{(2n-1)+}$$

However, while a value of $\Delta H = 2.9$ kcal/mol for Q_3 is entirely reasonable, it is difficult, if not impossible, to rationalize a +11-eu entropy change for the formation of a fluoride ion bridged intermediate. Cannon and Gardiner[42] and Gaswick and Haim[43] have reported redox systems in which precursor complex formation is featured, and Movius and Linck,[44] as well as Seewald, Sutin, and Watkins,[45] have reported systems involving successor complex formation. Since these systems and others are discussed in a review by Haim,[38] they will not be discussed further here.

Mechanism C requires the formation of an activated chromium(III) reactant species, perhaps involving a geometric isomerization or a change in coordination number. Linkage isomerization of the N-bonded thiocyanate ion is not considered here since it is the thermodynamically stable linkage isomer. There has been but one quantitative study of geometric isomerization for disubstituted aquochromium(III) species. Salzman and King[46] found the geometric isomerization *cis*-$\mathrm{CrCl_2}^{+} \rightleftharpoons$ *trans*-$\mathrm{CrCl_2}^{+}$ to be on the same order of magnitude as the thermal aquations. Carlyle and King[23] have also reported that spontaneous isomerization of *cis*- and *trans*-$\mathrm{Cr}(N\mathrm{CS})_2^{+}$ occurs, but much more slowly than does aquation. Since the observed pseudo-first-order rate coefficients for electron transfer are several orders of magnitude greater than the spontaneous geometric isomerizations noted above, it seems safe to conclude that such a process could not account for the necessary activation. There is no precedent for a change in coordination number in the redox chemistry of chromium(III). Moreover, light is without effect on the reaction (at least at 415 nm); therefore the required activation is not photochemical in origin. Hence, mechanism C is provisionally dismissed.

The kinetics of this system are unusual in that evidence for a precursor complex is obtained in a relatively slow electron-transfer reaction. Mechanism A is preferred in the present work because it best accommodates all of the experimental evidence including $\Delta S = +11$ eu for Q_1. If mechanism A is accepted, then the first step may represent the first example of adjacent attack at nitrogen in a metal–isothiocyanate complex. However, it should be noted that such an attack is at best only weakly competitive with fluoride ion bridged electron transfer.

Finally, in Table IV are summarized all of the available rate constants and activation parameters for the reactions of disubstituted tetraaquochromium(III) ions with chromium(II). The exchange reactions of the fluoro- and isothiocyanatopentaaquochromium(III) are included for purposes of comparison.

An examination of Table IV reveals that k_2 given for the $\mathrm{Cr}(N\mathrm{CS})\mathrm{F}^{+}$ (entry 4) is larger than that for any of the other fluoride ion complexes (entries 1, 2, 5). However, it is more astonishing that CrF^{2+} has a larger rate constant than either

Table IV. Summary of Kinetic Data for Reactions of Disubstituted Tetraaquochromium(III) Ions with Chromium(II) at 25 °C and $\mu = 1.0$ M

Entry no.	Oxidant	k, M^{-1} s^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu	Ref
1	*cis*-CrF_2^+	5.0×10^{-3} [g]	13	−24	*a*
2	*trans*-CrF_2^+	7.5×10^{-4} [g]			*a*
3	$Cr(NCS)_2^+$	$\leq 4.5 \times 10^{-4}$ [g]			*b*
4	$Cr(NCS)F^+$	5.4×10^{-2}	14.6	−15	*c*
5	CrF^{2+}	2.6×10^{-2}	13.7	−20	*d*
6	$Cr(NCS)^{2+}$	1.2×10^{-4}			*d*
7	*cis*-$CrCl_2^+$	1.4×10^{2} [g]	5.7	−28	*e*
8	*trans*-$CrCl_2^+$	2.0×10^{2} [g]	4.9	−30	*e*
9	*cis*-$Cr(N_3)_2^+$	3.8 [g,h]	8.1	−27	*f*

[a] References 3 and 4. [b] Calculated from data in footnote 18 of ref 36. [c] This work. [d] Reference 36. [e] J. H. Espenson and S. G. Slocum, *Inorg. Chem.*, **6**, 906 (1967). [f] A. Haim, *J. Am. Chem. Soc.*, 88, 2324 (1966). [g] Corrected for symmetry number factor. [h] Singly bridged pathway.

CrF_2^+ species. All have comparable activation parameters as anticipated for such similar systems. In view of the absence of any trend in rate constants among these species no firm conclusion can be reached concerning the reasonableness of k_2 for $Cr(NCS)F^+$. A comparison of the two constants for entries 5 and 6 indicates clearly that fluoride ion is superior to thiocyanate ion as a bridging group by a factor of $\sim 10^2$, a fact consistent with the observed stoichiometry.

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Registry No. $Cr(H_2O)_4(NCS)F^+$, 59110-00-8; Cr^{2+}, 22541-79-3; $[Co(NH_3)_5F](ClO_4)_2$, 36126-23-5; $[Co(NH_3)_5H_2O](ClO_4)_3$, 13820-81-0.

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Photochemistry of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$

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The photochemistry of *trans*-$[Cr(en)_2NH_3Cl]^{2+}$ has been studied in aqueous solution at irradiation wavelengths corresponding to excitation into the ^4E_a (546 nm), $^4B_2$ (436 nm), and $^4A_2$–^4E_b (366 nm) states of the molecule. For irradiation into the lowest energy ^4E state, the photosolvation mode is highly specific, corresponding to loss of ammonia ($\phi = 0.33$) more or less exclusively (100 ± 3%) to yield *cis*-$[Cr(en)_2H_2OCl]^{2+}$ (only 1 ± 2% trans product is found). For irradiation into the higher energy transitions the photochemistry becomes less specific, the quantum yield of ammonia falling somewhat to a constant value ($\phi = 0.30$), while ethylenediamine progressively increases with excitation energy (0.06 at 436 nm, 0.10 at 366 nm). Small temperature dependences of yields were observed. The results are discussed in the framework of existing models of chromium(III) photochemistry.

Introduction

The photochemistry of Cr(III) complexes has been the subject of a number of recent reviews[1-5] which, taken together, draw attention to a number of outstanding questions. Of particular interest to the authors are whether the existing models[6-10] are adequate to predict the reaction modes of chromium(III) complexes, the nature of the excited state(s) from which reaction may occur, and the mechanism of reaction including the nature of the stereochemistry.

In regard to the first two questions, Adamson[6] originally proposed a model in which the strong-field ligand on the weak-field axis would be preferentially labilized, with a loss of discrimination for irradiation at higher energies. Pyke and Linck[7] suggested that this should be modified to reflect that the axis of labilization is more a function of σ-bonding strength than overall ligand field strength. Wrighton[8] et al. and