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Temperature-Jump Studies on the Equilibration of Thiocyanate and Pyridine with the Di-μ-oxo-bis[aquooxalatooxomolybdenum(V)] Complex. Substitution Cis to a Terminal Oxo Ligand

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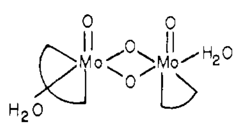
Received February 17, 1976 AIC60120P

The rapid 1:1 equilibrations of thiocyanate and pyridine with the title complex, $Mo_2O_4(C_2O_4)_2^{2-}$ (I), have been studied by the temperature-jump technique over a range of temperatures 10–32 °C, $I = 1.00$ M ($NaClO_4$). Replacement of an H_2O ligand cis to a terminal oxo group occurs in both cases. Rate constants k_f for complex formation ($M^{-1}\ s^{-1}$) and activation parameters $\Delta H^\ddagger$ (kcal mol^{-1}) and $\Delta S^\ddagger$ (cal $K^{-1}\ mol^{-1}$) at 25 °C are respectively 0.50×10^4, 11.2, −4.2 (NCS^-) and 0.30×10^4, 10.8, −6.5 (py). These values are consistent with a dissociative S_N1 nonlimiting (or I_d) mechanism for substitution. Comparisons are made with other studies of complexes having terminal oxo ligands, and features of reactions involving substitution at positions cis and trans to oxo ligands are discussed.

The kinetics of equilibration of NCS^- with the molybdenum(V)–aquo dimer $Mo_2O_4^{2+}$, have been studied previously.[1] On the basis of comparisons with data for reactions of VO^{2+} it was suggested that replacement of an H_2O cis (rather than trans) to one of the terminal oxo ligands is involved. Cotton and Morehouse[2] have carried out an x-ray crystallographic study of the barium salt of the di-μ-oxo-bis[aquooxalatomolybdenum(V)] complex, $Mo_2O_4(C_2O_4)_2^{2-}$,[3] and demonstrated that the H_2O ligands occupy positions cis to the terminal oxo groups (I). Derivatives of I have been prepared by Mitchell.[4] With a view to further clarifying mechanistic assignments for substitution at Mo(V) it seemed desirable to extend the earlier work to a consideration of substitution processes at the cis H_2O sites of I.



I

Experimental Section

Reactants. The Mo(V) oxidation state was generated by reduction of sodium molybdate (8.2 g) in 10 M HCl (180 ml) with hydrazine hydrochloride (6.6 g) at 80 °C for 2–3 h. The solution was concentrated ca. fourfold using a rotary evaporator. Aliquots of this green-brown solution (as required) were diluted ca. 100-fold by addition of oxygen-free water to give a final [H^+] of ca. 0.1 M. Under these conditions the Cl^- is aquated and the aquo dimer $Mo_2O_4^{2+}$ is formed. The solution was passed down a column of Dowex 50W-X8 ion-exchange resin using air-free conditions, and after being washed free of Cl^-, the $Mo_2O_4^{2+}$ eluted with 1 M $HClO_4$. Stock solutions obtained were standardized spectrophotometrically, $Mo_2O_4^{2+}$ peak at 384 nm (ϵ 103 $M^{-1}\ cm^{-1}$), and stored under N_2.

Sodium thiocyanate (Hopkin and Williams, GPR) was recrystallized from water and standardized by titration with Hg(II). All other reagents used were of Analar grade purity. Ionic strengths were adjusted to $I = 1.00$ M using $NaClO_4$.

The oxalato complex, $Mo_2O_4(C_2O_4)_2^{2-}$, was prepared freshly each day in situ by addition of a 5% excess of oxalic acid (BDH, Analar) to $Mo_2O_4^{2+}$ (ca. 10^{-3} M) and adjusting the pH to the range 3–4.5. From spectrophotometric measurements at λ 384 nm, [H^+] = 0.5–2.0 M, it was estimated that for the conditions of our experiments $Mo_2O_4(C_2O_4)_2^{2-}$ was in excess of $Mo_2O_4^{2+}$ by ca. 10^5:1. Identical kinetic behavior was observed when the oxalate added was in 10% excess. There is no evidence for coordination of a third oxalate.[4] The oxalato complex has a broad peak at ca. 384 nm, ϵ 297 $M^{-1}\ cm^{-1}$. Above pH 5.5 the spectrum of $Mo_2O_4(C_2O_4)_2^{2-}$ is pH dependent with drastic changes occurring in the 350–450-nm region. Such changes are consistent with acid dissociation processes involving the aquo ligands of I. Precipitation occurs at pH >6.0 with [$Mo_2O_4(C_2O_4)_2^{2-}$] = 6×10^{-4} M. Care was taken not to exceed pH 5 in the preparation of all $Mo_2O_4(C_2O_4)_2^{2-}$ solutions. The reactants NCS^- and pyridine were added to $Mo_2O_4(C_2O_4)_2^{2-}$ as required, followed by the buffer in the case of the pyridine study. The pH was adjusted by addition of NaOH.

Although it was necessary to store all Mo(V) solutions in air-free conditions, rigorous air-free techniques were not necessary for ~20-min periods as required for each temperature-jump experiment.

Solutions for studies on the complexing of pyridine to $Mo_2O_4(C_2O_4)_2^{2-}$ required a higher range of pH and were buffered with 0.05–0.10 M acetate. At these concentrations of acetate there is no observable effect on the visible spectrum of $Mo_2O_4(C_2O_4)_2^{2-}$,[5] and in kinetic studies relaxation times obtained were independent of buffer concentrations.

Protonation Constants. These were determined for pyridine at temperatures 17.9–31.9 °C, $I = 1.00$ M ($NaClO_4$) (eq 1). Solutions

$$H^+ + py \overset{K_p}{\rightleftharpoons} Hpy^+ \tag{1}$$

of pyridine (ca. 4×10^{-3} M, 100 ml) in a double-walled thermostated jacket were titrated potentiometrically with 0.25 M $HClO_4$. All pH measurements were made using a Radiometer (PHM 4d) meter with glass (Type G202C) and calomel (Type K401) electrodes. The salt bridge of the calomel electrode contained saturated NaCl, and the meter was standardized against perchloric acid solutions of known concentration, $I = 1.00$ M ($NaClO_4$). Protonation constants were evaluated from titration curves using the Miniquad computer program.[6]

Formation Constants. These were determined spectrophotometrically, λ 380 nm, for thiocyanate and pyridine binding to $Mo_2O_4(C_2O_4)_2^{2-}$. With NCS^- the pH was in the range 2.8–3.2 and $[NCS^-]$ (in large excess) was varied 0.03–0.50 M. The absorbance (A) of solutions is given by (2), where A_0 is the absorbance with no NCS^-

$$A = -\frac{1}{K_1}\frac{(A - A_0)}{[NCS^-]} + [Mo_2]_t\epsilon_c \tag{2}$$

added, $[Mo_2]_t$ is the total concentration of molybdenum dimer present (1.38×10^{-3} M), and ϵ_c is the absorption coefficient (M^{-1} cm^{-1}) of the complex formed. The formation constant K_1 for the 1:1 complex (eq 3) was obtained from the slope of a graph of A against $(A -$

$$Mo_2O_4(C_2O_4)_2^{2-} + NCS^- \overset{K_1}{\rightleftharpoons} Mo_2O_4(C_2O_4)_2(NCS)^{3-} \tag{3}$$

$A_0)/[NCS^-]$. A similar expression was obtained for 1:1 complexing with py (K_2) where allowances were made for the formation of Hpy^+. All spectrophotometric measurements were on a Unicam SP8000 recording spectrophotometer with cell compartment thermostated to 25.0 ± 0.1 °C.

Kinetic Measurements. These were done using the Messanlagen-Studiengesellschaft, Göttingen, temperature-jump apparatus. A temperature rise of typically 2.8 °C was obtained by applying a voltage of 35 kV to solutions. The temperature of the sample solution was measured immediately before the temperature jump using a Comark Type 1604 electronic thermometer. The temperature after the jump is accurate to ±0.2 °C. The kinetics were monitored by measuring absorbance changes at 380 nm. In all cases only one relaxation process, a decrease in absorbance due to the decrease in stability of the mixed-ligand complex at higher temperatures, was observed. Output from the photomultiplier was stored on a Tektronics 564B storage oscilloscope and photographed on 35-mm film. The relaxation time (τ) for the decay was obtained by curve matching using an exponential generator.[7] Each relaxation time is typically an average of five measurements. Complexing ligand concentrations were in >10-fold excess of $Mo_2O_4(C_2O_4)_2^{2-}$. Because of the low formation constants for ligand binding to $Mo_2O_4(C_2O_4)_2^{2-}$ no evidence was obtained for the formation of higher than 1:1 complexes.

Treatment of Data. Formation constants (and errors) were obtained from an unweighted least-squares treatment of absorbance data. Activation parameters for the reactions with NCS^- and py were determined using a nonlinear least-squares program.[8]

Results

Protonation constants (M^{-1}) as defined in (1) for pyridine ($10^{-5}K_p$) are 4.77 (17.9 °C), 3.62 (25.0 °C), and 2.71 (31.9 °C), giving $\Delta H = -7.3 \pm 0.3$ kcal mol^{-1} and $\Delta S = 1.5 \pm 1.0$ cal K^{-1} mol^{-1}, $I = 1.00$ M ($NaClO_4$). Existing literature values are, at 25 °C, $10^{-5}K_p = 5.18$ M^{-1}, $I = 0.1$ M ($NaClO_4$),[9] and 1.76 M^{-1}, $I = 1.0$ M ($NaClO_4$).[10]

Formation constants, e.g., as defined in (2), determined at 25 °C, $I = 1.00$ M ($NaClO_4$), were $K_1 = 4.3 \pm 0.2$ M^{-1} for NCS^- (see Figure 1) and $K_2 = 39.5 \pm 2.0$ M^{-1} for py. From the intercept of the A axis of Figure 1, the absorption coefficient for the thiocyanato complex is 890 M^{-1} cm^{-1} and for the pyridine complex 829 M^{-1} cm^{-1} at 380 nm. The point for $[NCS^-] = 0.50$ M lies on the line, Figure 1, and no evidence for formation of a bis(thiocyanato) complex is apparent. If the two molybdenum aquo sites are regarded as identical and independent then it can be reasoned on statistical grounds that the equilibrium constants for formation of the bis complexes are $K_1/4$ and $K_2/4$, respectively. Concentrations of reactants were chosen to minimize such complexing.

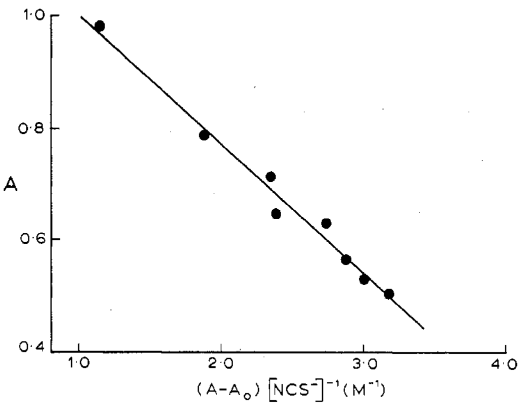


Figure 1. Spectrophotometric determination of the equilibrium constant K_1 for the formation of the 1:1 complex of NCS^- with $Mo_2O_4(C_2O_4)_2^{2-}$, eq 2, at 25 °C, $I = 1.00$ M ($NaClO_4$).

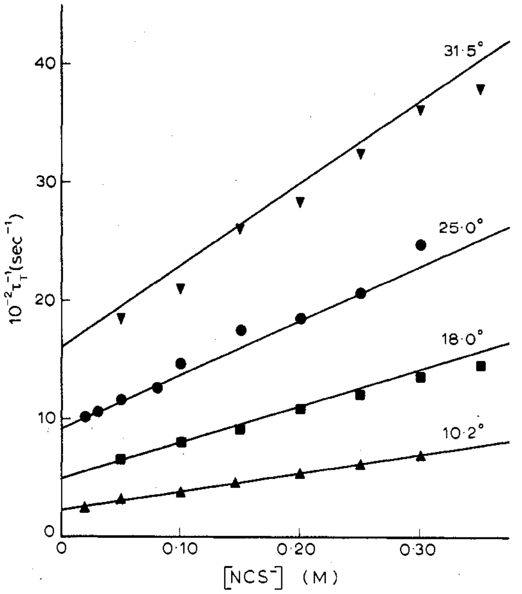


Figure 2. Dependence of reciprocal relaxation times on $[NCS^-]$ for the equilibration of NCS^- with $Mo_2O_4(C_2O_4)_2^{2-}$, eq 4, $I = 1.00$ M ($NaClO_4$).

Reciprocal relaxation times from temperature-jump studies for the equilibration of NCS^- with $Mo_2O_4(C_2O_4)_2^{2-}$ at temperatures 10.2–31.5 °C, with the complex ca. 1.5×10^{-3} M and $[NCS^-]$ in the range 0.02–0.35 M, are given in Table I.[11] A linear dependence on $[NCS^-]$ is obtained (eq 4), Figure

$$\tau_T^{-1} = k_{1f}[NCS^-] + k_{1b} \tag{4}$$

2, from which forward (k_{1f}) and back (k_{1b}) rate constants can be obtained. Computed lines (using best fit of data at all temperatures) are shown. The variation of pH 2.8–3.2 did not affect values of τ_T^{-1}. The temperature was varied within the range 10–32 °C and activation parameters for k_{1f} and k_{1b} were obtained.

Details of reciprocal relaxation times for the equilibration of $Mo_2O_4(C_2O_4)_2^{2-}$ (ca. 1.4×10^{-3} M) with pyridine (0.156–0.467 M) are given in Table II.[11] A dependence on $[H^+]$, $(1.4–5.4) \times 10^{-5}$ M, was observed and a good fit was obtained in (5), where k_{2f} and k_{2b} are forward and back rate constants for the equilibration with py (pyH^+ is not reactive) and $[py]_t$ is the total pyridine concentration. Rate constants

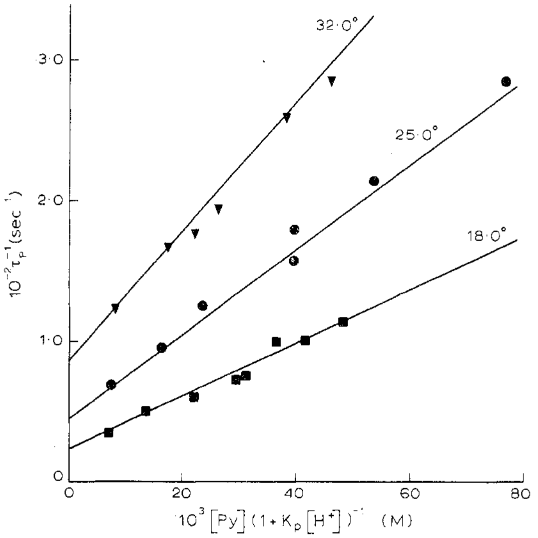


Figure 3. Dependence of reciprocal relaxation times on the concentration of unprotonated pyridine for the equilibration of pyridine with $Mo_2O_4(C_2O_4)_2^{2-}$, eq 5, $I = 1.00$ M ($NaClO_4$).

Table III. Summary of Rate Constants (25 °C) and Activation Parameters for Forward (k_f) Reactions Involving 1:1 Complex Formation of $Mo_2O_4(C_2O_4)_2^{2-}$ (k_{1f} and k_{2f}) and $Mo_2O_4^{2+}$

Reactant	$10^{-4}k_f$, M^{-1} s^{-1}	$\Delta H_f^‡$, kcal mol^{-1}	$\Delta S_f^‡$, cal K^{-1} mol^{-1}
NCS^- (k_{1f})^a	0.50 ± 0.02	11.2 ± 0.7	−4.2 ± 2.4
py (k_{2f})^a	0.30 ± 0.02	10.8 ± 1.6	−6.5 ± 5.5
NCS^- ^{b,c}	2.9 ± 0.10	11.3 ± 0.9	−0.3 ± 3.1

^{a} $I = 1.00$ M ($NaClO_4$). ^{b} $I = 2.00$ M ($LiClO_4$); ref 1. ^{c} Reaction with the aquo ion $Mo_2O_4^{2+}$. Statistical factor of 2 should be applied since four equatorial cis H_2O sites are available, whereas there are only two for the oxalato complex I.

$$\tau_P^{-1} = \frac{k_{2f}[\mathrm{py}]_t}{1 + K_P[\mathrm{H}^+]} + k_{2b} \tag{5}$$

(25 °C) and activation parameters are listed in Tables III and V below.

Discussion

Kinetic data for the formation of 1:1 complexes of the dimer $Mo_2O_4(C_2O_4)_2^{2-}$ (I) with NCS^- and py are summarized in Table III. One of the two identical H_2O sites in I is utilized for complex formation. The enthalpy terms $\Delta H_f^‡$ are virtually identical which suggests that the mechanism of substitution is dissociative SN1 nonlimiting (or I_d). This is supported by $\Delta S_f^‡$ values which are close to zero and similar K_f values at 25 °C. Data for 1:1 complex formation between the aquo dimer $Mo_2O_4^{2+}$ and NCS^- are also given in Table III.[1] Since there are four H_2O's occupying cis sites in $Mo_2O_4^{2+}$, the value of k_f requires division by a statistical factor of 2 thus enabling direct comparison. Good agreement is observed with the kinetic data for $Mo_2O_4(C_2O_4)_2^{2-}$.

For a dissociative process k_f is equal to the product $k_{ex}K_{os}$, where k_{ex} (s^{-1}) is the rate constant for loss of H_2O (which is expected to show little variation for the reactants under consideration) and K_{os} is the outer-sphere association constant for the complex with the incoming ligand. Values of K_{os} introduced by the variations in charge on the reactants can be estimated assuming each molybdenum coordination sphere has a net charge of 1− in the case of I and 1+ in the case of the aquo dimer $Mo_2O_4^{2+}$. Electrostatic interactions of (1−, 1−), (1−, 0), and (1+, 1−) pairs are not expected to give very different values of K_{os} (possibly within a factor of 3).[12] Thus trends in k_f values in Table III directly attributable to charge are not expected to be large, which is in fact the case.

Table IV. Comparison of Formation Constants (25 °C) for 1:1 Complexes of $Mo_2O_4(C_2O_4)_2^{2-}$ (I) As Determined by Spectrophotometric Means and from Kinetic Data (k_f/k_b), $I = 1.0$ M ($NaClO_4$)

Reactant	K(spec), M^{-1}	K(kin), M^{-1}
NCS^- (K_1)	4.3 ± 0.2	5.5 ± 0.4
py	39.5 ± 2.0	68.2 ± 12.0

Table V. Summary of Rate Constants (25 °C) and Activation Parameters for Back-Reactions Involving Aquation of 1:1 Complexes of $Mo_2O_4(C_2O_4)_2^{2-}$ (k_{1b} and k_{2b}) and $Mo_2O_4^{2+}$

Complex	k_b, s^{-1}	$\Delta H_b^‡$, kcal mol^{-1}	$\Delta S_b^‡$, cal K^{-1} mol^{-1}
$Mo_2O_4(C_2O_4)_2NCS^{3-}$ (k_{1b})^a	916 ± 38	15.1 ± 1.2	5.6 ± 4.1
$Mo_2O_4(C_2O_4)_2py^{2-}$ (k_{2b})^a	48.7 ± 6.3	16.3 ± 4.2	3.8 ± 14.0
$Mo_2O_4NCS^+$ ^{b}	120 ± 10	13.7 ± 2.5	−3.0 ± 8.0

^{a} $I = 1.00$ M ($NaClO_4$). ^{b} $I = 2.00$ M ($LiClO_4$); ref 1.

Comparisons of the substitution behavior of $Mo_2O_4^{2+}$ and VO^{2+} are believed to be relevant due to structural similarities arising from the presence of terminal oxo ligands and labilization of ligands in the trans position.[13] Wüthrich and Connick[14] have obtained evidence from NMR studies for a rapid (solvent) water exchange of the H_2O trans to the oxo group (ca. 10^{11} s^{-1}). Occupancy of the trans position is possibly to be regarded as little different to outer-sphere complexing. The cis H_2O's exchange at a much slower rate. Formation of the 1:1 cis complex of NCS^- with VO^{2+} has also been studied and kinetic data ($k_f = 11.5 \times 10^3$ M^{-1} s^{-1}, $\Delta H_f^‡ = 10.8$ kcal mol^{-1}, $\Delta S^‡ = -3.7$ cal K^{-1} mol^{-1}, $I \to 0$) are very similar to those obtained for $Mo_2O_4(C_2O_4)_2^{2-}$ and $Mo_2O_4^{2+}$.[15] On the basis of this comparison there seems little doubt that structure I is retained in these studies and that the kinetic data for $Mo_2O_4(C_2O_4)_2^{2-}$ and $Mo_2O_4^{2+}$ correspond to replacement of a cis H_2O.[20] What is interesting with regard to I is the preference oxalate shows for chelating at positions cis and trans to the oxo group.

Formation constants determined spectrophotometrically, Table IV, are in satisfactory agreement with kinetic values (k_f/k_b). In contrast to k_f values, formation constants are influenced by the charge on the complex. Thus the value for NCS^- complexing with $Mo_2O_4^{2+}$ (240 M^{-1}) is significantly greater than for complexing with $Mo_2O_4(C_2O_4)_2^{2-}$ (4.3 M^{-1}). The basicity of the ligand is also important in explaining the difference in formation constants for $Mo_2O_4(C_2O_4)_2^{2-}$ with NCS^- (4.3 M^{-1}) and py (39.5 M^{-1}). These trends can be explained by consideration of the back-reactions, Table V, involving dissociation of NCS^- and py, from the 1:1 complexes. For a dissociative process bond strengths, as determined by such factors as charge and basicity of the leaving group, influence the bond-breaking process. The net negative charge of I favors bond breaking in the case of NCS^-. Pyridine is known to be more basic than NCS^- thus again favoring bond breaking for NCS^-.

Finally attention must be drawn to the different interpretations as required in this work (cis substitution) and for the reactions in CH_2Cl_2 solvent of the mononuclear Mo(V) complex $MoOCl_3(OPPh_3)_2$.[16] Replacement of a triphenylphosphine oxide ligand by Cl^- and Br^- has been studied in the latter case, where the simplest interpretation is in terms of an SN1 limiting (or D) mechanism involving the $OPPh_3$ ligand trans to the oxo group. Kinetic data for the dissociation step are typically the rate constant 42 s^{-1}, $\Delta H^‡ = 16.5$ kcal mol^{-1}, and $\Delta S^‡ = 4.2$ cal K^{-1} mol^{-1}.[16] We have considered the possibility that a rapid isomerization occurs in the present study, so that an H_2O ligand of I occupies the trans position and rate constants for $Mo_2O_4(C_2O_4)^{2-}$ in Table III therefore correspond to a composite term $k_{trans}K_{isom}$. However a strong feature of the present interpretation is the correspondence of data for $Mo_2O_4(C_2O_4)_2^{2-}$, $Mo_2O_4^{2+}$, and VO^{2+}. The behavior of VO^{2+} is now well established,[17] and the high lability of the trans H_2O has been confirmed using EPR[18,19] as well as NMR line-broadening techniques.[14] Structural similarities of V(IV) and Mo(V) complexes having terminal oxo ligands must again be stressed.[13]

Acknowledgment. G.R.C. is grateful to ICI Ltd. for a postdoctoral fellowship. Helpful discussions with Drs. Garner and Hyde are also acknowledged.

Registry No. $Mo_2O_4(C_2O_4)_2^{2-}$, 60209-19-0; NCS^-, 302-04-5; py, 110-86-1.

Supplementary Material Available: Tables I and II listing reciprocal relaxation times (3 pages). Ordering information is given on any current masthead page.

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(20) **Note Added in Proof.** Dr. Y. Sasaki of the Tohoku University, Sendai, Japan, has recently observed that the ^{13}C NMR spectrum of $K_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ in water, pH ~4, gives only one sharp peak at 168.0 ppm at 34 °C. This suggests that there may be some rapid process in solution by which the C atoms assume equivalence.

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Mechanistic Implications of Kinetic Data for the Formation and Aquation of Acidopentaamminechromium(III) Complexes, $Cr(NH_3)_5X^{2+}$, $X^- = NCS^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$, Cl^-, Br^-, and I^-. Evidence for a Dissociative Mechanism

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Received March 22, 1976 AIC60210U

Rate constants (k_{aq}) for the aquation of six different acidopentaamminechromium(III) complexes, $Cr(NH_3)_5X^{2+}$, with $X^- = NCS^-$, $CCl_3CO_2^-$, $CF_3CO_2^-$, Cl^-, Br^-, and I^-, have been determined at 50 °C, $I = 1.00$ M ($LiClO_4$). Rate constants (k_f) for the corresponding anation reactions of $Cr(NH_3)_5H_2O^{3+}$ have been obtained for all except $X^- = I^-$. Information regarding equilibrium constants, $K_{OS}K_{IS}$, for the formation of $Cr(NH_3)_5X^{2+}$ from $Cr(NH_3)_5H_2O^{3+}$, using procedures involving ion-exchange separation and determination of products, is reported. The values obtained are in satisfactory agreement with kinetically determined values (k_f/k_{aq}) at 50 °C, $I = 1.00$ M ($LiClO_4$). A graph of log k_{aq} against $-\log K_{OS}K_{IS}$ gives a slope of 0.91 ± 0.05. A narrow range of formation rate constants, k_f, is observed and when allowance is made for the outer-sphere association constants in cases where K_{OS} has been evaluated (the NCS^- study only in this work) values of k_f/K_{OS} are comparable with the water exchange rate constant for $Cr(NH_3)_5H_2O^{3+}$ at 50 °C. The results suggest that $Cr(NH_3)_5H_2O^{3+}$ exhibits more dissociative character than $Cr(H_2O)_6^{3+}$ in the substitution of H_2O.

The aquation rate constants for the acidopentaamminechromium(III) complexes, $Cr(NH_3)_5X^{2+}$, $X^- = NCS^-$,[1] $CCl_3CO_2^-$,[2] $CF_3CO_2^-$,[3] Cl^-,[4] Br^-, and I^-,[5] have been determined previously. Different ionic strengths and media were used, however, and a meaningful comparison of data is therefore difficult. Duffy and Earley[4] have determined the rate constants for water exchange of $Cr(NH_3)_5H_2O^{3+}$ as well as the anation of this complex with Cl^- and NCS^- and have proposed a dissociative interchange (I_d) mechanism. For a part of their study (the NCS^- anation reaction), NaBr was used to adjust the ionic strength and the inner- and outer-sphere associations of Br^- appear to have been neglected. It has been observed in earlier work that after allowing for outer-sphere association (K_{OS} obtained from kinetics) the rate constants for $C_2O_4^{2-}$, $HC_2O_4^-$,[6] and $^+NH_3CH_2CO_2^-$ [7] are about the same as for water exchange. Hence a dissociative I_d mechanism has been suggested. Swaddle and Stranks,[8] on the other hand favor an associative interchange, I_a, for the water exchange reaction on the basis that a negative volume of activation (-5.8 cm^3 mol^{-1}) has been obtained. It is not clear therefore from these various studies whether the interchange mechanism involved is associative or dissociative.

The aim of this investigation is to extend previous studies to include all relevant kinetic and thermodynamic measurements, thus enabling a firm mechanistic assignment to be made.

Experimental Section

Materials. Literature methods were used to prepare the complexes $[Cr(NH_3)_5H_2O](ClO_4)_3$,[9] $[Cr(NH_3)_5(NCS)](ClO_4)_2$,[10] $[Cr(NH_3)_5(O_2CCCl_3)](ClO_4)_2 \cdot H_2O$,[11] $[Cr(NH_3)_5(O_2CCF_3)](ClO_4)_2$,[11] $[Cr(NH_3)_5Cl](ClO_4)_2$,[12] and $[Cr(NH_3)_5I]Cl_2$.[13] The complex $[Cr(NH_3)_5Br]Br_2$ was prepared by heating $[Cr(NH_3)_5H_2O](ClO_4)_3$ (1.0 g) in 50 ml of solution containing 2.5 M NaBr and 0.1 M $HClO_4$ at 50 °C. Crystals of $[Cr(NH_3)_5Br]Br_2$ were obtained within about