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The Methanol Catalysis of the Chromium(III)-Thiocyanate Reaction in Aqueous-Methanol Acid Solutions

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Methanol bound in the first coordination sphere of chromium(III) increases the rate of substitution of chloride compared to the completely aquated species. The relative slowness of the equilibrium reaction

$$Cr(H_2O)_6{}^{3+} + CH_3OH \rightleftharpoons Cr(H_2O)_5(CH_3OH)^{3+} + H_2O \quad (1)$$

has made it possible to specify the rates of the two types of solvated Cr(III) species. The relative rate coefficients, k_2/k_1, of the two substitution reactions

$$Cr(H_2O)_6{}^{3+} + Cl^- \xrightarrow{k_1} CrCl^{2+} \quad (2)$$

$$Cr(H_2O)_5(CH_3OH)^{3+} + Cl^- \xrightarrow{k_2} CrCl^{2+} \quad (3)$$

were found to be 3.75 in methanol–water solutions containing 0.128 and 0.306 mol of methanol.[3]

In the present work, the effect of methanol coordination on Cr(III) on the substitution reaction with thiocyanate was studied. The ratio of rate coefficients, k_2/k_1, of reactions 2 and 3 when thiocyanate is used in place of chloride is 1.5 in both 0.12 and 0.30 mol of methanol. Ligand-substitution dynamics has been recently reviewed by Langford and Stengle[4] in which evidence for interchange and dissociative pathways is discussed. The interchange mechanism may be the more common stoichiometric pathway for octahedral substitution reactions although evidence is available supporting dissociative pathways in some cases. In the present study evidence against the formation of a pentacoordinated intermediate is assembled by the comparison of the relative rate coefficients of reactions 2 and 3 with possible mechanisms.

Experimental Section

Reagents and Analyses.—The procedure for the preparation of reagents used in this work and the methods of analyses were by the same techniques as those reported in earlier work on the chromium–chloride system.[3] Thiocyanate analyses were performed by titration using standard silver nitrate solution.

Separation of chromium(III) species of charges +2 and +3 was carried out using ion-exchange techniques. Elution of the chromium(III) species with bound methanol was made with 3 *M* sulfuric acid. The methanol content of the chromium(III) species was measured by titration with a standard Ce(IV)–Cr(VI) solution. The details of this separation and titration procedure are described earlier.[3]

Preequilibrated Solutions.—Preequilibrated solutions of chromium(III) perchlorate, perchloric acid, and methanol–water were prepared from stock solutions of known concentrations and density. The solutions were equilibrated at 30.0 ± 0.1° for 8 weeks. The solutions were judged to be at equilibrium when the average number of methanol molecules bound per chromium(III), $\bar{n}$, reached a constant value. The value of $\bar{n}$ was measured by titrimetric procedures described earlier. The values of $\bar{n}$ measured at an ionic strength of 1.98 *M* were 0.15 (0.145), 0.23 (0.190), 0.41 (0.306), 0.51 (0.391), and 0.63 (0.505). The value of the mole fraction of methanol in the solvent is given in the parentheses. The concentrations of chromium(III) and hydrogen ions were 0.314 and 0.100*M*, respectively. The ionic strength of the preequilibrated solutions were higher than the final ionic strength of the kinetic solutions. The ionic strength of the kinetic solutions was adjusted by proper dilution and addition of sodium perchlorate and sodium thiocyanate solutions.

Kinetic Solutions.—The required volumes of preequilibrated chromium(III) perchlorate, sodium thiocyanate, methanol, water, sodium perchlorate, and perchloric acid stock solutions were mixed to give a final ionic strength of 0.418 *M*. The solutions were placed in a volumetric flask immersed in a water bath at 30.0°. The rate of substitution of chromium(III) ion was followed by analysis of the product isothiocyanatochromium(III) ion separated from quenched reaction solution by absorbing chromium(III) ions on a 15-cm cation-exchange column and washing through the isothiocyanatochromium(III) ion. Two different methanol–water mixtures of methanol mole fractions equal to 0.128 and 0.306 were used in this study.

Results

Rate of Formation of Isothiocyanatochromium(III) Ion.—The rates of substitution of hexaaquochromium(III) and methanolpentaaquochromium(III) ions with thiocyanate ion were determined in acidic solutions. The concentrations of chromium(III) ion and thiocyanate ion did not change during the reaction period. The rate law is of the form

$$\frac{d[CrNCS^{2+}]}{dt} = k_f[Cr^{3+}][SCN^-] \quad (4)$$

Table I presents the second-order rate constants derived from values of $\Delta[CrSCN^{2+}]/\Delta t$. Rates measured in water were found to be first order in both thiocyanate and chromium(III). The reaction was run at short times where $\bar{n}$ was reasonably constant and the backward reaction could be ignored. This limited the experiments to within the first 10-hr period of the reaction.

Methanol influences the rate of the reaction because it is part of the first coordination sphere of chromium(III) ion and/or because it is in the solvent exerting a medium effect. The effect of methanol in the medium is small as evidenced by values of k_f equal to 2.94, 2.62, and 2.52 × 10^{-6} M^{-1} sec^{-1} at almost constant solvation of $\bar{n}$ near zero in water and in 0.128 and 0.306 mol of methanol. However, when methanol is added to the first coordination sphere, the rate of the reaction increases as seen in Table I. The second-order rate coefficient is made up of two terms

$$k_f = (1 - \bar{n})k_1 + \bar{n}k_2 \quad (5)$$

where k_1 and k_2 are the second-order rate coefficients for reactions 2 and 3, respectively. For each solvent mixture the values of k_1 and k_2 were calculated from the dependence of an average value of $\bar{n}$ during the 10-hr

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TABLE I

RATE OF FORMATION OF ISOTHIOCYANATOCHROMIUM(III) ION AT 30°[a]

$\bar n$, $t = 0$	$\bar n$, $t = 10$ hr	[SCN$^-$], M	[Cr^{3+}], M	10^6k_f, M^{-1} sec^{-1}
		$Z_{CH_3OH} = 0$		
0	0	0.0713	0.0314	2.94
0	0	0.119	0.0314	2.95
0	0	0.119	0.0314	2.87
0	0	0.0714	0.0440	2.91[b]
		$Z_{CH_3OH} = 0.128$		
0	0.04	0.119	0.0314	2.62
0.15	0.15	0.119	0.0317	2.80
0.23	0.21	0.119	0.0319	2.90
0.41	0.34	0.119	0.0318	3.09
0.51	0.41	0.119	0.0327	3.16
0.63	0.50	0.119	0.0341	3.20
		$Z_{CH_3OH} = 0.306$		
0	0.08	0.119	0.0314	2.52
0.15	0.20	0.119	0.0317	2.71
0.23	0.27	0.119	0.0319	2.80
0.41	0.39	0.119	0.0318	2.95
0.51	0.46	0.119	0.0327	3.06
0.63	0.55	0.119	0.0341	3.10

[a] $[H^+] = 0.1000$ M; $I = 0.420$ M; $k_f = [\Delta CrSCN^{2+}]/\Delta t(1/[Cl^-][Cr^{3+}]$. [b] $[H^+] = 0.073$ M. Uncertainty in any measurement of k is indicated by the range of values found for $Z_{CH_3OH} = 0$.

TABLE II

FIRST COORDINATION SPHERE SOLVATION DEPENDENCE OF K_f AT 30°

$Z_{CH_3OH} = 0.128$			$Z_{CH_3OH} = 0.306$		
	10^6k_f, M^{-1} sec^{-1}			10^6k_f, M^{-1} sec^{-1}	
$\bar n_{av}$	Obsd	Calcd[a,b]	$\bar n_{av}$	Obsd	Calcd[a,c]
0.02	2.62	2.64	0.02	2.52	2.54
0.15	2.80	2.79	0.17	2.71	2.71
0.22	2.90	2.87	0.25	2.80	2.81
0.38	3.09	3.05	0.40	2.99	2.98
0.46	3.16	3.13	0.48	3.06	3.07
0.56	3.20	3.28[d]	0.59	3.10	3.20[d]

[a] Calculated from $k_f = (1 - \bar n)k_1 + \bar n k_2$. [b] $k_1 = (2.63 \pm 0.10) \times 10^{-6}$; $k_2 = (3.73 \pm 0.19) \times 10^{-6}$. [c] $k_1 = (2.52 \pm 0.10) \times 10^{-6}$; $k_2 = (3.68 \pm 0.18) \times 10^{-6}$. [d] At values of $\bar n$ greater than 0.5 dimethanol species could be present in large enough quantities to influence the value of k_f.

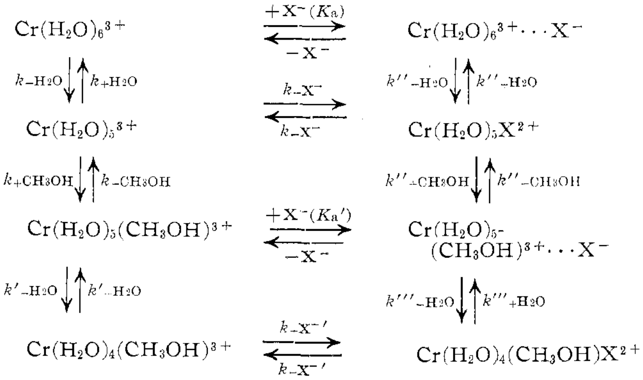
experimental period. The values of k_1 and k_2 are reported in Table II. The relative rate of the two reactant chromium(III) species is given by the ratio k_2/k_1, which is equal to 1.5 within experimental uncertainty in both solvent mixtures. A least-squares analysis of the data fit to eq 5 yields values of k_2/k_1 equal to 1.42 ± 0.12 and 1.46 ± 0.12 for the two solvent mixtures. The error is reported here at a 95% confidence level. The value of $\bar n$ changes during the 10-hr kinetic run so the value is measured initially and at the end of the time period. An average value of $\bar n$ is then used in eq 5. In the range of $\bar n$ values up to 0.5 previous work indicates that only the mono(methanol)chromium(III) ionic species exists in solution with the completely aquated form.[3]

Discussion

Substitution reactions in nonaqueous solvents have been reviewed by Tobe,[5] who concluded that Co(III) octahedral substitution occurs mainly by a dissociative mode of activation and by means of an interchange mechanism. Our work shows some interesting results when the ratio of the two rate constants k_1/k_2 is compared to those of possible mechanisms consistent with a dissociative activation mode. Scheme I presents a limiting SN1 mechanism and an interchange mechanism where bond breaking of the bound solvent molecule occurs in the transition state.

SCHEME I

MECHANISMS CONSISTENT WITH A DISSOCIATIVE ACTIVATION



The rate law relating concentration of solvent to the solvent dependence of k_1 and k_2 can be derived in the case a long way from equilibrium where the dissociation of CrX^{2+} can be ignored and where $\bar n$ remains constant. In the limiting SN1 case steady-state approximation leads to a rate law of the form

$$\frac{d[CrX^{2+}]}{dt} = [X^-][Cr^{3+}]_{total} \times \left[\frac{k_{+X^-}k_{-H_2O}(1 - \bar n) + k_{-CH_3OH}\bar n}{k_{+H_2O}a_{H_2O} + k_{+CH_3OH}a_{CH_3OH} + k_{+X^-}[X^-]} + \frac{k'_{+X^-}\bar n k'_{-H_2O}}{k'_{+H_2O}a_{H_2O} + k'_{+X^-}[X^-]}\right] \quad (6)$$

The values of k_1 and k_2 can be derived from the rate law and give the ratio

$$k_2/k_1 = \frac{k_{-CH_3OH}}{k_{-H_2O}} + \frac{k'_{+X^-}k'_{-H_2O}(k_{+H_2O}a_{H_2O} + k_{+CH_3OH}a_{CH_3OH} + k_{+X^-}[X^-])}{k_{+X^-}\,k_{-H_2O}(k'_{+H_2O}a_{H_2O} + k'_{+X^-}[X^-])} \quad (7)$$

Steady-state approximation in the interchange mechanism leads to the rate law

$$\frac{d[CrX^{2+}]}{dt} = [Cr^{3+}][X^-][K_a(1 - \bar n)k''_{-H_2O} + K_a'\bar n(k''_{-CH_3OH} + k'''_{-H_2O})] \quad (8)$$

The value of the ratio k_2/k_1 is

$$k_2/k_1 = \frac{K_a'}{K_a}\,\frac{k''_{-CH_3OH} + k'''_{-H_2O}}{k''_{-H_2O}} \quad (9)$$

It should be noted the distribution of methanol in the product isothiocyanatochromium(III) was not measured so that no attempt is made to separate the terms containing k''_{-CH_3OH}, k'''_{-H_2O}, k_{+X^-}, and k'_{+X^-}.

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(5) M. L. Tobe, Advances in Chemistry Series, No. 49, American Chemical Society, Washington, D. C., 1965, p 7.

However, because the distribution of methanol in the reactant chromium(III) ion was known, some terms were eliminated when the ratio of the measured rate constants was taken. The experimental data are consistent with both mechanisms and are also consistent with SN2 (limited) or SN2 if these mechanisms were derived. At this point one would say the kinetic study in mixed solvent does not settle the question of solvent participation in the mechanism.

The ratio of k_2/k_1 in the limiting SN1 mechanism has the term k_{-CH_3OH}/k_{-H_2O}, which can be isolated experimentally. This fact allows one to comment further about the possible mechanisms described above. In previous work the rate coefficients for the displacement of water by methanol and of methanol by water in the first coordination sphere were found to be consistent with both the SN2 and the SN1 (limited) mechanisms.[3,6] Experimentally the binding of methanol by chromium(III) ion in water–methanol mixtures was followed as a function of time at 30°. The approach to equilibrium of $\bar{n}$ was first order given by the rate expression

$$\frac{d\bar{n}}{dt} = k_f(1 - \bar{n}) - k_b\bar{n} \qquad (10)$$

The values of k_f and k_b are related to solvent activities in the limiting SN1 mechanism by

$$k_f = \frac{k_{-H_2O}k_{+CH_3OH}a_{CH_3OH}}{a_{H_2O}k_{+H_2O} + a_{CH_3OH}k_{CH_3OH}} \qquad (11)$$

and

$$k_b = \frac{k_{-CH_3OH}k_{+H_2O}a_{H_2O}}{a_{H_2O}k_{+H_2O} + a_{CH_3OH}k_{+CH_3OH}} \qquad (12)$$

Equations 11 and 12 can be written in the forms

$$1/k_f = K/R(1/k_{-H_2O}) + 1/k_{-H_2O} \qquad (13)$$

$$1/k_b = R/K(1/k_{-CH_3OH}) + 1/k_{-CH_3OH} \qquad (14)$$

where R is the activity ratio, methanol to water, and K is the ratio k_{+H_2O}/k_{+CH_3OH}. In previous work[3,6] the values of k_f and k_b were found to be: 1.8×10^{-6} and 7.3×10^{-6} sec^{-1} ($R = 0.235$), 2.4×10^{-6} and 5.3×10^{-6} sec^{-1} ($R = 0.441$), and 2.9×10^{-6} and 4.0×10^{-6} sec^{-1} ($R = 0.639$). The ratio of mole fractions of solvent was used for the activity term, R, in all calculations. A least-squares analysis of the data fit to eq 13 yielded values of k_{-H_2O} and K equal to $(4.3 \pm 0.3) \times 10^{-6}$ sec^{-1} and 0.33 ± 0.04. The fit of data to eq 14 yielded values of k_{-CH_3OH} and K equal to $(1.43 \pm 0.3) \times 10^{-5}$ sec^{-1} and 0.25 ± 0.02. The least-squares analysis was run on a Wang 370 desk calculator. The program also included a calculation of the standard deviation. The uncertainty reported for the constants is at the 95% confidence level.

The values of K from eq 13 and 14 are in reasonable agreement considering the range of uncertainty associated with the calculation. The values of k_f and k_b are obtained from a sum of terms so that an error in this calculation would further magnify itself in certainty of K, k_{-H_2O}, and k_{-CH_3OH}. The ratio k_{-CH_3OH}/k_{-H_2O} is 3.3 ± 0.3 at 95% confidence level. If one makes the assumption that the solvent and ligand substitution reactions occur by an SN1 (limited) mechanism, all ratios of k_2/k_1 should be greater than 3.3 ± 0.3 because of the single term k_{-CH_3OH}/k_{-H_2O} in eq 7. At 30° the reaction of chromium(III) and chloride gives a value of k_2/k_1 equal to 3.75 at 0.128 and 0.306 mol of methanol[3] while the reaction of chromium(III) and thiocyanate gives a ratio of 1.4 ± 0.15 at similar solvent compositions. The low value of k_2/k_1 compared to 3.3 for the thiocyanate system would not be consistent with the SN1 (limited) case as a possible mechanism for the substitution reactions observed. The value of k_{-H_2O} calculated from eq 13 should predict the value from the rate of oxygen-18 exchange measured by Hunt and Plane.[7] A value of 3.2×10^{-5} sec^{-1} was measured in the ^{18}O-exchange experiments which is inconsistent with the value derived from the methanol exchange assuming an SN1 (limited) mechanism. An interpretation of the experimental data is that the exchange of solvent and ligand substitution reactions of chromium(III) in methanol–water mixtures does not occur by an SN1 (limited) mechanism.

This interpretation of the data raises some questions concerning medium effects that are difficult to answer. In order to separate the SN1 (limited) rate coefficients from the exchange data the assumption must be made that medium effects on the coefficient are constant over the solvent composition range studied. Unfortunately the solvent participation in the reactions cannot be isolated in the systems. King, *et al.*, have isolated equilibrium quotient medium effects in water–ethanol[8] and water–DMSO[9] systems where 10–20% variations were noted over 0.35-mol changes in solvent composition. In the DMSO–water system the rate of formation of mono(dimethyl sulfoxide)chromium(III) ion was followed at concentrations of less than 2 mol % DMSO. The pseudo-first-order rate constant measured in the approach to equilibrium was approximately first order in dependence upon the dimethyl sulfoxide concentration.

The medium dependence of the rate of formation in methanol–water mixtures of the thiocyanato- and chlorochromium(III) species is confusing. In the chloride system k_1 varies from 1.6×10^{-7} M^{-1} sec^{-1} in water to 2.4×10^{-7} M^{-1} sec^{-1} in 0.30 mol of methanol. However, in the thiocyanate system k_1 varies from 3.0×10^{-6} M^{-1} sec^{-1} in water to 2.5×10^{-6} M^{-1} sec^{-1} in 0.30 mol of methanol. In both systems the ratio k_2/k_1 remains constant at two different solvent compositions. The medium dependence of the rate coefficients k_{-CH_3OH} and k_{-H_2O} may be important. Therefore, a limit can be set on the value of k_{-CH_3OH}/k_{-H_2O} when the reactions proceed by a limiting SN1 mechanism. If all the reactions were to occur by a limiting SN1 mechanism, then the thiocyanate reaction ratio

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k_2/k_1 limits k_{-CH_3OH}/k_{-H_2O} to a maximum value of 1.5 from eq 7. This in turn limits the second term to a value less than 0.1. The data for the chloride system for k_2/k_1 with the value of 1.5 equal to k_{-CH_3OH}/k_{-H_2O} limit the second term to a value of 2.0. The value of k'_{+X^-}/k_{+X^-} is the only variable at constant solvent composition in the second term of eq 7 when $k_{+H_2O} \cdot a_{H_2O} + k_{+CH_3OH}a_{CH_3OH} > k_{+X^-}/X^-]$ and $k'_{+H_2O} \cdot a_{H2O} > k'_{+X^-}[X^-]$. The implication is that the rate coefficients k'_{+X^-} and k_{+X^-} show considerable dependence upon the entering group. Differences between k'_{+Cl^-} and k'_{+SCN^-} are expected in limiting SN1 mechanisms. Halpern[10] and Haim and Wilmarth[11] found evidence of a limiting SN1 mechanism in some cobalt(III) complexes where the reactivity of the intermediate followed the order $OH^- > CN^- > SCN^- > Br^-$. However, the dependence of the ratio k'_{+X^-}/k_{+X^-} upon entering group is not expected. The thermodynamic stabilities of chloromethanoltetraaquochromium(III) and chloropentaaquochromium(III) ions relative to hexaaquochromium(III) and methanolpentaaquochromium(III) are identical.[3] If the rate coefficients follow the thermal stability, then the ratio k'_{+X^-}/k_{+X^-} should be near unity. The evidence indicates that all of the reactions do not proceed through a five-coordinated intermediate. If medium effects are unimportant, then argument can be made that all values of k_2/k_1 must be greater than 3.3 to be consistent with a limiting SN1 mechanism. If medium effects are important, the dependence of k'_{+X^-}/k_{+X^-} on the entering group is not consistent with a limiting SN1 mechanism.

The kinetic data are consistent with the interchange mechanism described in eq 8 and 9, but there is an obvious dependence of the rate coefficients upon the entering group. The ligand dependence of the ratio k_2/k_1 is very interesting and it appears to be very worthwhile to perform additional experiments particularly on the acid dependence of the rates and ratio of the various products in the reactions. Several authors have discussed the dependence of rate upon the entering group.[12] The reactions can be associative in nature[13] or the proton transfer to the anion in an ion interchange transition state could make the entering group become HX in place of X^-.[12,14]

The study has shown that the methanol catalysis of the substitution reaction of chromium(III) with thiocyanate is not as great as in the chloride case, but still an important factor in measuring rate coefficients in mixed solvents. The value of k_1 measured in water agrees with a previous study of Postmus and King in which a value of k_f $(= k_1 + k_2[H^+]^{-1} + k_3[H^+]^{-2})$ is $2 \times 10^{-6}\ M^{-1}\ sec^{-1}$ in 0.1 M hydrogen ion concentration and in ionic strength of 0.600 M at 25°. In 0.1 M hydrogen ion 96% of the reaction goes by the acid-independent step.[13]

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Complexes with Sulfur and Selenium Donors. I. Tris(O,O′-dialkyldithiophosphato)-chromium(III) Compounds

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A wide variety of complexes with sulfur and selenium donor atoms has been described[2] and such compounds continue to be of considerable interest.[3] O,O′-Dialkyldithiophosphoric acids have long been known to form highly colored complexes with transition metal ions. Of these, complexes of O,O′-diethyldithiophosphoric acid (Et-dtp) have undoubtedly been the most extensively investigated.[4-8] The electronic spectrum of $Cr(Et\text{-}dtp)_3$ has shown that Et-dtp should be placed below water in the spectrochemical series.[7] However, the very low value for the nephelauxetic parameter,[9] β, and the appreciable intensities[7,9] of the electronic absorption bands of $Cr(Et\text{-}dtp)_3$ are indicative of considerable metal–ligand covalency. The high degree of covalency of metal ion–O,O′-dialkyldithiophosphate bonds is also demonstrated by the observation of the ^{31}P superhyperfine splitting in the electron spin resonance (esr) spectra of oxovanadium(IV) and copper(II) chelates.[10] As there are slight, albeit not dramatic, changes in the pK_a's of O,O′-dialkyldithiophosphoric acids with substituent variations,[11] the spectral and magnetic properties of a series of tris(O,O′-dialkyldithiophosphato)chromium(III) compounds were prepared and characterized in order to determine the effects of substituent variation and to document further the properties of complexes with dithiophosphate ligands.

Experimental Section

Phosphorus(V) sulfide was obtained from Matheson Coleman and Bell, Norwood, Ohio. All other chemicals were of the best available reagent or spectroscopic grade. Carbon and hydrogen

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