Registry No. *p*-Hydroxybenzoic acid, 99-96-7; Cr^{3+}, 16065-83-1.

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Synthesis and Kinetics of Formation and Aquation of *cis*-Bis(oxalato)bis(dimethylformamide)chromate(III)

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The isolation by ion-exchange chromatography of *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$ has been effected. The complex has visible maxima at 418 and 565 nm with molar absorptivities of 87.5 and 96.5 M^{-1} cm^{-1}, respectively. The aquation of this compound occurred in consecutive first-order reactions with the first step corresponding to the replacement of the first $HCON(CH_3)_2$ and the second step corresponding to the replacement of the second $HCON(CH_3)_2$. The intermediate was concluded to be *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^-$. The reactions are independent of pH between pH 1 and 5 with $k_1 = (6.95 \pm 0.28) \times 10^{-4}$ s^{-1} and $k_2 = (3.27 \pm 0.18) \times 10^{-4}$ s^{-1} at 25 °C and $\mu = 1.00$ M ($NaNO_3$). The activation parameters are $\Delta H^* = 14.3 \pm 0.4$ and 14.2 ± 0.9 kcal/mol and $\Delta S^* = -24.9 \pm 1.3$ and -26.9 ± 3.0 cal/(deg mol) for the first and second steps, respectively. An I_a mechanism was assigned for both steps. The solvolysis reaction of *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ in $HCON(CH_3)_2$ is very similar to the aquation reaction. The value of k_{-2} (first step) is $(1.75 \pm 0.04) \times 10^{-3}$ s^{-1} and k_{-1} (second step) is $(1.87 \pm 0.05) \times 10^{-4}$ s^{-1} at 25 °C. The values of the activation parameters are $\Delta H^* = 14.4 \pm 0.2$ and 14.7 ± 0.3 kcal/mol and $\Delta S^* = -22.8 \pm 0.7$ and -26.1 ± 0.9 cal/(deg mol) for the first and second steps, respectively. The equilibrium behavior was studied at 25 °C, $[H^+] = 10^{-3}$ M, and $\chi_{DMF} = 0.028$–0.90 in aqueous dimethylformamide solutions. The equilibrium quotients are $Q_1 = 5.55 \pm 0.27$ and $Q_2 = 0.437 \pm 0.069$.

Introduction

The mechanism of the reactions of the *cis*-$Cr(C_2O_4)_2$ moiety have been of continuing interest. The complexes involving the monodentate ligands $(CH_3)_2SO$,[1] CH_3COO^-,[2] NCS^-,[3] N_3^-,[4] C_5H_5N,[2,5] and CN^-[6,7] have been studied. With the exception of $(CH_3)_2SO$, all of the complexes were in aqueous solutions, and the aquation reactions only were studied. With $(CH_3)_2SO$, both H_2O and $(CH_3)_2SO$ were used as solvents, and both the aquation and solvolysis reactions were studied. The results implied that the reactions of *cis*-$Cr(C_2O_4)_2(OH_2)L^{n-}$, where L is $(CH_3)_2SO$, CH_3COO^-, NCS^-, and N_3^-, occurred by an I_a mechanism.[4] That is, the rate constants and activation parameters for aquation are relatively insensitive to the nature of the leaving group. However, only the equilibrium constant with NCS^- has been determined.

In the effort to better understand this system, the present investigation was undertaken. The reactions of the *cis*-$Cr(C_2O_4)_2$ moiety with $HCON(CH_3)_2$(DMF) were studied. Both aquation and solvolysis reactions were investigated. This paper presents the results.

Experimental Section

Chemicals and Instruments. All chemicals used were reagent, analytical, or primary-standard grade, depending upon the need. Mallinckrodt AR grade dimethylformamide was used. Before being used, it was vacuum distilled from anhydrous barium oxide or Davison 4A molecular sieves. The ion-exchange resin was 200–400 mesh Bio-Rad Ag 1-X8 anion-exchange resin in the nitrate form. The instrumentation has been described before.[4]

Analytical Methods. The analyses for chromium were performed as previously described.[8] For the analyses of DMF, a solution containing about 0.50 mmol of DMF was hydrolyzed to dimethylamine with 5 mL of 1.0 M H_2SO_4 at 60 °C for 1 h. The solution was cooled and made basic with 10 mL of 3.6 M KOH. The dimethylamine was distilled from the basic solution into 2 mL of 0.48 M HCl. The resulting dimethylamine solution was analyzed spectrophotometrically by a method described by Cullis and Waddington.[9] The ion-exchange techniques have been described.[10]

Preparation of Compounds. The sodium *trans*-bis(oxalato)diaquochromate(III) was prepared by the method described by Werner.[11] Sodium *cis*-bis(oxalato)bis(dimethylformamide)chromate(III) was prepared by adding 10 g of sodium *trans*-bis(oxalato)diaquochromate(III) to 70 mL of DMF. The temperature was raised to 90 °C and maintained for 4 h. The solution was cooled to room temperature and kept in the refrigerator overnight. The crystals that formed were collected on a filter and washed with absolute ethanol and anhydrous diethyl ether. The product was recrystallized by dissolving 10 g of the product in 50 mL of DMF at 90 °C. The solution was cooled to room temperature and kept in the refrigerator overnight. The crystals that formed were collected and treated as before. The final product was dried for 6 h in a vacuum desiccator at 20 torr at room temperature. Attempts to isolate *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^-$ by using ion-exchange chromatography at 1 °C were unsuccessful. The complexes aquated on the column too fast to be separated by this technique. Both very fast and very slow elution rates were used.

Equilibrium Measurements. The values of $\bar{n}$, the average number of DMF molecules bound to chromium, as a function of χ_{DMF} were determined in the following manner. A series of solutions of DMF and H_2O with χ_{DMF} from 0.028 to 0.90 containing about 0.01 M *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$ were equilibrated for 24 h at 25 °C. Then, 5 mL of each solution was added to an anion-exchange column. The column capacity was about 10 mequiv. The solution was run into the column, and 15 mL of ice-cold H_2O was passed through the column. Blank experiments established that this would remove all of the solvent DMF. The 1– complexes were eluted then with ice-cold 0.10 M $NaNO_3$. The complete time required for this separation was about 5 min. The eluted solutions were analyzed for chromium and DMF as described above.

Kinetic Measurements. The kinetic runs were made on a Cary 11 or 15 recording spectrophotometer. Both instruments were fitted with 10-cm constant-temperature cell blocks that maintained the temperature to within ±0.1 °C of that desired. The change in absorbance was measured at 565 nm. The pH was adjusted with HNO_3 and $\mu = 1.00$ M ($NaNO_3$). The complex concentration was 0.50 mM. In the solvolysis reactions and in the reactions in DMF–H_2O solutions,

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no $NaNO_3$ was added. The HNO_3 concentration was adjusted to about 10^{-3} M.

However, in the solvolysis reactions, it was found that Na[*cis*-$Cr(C_2O_4)_2(OH_2)_2$] required several hours to dissolve in DMF. Hence, it was necessary to prepare a concentrated solution of Na[*cis*-$Cr(C_2O_4)_2(OH_2)$] in aqueous solution. A desired amount of this solution was added to the DMF solvent in order to initiate the kinetic run. The final water concentration in the DMF was 0.028 M (χ_{DMF} = 0.998), and the complex concentration was 0.75 mM. All kinetic runs were made in triplicate.

Results and Discussion

Preparation and Spectrum. Attempts to prepare pure Na[*cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2$] were unsuccessful. The impurities were separated by ion-exchange chromatography and identified by their molar absorptivities to be $Cr(C_2O_4)(OH_2)_4^+$ and $Cr(C_2O_4)_3^{3-}$. Various temperatures and times were used in the preparation. A temperature of 90 °C and a time of 4 h was found to give the optimum purity of 90–95%. Recrystallization of the product did not increase the purity. This implied that all these species are in equilibrium. The analysis of *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$ was obtained after a solution of the compound was purified by ion-exchange chromatography. The Cr:DMF ratio was 1.00:(1.96 ± 0.14). This and all other uncertainties reported are one standard deviation. Upon aquation, *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ was obtained. The spectrum of *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$ is similar to that of *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ except that the relative values of the molar absorptivities of the two maxima were reversed. The maxima were at 565 and 418 nm with molar absorptivities of 96.5 and 87.5 M^{-1} cm^{-1}, respectively. The assignment of the cis geometry to $Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$ was made because of the similarity of the spectrum to *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$.[4] The small change in the spectrum from *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ to *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$ implies that the DMF complex is oxygen bonded. Attempts to confirm this by IR measurements were nonconclusive.

Aquation of *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$. The overall reaction studied was eq 1. However, this reaction did not

$$cis\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)_2^- \xrightarrow{H_2O} cis\text{-}Cr(C_2O_4)_2(OH_2)_2^- + 2HCON(CH_3)_2 \quad (1)$$

follow simple first-order kinetics. Since there were two ligands being replaced by two water molecules, it was assumed that consecutive reactions were occurring (eq 2 and 3). It can be

$$cis\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)_2^- + H_2O \xrightarrow{k_1} cis\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^- + HCON(CH_3)_2 \quad (2)$$

$$cis\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^- + H_2O \xrightarrow{k_2} cis\text{-}Cr(C_2O_4)_2(OH_2)_2^- + HCON(CH_3)_2 \quad (3)$$

shown that for a system of this type that follows pseudo-first-order kinetics eq 4 is valid.[1] A is the absorbance at time

$$A - A_\infty = a_1 e^{-k_1 t} + a_2 e^{-k_2 t} \quad (4)$$

t and A_∞ is the absorbance at infinite time (10 half-lives). The constants a_1 and a_2 are defined by eq 5 and 6, where l is the

$$a_1 = l\epsilon_1[Cr]_{tot} + \frac{l\epsilon_2[Cr]_{tot}k_1}{k_2 - k_1} + \frac{l\epsilon_3[Cr]_{tot}k_2}{k_1 - k_2} \quad (5)$$

$$a_2 = \frac{lk_1[Cr]_{tot}(\epsilon_3 - \epsilon_2)}{k_1 - k_2} \quad (6)$$

cuvette length, $[Cr]_{tot}$ is the total complex concentration, and ϵ_1, ϵ_2, and ϵ_3 are the molar absorptivities of *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$, *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^-$, and *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$, respectively. Equation 4 was solved graphically for k_1 and k_2.[1] The results as well as the least-squares calculated values of the activation parameters are in Table I. The ionic strength was maintained constant at 1.00 M ($NaNO_3$). The pH was varied from 2 to 5 at 25 °C. There is no apparent effect of pH in this range.

Table I. Rate Data for the Aquation of *cis*-Bis(oxalato)bis(dimethylformamide)chromate(III)[a,f]

temp, °C	k_1, 10^{-4} s^{-1}	k_2, 10^{-4} s^{-1}
20	4.45 ± 0.10[c]	1.98 ± 0.09[c]
25	6.59 ± 0.65[b]	3.31 ± 0.38[b]
25	6.58 ± 0.33[c]	3.29 ± 0.59[c]
25	7.06 ± 0.24[d]	3.45 ± 0.21[d]
25	7.56 ± 0.17[e]	3.04 ± 0.15[e]
30	9.70 ± 0.91[c]	5.24 ± 0.35[c]
35	14.5 ± 0.3[c]	8.70 ± 0.56[c]
40	19.6 ± 0.6[c]	9.94 ± 0.22[c]
45	31.1 ± 0.4[c]	15.1 ± 0.6[c]
ΔH^*, kcal/mol	14.3 ± 0.4	14.2 ± 0.9
ΔS^*, cal/(deg mol)	−24.9 ± 1.3	−26.9 ± 3.0

[a] All uncertainties are one standard deviation. [b] pH 2.0. [c] pH 3.0. [d] pH 4.0. [e] pH 5.00. [f] μ = 1.00 M ($NaNO_3$).

In the aquation reactions of *cis*-$Cr(C_2O_4)_2(N_3)_2^{3-}$[4] and *cis*-$Cr(C_2O_4)_2(CN)_2^{3-}$,[6,7] similar kinetic behavior was observed. In these cases, the intermediates could be isolated and the aquation reactions of the intermediates observed. The agreement between the slow rate constant obtained from the graphical solution of eq 4 and the rate constant obtained from the aquation of the isolated intermediate was excellent. Hence, this method in this case is valid even though the intermediate could not be isolated.

The assignment of k_1 to the first step and k_2 to the second step is not arbitrary. In eq 4–6, l, $[Cr]_{tot}$, ϵ_1, and ϵ_3 are known. The values of the two rate constants (k_1 and k_2) were determined. However, what is actually determined is a faster rate constant (k_{fast}) and a slower rate constant (k_{slow}). The values of ϵ_2 are not known. By selection of an optimum time when [*cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^-$] was at a maximum, the values of ϵ_2 at various wavelengths can be calculated. If the k_{slow} is assigned to k_1 and k_{fast} is assigned to k_2, very low values of molar absorptivities are calculated for the maxima. In addition, the molar absorptivities between 580 and 630 nm have negative values. When k_{fast} is assigned to k_1 and k_{slow} is assigned to k_2, very reasonable values are obtained. The maxima are at 567 and 420 nm with molar absorptivities of 71 M^{-1} cm^{-1} at both maxima. Hence, k_{fast} is concluded to correspond to k_1 and k_{slow} to k_2.

In addition, because of the shape of the visible spectrum of the intermediate, it is assigned a cis geometry.[4] It is possible to devise a reaction scheme in which there is cis–trans and trans–cis isomerization of reactant, intermediate, and product. This has been discussed for the reaction with dimethyl sulfoxide (Me_2SO).[1] The arguments presented there are applicable here, and the more complex scheme is discarded.

The rate constants at 25 °C for the aquation of *cis*-$Cr(C_2O_4)_2X_2^-$ to *cis*-$Cr(C_2O_4)_2XOH_2^-$ where X is C_5H_5N,[5] $NH_2CH_2COO^-$,[13] $NH_2(CH_2)_2NH_2$,[14] $HCON(CH_3)_2$, or $(CH_3)_2SO$[1] are 9.5×10^{-6}, 7.9×10^{-5}, 1.7×10^{-5}, 6.6×10^{-4}, and 1.1×10^{-3} s^{-1}, respectively. The values of ΔH^* are 23, 18, 21, 14, and 12 kcal/mol, respectively. The values of ΔS^* are −5, −19, −11, −25, and −31 cal/(deg mol), respectively. These activation parameters could imply that there is more associative activation in the aquation of the $(CH_3)_2SO$ and the $HCON(CH_3)_2$ complexes than in the aquation of the $NH_2CH_2COO^-$, $NH_2(CH_2)_2NH_2$, and C_5H_5N complexes. A second possibility is that the degree of associative activation is similar but that the $NH_2CH_2COO^-$, $NH_2(CH_2)_2NH_2$, and C_5H_5N complexes are much more stable than the $(CH_3)_2SO$ and $HCON(CH_3)_2$ complexes. Also, these activation pa-

Table II. Rate Data for the Solvolysis of *cis*-Bis(oxalato)diaquochromate(III) in DMF[a,b]

temp, °C	k_{-2}, 10^{-4} s^{-1}	k_{-1}, 10^{-5} s^{-1}
5	2.76 ± 0.10	2.99 ± 0.30
10	4.40 ± 0.21	4.51 ± 0.26
15	7.23 ± 0.31	7.71 ± 0.48
20	11.7 ± 0.6	12.3 ± 0.3
25	17.5 ± 0.4	18.7 ± 0.5
35	25.6 ± 0.5	27.9 ± 0.3
ΔH^*, kcal/mol	14.4 ± 0.2	14.7 ± 0.3
ΔS^*, cal/(deg mol)	−22.8 ± 0.7	−26.1 ± 0.9

[a] $[H_2O] = 0.028$ M. [b] All uncertainties are one standard deviation.

rameters could imply that a change in intimate mechanism from associative activation in the $(CH_3)_2SO$ and $HCON(CH_3)_2$ complexes to dissociative activation in the $NH_2CH_2COO^-$, $NH_2(CH_2)_2NH_2$, and C_5H_5N complexes occurs. Until the equilibrium quotients are determined, not a great deal can be concluded about these reactions. However, the activation parameters imply that the aquation reactions of the $(CH_3)_2SO$ and $HCON(CH_3)_2$ complexes are associatively activated.

For the aquation at 25 °C of *cis*-$Cr(C_2O_4)_2X(OH_2)^{n-}$, where X = $NH_2(CH_2)_2NH_3^+$,[14] CH_3COO^-,[2] $HCON(CH_3)_2$, $(CH_3)_2SO$,[1] N_3^-,[4] and NCS^-,[3] the rate constants are 1.9×10^{-5}, 51.0×10^{-5}, 33.1×10^{-5}, 30.3×10^{-5}, 2.19×10^{-5}, and 1.61×10^{-5} s^{-1}, respectively. This is a 32-fold change. For $Co(NH_3)_5X^{2+}$, where X = CH_3COO^-, N_3^-, or NCS^-, there is a 4200-fold change. The aquation of $Co(NH_3)_5X^{2+}$ has been concluded to occur by an I_d mechanism.[15] The apparent insensitiveness of the rate constant for aquation of *cis*-$Cr(C_2O_4)_2X(OH_2)^{n-}$ implies associative activation.

However, if the stability constants of these complexes were very similar, the insensitiveness could be interpreted to imply dissociative activation. But this type of activation seems to be excluded by the values of the activation parameters. When X is $HCON(CH_3)_2$, CH_3OO^-,[2] $(CH_3)_2SO$,[1] N_3^-,[4] and NCS^-,[3] the activation enthalpies are 14, 16, 18, 18, and 20 kcal/mol. The activation entropies for this same order of ligands are −27, −19, −18, −18, and −13 cal/(deg mol). The values of these activation parameters imply associative activation. In fact, it seems that the aquation reaction of the $HCON(CH_3)_2$ ligand is even more associative in nature than the other ligands, including $(CH_3)_2SO$.

Solvolysis of *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ in DMF. Because of the very long time that it took Na[*cis*-$Cr(C_2O_4)_2(OH_2)_2$] to dissolve in DMF, it was necessary to add an aqueous solution of Na[*cis*-$Cr(C_2O_4)_2(OH_2)_2$] to DMF. This resulted in at least 0.028 M water ($\chi_{DMF} = 0.998$) in these kinetic runs. However, kinetic runs with additional water indicated that these kinetic results can be treated as if the DMF contains no water. The reaction studied was eq 7. As in the aqueous solutions, simple

$$\textit{cis}\text{-}Cr(C_2O_4)_2(OH_2)_2^- \xrightarrow{\text{DMF}} \textit{cis}\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)_2^- + 2H_2O \quad (7)$$

first-order kinetics were not observed. Again, it was assumed that consecutive first-order reactions were occurring.

The values of k_{fast} and k_{slow} were obtained as before. As to what steps to assign k_{fast} and k_{slow}, the same technique as before was used. Essentially the same results were obtained. The results as well as the least-squares calculated values of the activation parameters are shown in Table II.[12] The faster rate constant was ascribed to k_{-2} and the slower one to k_{-1}. Equations 8 and 9 define k_{-2} and k_{-1}. The calculated maxima

$$\textit{cis}\text{-}Cr(C_2O_4)_2(H_2O)_2^- + \text{DMF} \xrightarrow{k_{-2}} \textit{cis}\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^- + H_2O \quad (8)$$

$$\textit{cis}\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^- + \text{DMF} \xrightarrow{k_{-1}} \textit{cis}\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)_2^- + H_2O \quad (9)$$

were at 565 and 420 nm with molar absorptivities of 75 and 74 M^{-1} cm^{-1}, respectively. This agrees well with those calculated before. The high molar absorptivities and the shape of the visible absorption spectrum implied that the intermediate was the cis isomer.[4] The arguments against a more complex reaction scheme than eq 8 and 9 were the same as used for the aquation reactions. The activation parameters are indicative of associative activation in both reactions. However, the fact that these reactions are occurring in a nonaqueous solvent made this conclusion very tentative. The effect of solvation in DMF on the reaction kinetics could be drastically different from the effects in water. The closet comparison is the solvolysis of *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ in Me_2SO. The activation parameters associated with k_{-2} and k_{-1} in Me_2SO are 29 and 30 kcal/mol and +20 and +22 cal/(deg mol) for ΔH^* and ΔS^*, respectively. These values are drastically different than those for DMF. The high ΔH^* values and the positive ΔS^* values would imply dissociative activation for the reactions in Me_2SO.

It seems unlikely, although possible, that a complete change in the type of mechanism of the reaction would occur when changing from one dipolar aprotic solvent to another dipolar aprotic solvent. It is more reasonable to ascribe the large difference in activation parameters to solvation effects.

The rate constant for H_2O exchange in *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ has been reported to be 7.8×10^{-6} s^{-1} at 25 °C.[16] No activation parameters were reported. On the assumption that there is no increase in the rate constant for H_2O exchange as a function of solvent, it is clear that the reactions must be associatively activated.[17]

Equilibrium Quotients. The equilibrium quotients can be defined as in eq 10 and 11, where γ_i are the activity coefficients

$$Q_1 = K_1\frac{\gamma_3\gamma_{\text{DMF}}}{\gamma_2\gamma_{H_2O}} = \frac{[\textit{cis}\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^-][H_2O]}{[\textit{cis}\text{-}Cr(C_2O_4)_2(OH_2)_2^-][HCON(CH_3)_2]} \quad (10)$$

$$Q_2 = K_2\frac{\gamma_2\gamma_{\text{DMF}}}{\gamma_1\gamma_{H_2O}} = \frac{[\textit{cis}\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-][H_2O]}{[\textit{cis}\text{-}Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^-][HCON(CH_3)_2]} \quad (11)$$

and 1, 2, and 3 refer to *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$, *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)(OH_2)^-$, and *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$, respectively.

The quantity $\bar{n}$ is defined by eq 12, where $[\text{DMF}]_{\text{complex}}$ is

$$\bar{n} = \frac{[\text{DMF}]_{\text{complex}}}{[\text{Cr}]_{\text{tot}}} = \frac{Q_1\dfrac{[HCON(CH_3)_2]}{[H_2O]} + 2Q_1Q_2\dfrac{[HCON(CH_3)_2]^2}{[H_2O]^2}}{1 + Q_1\dfrac{[HCON(CH_3)_2]}{[H_2O]} + Q_1Q_2\dfrac{[HCON(CH_3)_2]^2}{[H_2O]^2}} \quad (12)$$

the total amount of DMF in $[\text{Cr}]_{\text{tot}}$ and $[HCON(CH_3)_2]$ and $[H_2O]$ are the molar concentrations in the mixed solvents. The data in Figure 1 were fit to eq 12 by using the least-squares program.[12] The solid line is the least-squares calculated values of n̄. The values of Q_1 and Q_2 are 5.55 ± 0.27 and 0.437 ±

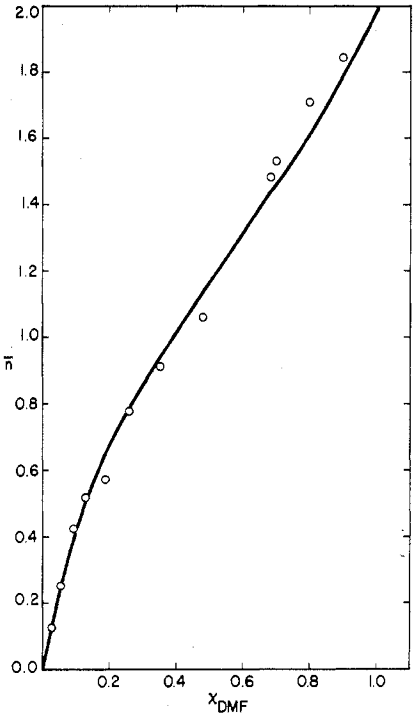

Figure 1. Plot of $\bar{n}$ vs. χ_{DMF} at 25 °C and $[H^+] \approx 10^{-3}$ M. The solid line is the least-squares fit of the data.

0.069, respectively. The value of Q_1 for NCS^- is 4.50 ± 0.06.[3]

Unfortunately, no other values of Q have been measured for *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$. Hence, comparisons and trends cannot be discussed yet.

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Registry No. *cis*-$Cr(C_2O_4)_2(HCON(CH_3)_2)_2^-$, 69847-06-9; *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$, 15489-30-2; $HCON(CH_3)_2$, 68-12-2.

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Mechanistic Information from the Effect of Pressure on the Kinetics of Some Anation Reactions of Aquopentaamminecobalt(III), -rhodium(III), and -chromium(III) Ions in Acidic Aqueous Solution[1]

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The anations of $Co(NH_3)_5OH_2^{3+}$ by Cl^- and SO_4^{2-}, $Rh(NH_3)_5OH_2^{3+}$ by Cl^-, and $Cr(NH_3)_5OH_2^{3+}$ by NCS^- were studied in acidic aqueous solution as a function of nucleophile concentration and pressure up to 1.5 kbar. No kinetic evidence for the participation of ion pairs could be found. The volumes of activation for the anation reactions are +1.4 ± 0.8 (μ = 2 M, 60 °C), +2.3 ± 1.8 (μ = 2 M, 60 °C), +3.0 ± 0.7 (μ = 2 M, 60 °C), and −4.9 ± 0.6 cm^3 mol^{-1} (μ = 1 M, 50 °C), respectively. These values were used in conjunction with the volumes of activation for the corresponding aquation reactions to estimate the overall volume changes incurred in the reactions. The latter could then be compared with independently obtained values of $\Delta\bar{V}$. The results are discussed in terms of an interchange mechanism and compared with data reported in the literature.

Introduction

The anation reactions of Co(III), Rh(III), and Cr(III) pentaammine complexes have been extensively studied for a wide range of organic and inorganic entering ligands in aqueous medium.[4-21] During the anation process, the ammonia ligands are tightly bound to the metal ion[22] and, in most cases,[20] are substitution inert. These reactions are generally accepted[5] to proceed according to an interchange mechanism:[7,23]

$$M(NH_3)_5OH_2^{3+} + X^- \overset{K_x}{\rightleftharpoons} \{M(NH_3)_5OH_2^{3+},X^-\} \quad (1)$$

$$\{M(NH_3)_5OH_2^{3+},X^-\} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} M(NH_3)_5X^{2+} + H_2O \quad (2)$$

where M = Co(III), Rh(III), or Cr(III) and X = Cl, Br, NCS, CH_3COO, etc. Burnett[18] suggested that ion triplets also participate in the above mechanism at high concentrations of X^-, although this suggestion was criticized in later work.[24]

In many of these studies, K_x, k_a, and k_b were estimated from the dependence of k_{obsd} (observed first-order rate constant) on $[X^-]$. Various independent methods have been used[19,25-27] to estimate values for K_x. These measurements were usually restricted to low ionic strengths, whereas the kinetic studies