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Trans-Cis Isomerization of *trans*-Bis(oxalato)diaquochromate(III) and the Corresponding Hydroxy Complexes

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The trans-cis isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ and the corresponding hydroxy complexes has been studied at 15, 25, and 35 °C in 0.010 M buffers between pH 3.0 and 11.5 and at μ = 1.00 M ($NaClO_4$). The first-order rate constants at 25.0 °C for the isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$, *trans*-$Cr(C_2O_4)_2(OH)H_2O^{2-}$, and *trans*-$Cr(C_2O_4)_2(OH)_2^{3-}$ are $(4.89 \pm 0.45) \times 10^{-4}$, $(3.93 \pm 0.27) \times 10^{-3}$, and $(7.70 \pm 0.38) \times 10^{-2}$ s^{-1}, respectively. The values of ΔH^* respectively are 18.1 ± 0.1, 20.3 ± 0.6, and 20.4 ± 0.7 kcal/mol. The values of ΔS^* are −12.8 ± 0.4, −1.3 ± 2.0, and +4.7 ± 2.5 cal/(deg mol), respectively. The values of the acid dissociation constants, ${}^tK_{a_1}$ and ${}^tK_{a_2}$, of the trans isomer are $(1.08 \pm 0.24) \times 10^{-6}$ and $(2.28 \pm 0.34) \times 10^{-10}$ M at 25 °C. The relative values of the activation parameters can be interpreted to imply that the hydroxide ligand stabilizes the ground-state complex and allows for a more expanded activation complex for the isomerization.

Introduction

The alteration of the reactivity of metal ions, including that of Cr(III), as a function of the coordinated ligands has long been of interest in this laboratory.[1-4] The labilization of Cr(III) when coordinated to a hydroxide ion,[5,6] a porphyrin,[1-3,7,8] an alkyl group,[9] a sulfite ion,[10] a nitrate ion,[10] a nitrite ion,[10] an acetate ion,[10] a carbonate ion,[10] and some hexadentate ions[11] is documented.

The labilization of the Cr(III) ion has added significance in view of the report of the presence of Cr(III) in the glucose tolerance factor obtained from brewer's yeast.[12] If indeed an aquo Cr(III) species is present, the environment in which it is most likely to exist would be such that the Cr(III) species would exist as a hydroxy species. The reactivity of the species would be greatly altered from that in acidic solution if it were to behave as the reported Cr(III) compounds.

This labilization by the hydroxide ligand had been studied earlier in the aquation of *cis*-$Cr(C_2O_4)_2(N_3)H_2O^{2-}$ and *trans*-$Cr(C_2O_4)_2(CH_3CO_2)H_2O^{2-}$.[4,13] It was decided additionally to investigate in basic solutions some previously studied systems. The trans-cis isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ was chosen as a first reaction for study. The isomerization of *trans*-$Cr(C_2O_4)_2(OH)H_2O^{2-}$ and *trans*-$Cr(C_2O_4)_2(OH)_2^{3-}$ has been studied previously.[13] However, preliminary experiments demonstrated that the method used in this previous study of adding 1.1 and 2.8 equiv of sodium hydroxide to a solution of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ and then observing the kinetics of the isomerization reaction would give erroneous kinetic results. This is a report of the detailed investigation of the kinetics of the isomerization of *trans*-$Cr(C_2O_4)_2(OH)H_2O^{2-}$ and *trans*-$Cr(C_2O_4)_2(OH)_2^{3-}$.

Experimental Section

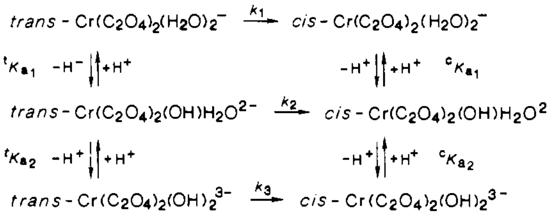
All chemicals used were of analytical or primary standard grade, depending upon the need. The Na[*trans*-$Cr(C_2O_4)_2(H_2O)_2$]·$3H_2O$ was prepared by the method described by Werner.[14] Sodium perchlorate was prepared from Na_2CO_3 and $HClO_4$. The buffers used were sodium acetate (pH 3.5–6.5), 2,6-dimethylpyridine (pH 5.8–7.6), boric acid (pH 7.2–9.6), and sodium dihydrogen phosphate (pH 10.5–11.5).

The kinetic runs were performed by using a Beckman DU equipped with upgraded electronics and interfaced to an Apple II+ via an Interactive Microwave, Inc., fast A to D data acquisition system. The cell compartment was fitted with a block through which water at the desired temperature was circulated. The kinetic runs were made in one of two ways, depending upon the rate of the reaction. In those reactions that took longer than 700 s to complete, conventional mixing techniques were used. A solution containing 0.01 M of the desired buffer, the required amount of $HClO_4$ or NaOH to give the desired pH, and the proper amount of $NaClO_4$, such that μ = 1.00 M, was thermostated at the desired temperature. Then, solid Na[*trans*-$Cr(C_2O_4)_2(H_2O)_2$]·$3H_2O$ was added (0.010 M) and dissolved. The thermostated cuvette then was filled and placed in the spectrophotometer. The absorbance-time (A–t) data at 416 nm were collected, the ln $(A - A_\infty)$ vs. t plots were made, and the pseudo-first-order rate constants were determined. The plots were linear for at least 4 half-lives. When the time for completion of the reaction was less than 700 s, a Hi-Tech manual stopped-flow mixing device was used. This device allowed the unmixed solutions to be thermostated at the desired temperature. In these cases, two solutions were prepared: one a solution of 1.00 M $NaClO_4$ at pH 4 and the other a solution of the buffer (0.020 M) adjusted to the desired pH with NaOH or $HClO_4$ with μ = 1.00 M ($NaClO_4$). These solutions were both thermostated at the desired temperature. Then, Na[*trans*-$Cr(C_2O)_4(H_2O)_2$]·$3H_2O$ (0.020 M) was dissolved in the $NaClO_4$ solution. Both solutions were loaded into the syringes of the mixing device and the runs made. The data were collected and treated as before. The pH of the solution was measured within 30 s of mixing and found to be constant during the time of the reaction.

Results and Conclusions

The isomerization reactions were pseudo first order in the trans isomer. The pseudo-first-order rate constants, k_{obsd}, were dependent upon the pH in a complex manner. Figure 1 is a plot of the pk_{obsd}–pH data at 25 °C. Similar plots were obtained at 15 and 35 °C. At 15, 25, and 35 °C the number of different pH values studied was 41, 41, and 57, respectively.

The shape of these plots is reminiscent of a pH titration curve of a weak diprotic acid. Hence, the following scheme is proposed to explain the data:



The pseudo-first-order rate constant for this scheme can be expressed as eq 1. The constants are defined in the above scheme.

$$k_{obsd} = \frac{k_1[H^+]^2 + k_2{}^tK_{a_1}[H^+] + k_3{}^tK_{a_1}{}^tK_{a_2}}{[H^+]^2 + {}^tK_{a_1}[H^+] + {}^tK_{a_1}{}^tK_{a_2}} \qquad (1)$$

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Table I. Acid Dissociation Constants, First-Order Rate Constants, and Activation Parameters for Trans–Cis Isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ and the Hydroxy species

	T, °C			ΔH^*, kcal/mol	ΔS^*, cal/(deg mol)
	15	25	35		
k_1, s^{-1}	$(1.65 \pm 0.29) \times 10^{-4}$	$(4.89 \pm 0.45) \times 10^{-4}$	$(1.38 \pm 0.10) \times 10^{-3}$	18.1 ± 0.1	-12.8 ± 0.4
k_2, s^{-1}	$(1.22 \pm 0.83) \times 10^{-3}$	$(3.93 \pm 0.27) \times 10^{-3}$	$(1.31 \pm 0.13) \times 10^{-2}$	20.3 ± 0.6	-1.3 ± 2.0
k_3, s^{-1}	$(2.09 \pm 0.83) \times 10^{-2}$	$(7.70 \pm 0.38) \times 10^{-2}$	$(2.26 \pm 0.15) \times 10^{-1}$	20.4 ± 0.7	$+4.7 \pm 2.5$
${}^tK_{a_1}$, M	$(1.00 \pm 0.56) \times 10^{-6}$	$(1.08 \pm 0.24) \times 10^{-6}$	$(8.43 \pm 1.98) \times 10^{-7}$		
${}^tK_{a_2}$, M	$(3.33 \pm 2.56) \times 10^{-10}$	$(2.28 \pm 0.34) \times 10^{-10}$	$(4.60 \pm 0.60) \times 10^{-10}$		

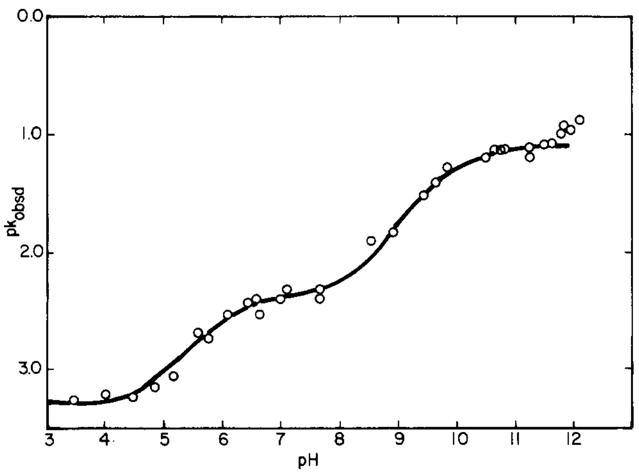

Figure 1. Plot of pK_{obsd} vs pH of the trans–cis isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ at 25 °C and μ = 1.00 M.

The k_{obsd}–pH data at each temperature were fit to eq 1 by using a nonlinear least-squares program.[15] Table I gives the results of these calculations. All uncertainties in Table I and elsewhere are one standard deviation. The solid line in Figure 1 represents the least-squares fit of the data. The activation parameters were calculated with the same program, and the results also are in Table I. The calculations were made with a weighting of $(1/k_{obsd})^2$ or $(1/k_i)^2$.

The values of pK_{a_i} are reported in Table II. There is a dearth of similar data to which comparisons can be made, but several observations are possible. The values of pK_{a_i} for the negatively charged complexes are about 2 larger than for the positively charged complexes. The direction of the change is what is expected from a simple charge consideration. The values of pK_{a_1} for the trans isomers are about 1 smaller than those for the cis isomers whereas pK_{a_2} is about 0.3 larger. This would suggest that the negative charge is more stabilized in the trans isomer than in the cis isomer. This could result from better solvation of the trans species since it is more polar. This line of reasoning could explain the values of pK_{a_2} for the cis and trans isomers since the cis isomer now is the more polar species.

From the data in Table I, it is clear that there has been a labilization of the isomerization of the trans isomer. At 25 °C, there are an 8- and a 20-fold increase in the rate constant in the isomerization reaction in going from *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ to *trans*-$Cr(C_2O_4)_2(OH)H_2O^{2-}$ to *trans*-$Cr(C_2O_4)_2(OH)_2^{3-}$. This labilization is due to a positive increase of 11.5 and 6.0 cal/(deg mol), respectively, in the value of ΔS^*. The value of ΔH^* increases by about 2 kcal/mol. These changes can be rationalized in several different ways. One of the ways is as follows. The formation of the hydroxy ligand results in an increase in the oxygen–chromium bond strength and thus in a stabilization of the ground state of the trans isomer. This also allows extra electron density to be given to the chromium when the oxalate oxygen–chromium bond is either stretched or broken in the activated complex. This allowed "loosening" of the oxalate oxygen–chromium bond results in a more expanded activated complex and hence in a more positive entropy of activation. This line of reasoning would imply that in the *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ isomer the isomerization is occurring via a twist mechanism and that it becomes more dissociative in character in the hydroxyaquo and the dihydroxy isomers.[16] This idea of a twist mechanism is consistent with the observation that no oxygen or oxalate exchange occurs in slightly acidic solutions in 8 days.[17,18]

Table II. Selected Acid Dissociation Constants at 25 °C

complex	pK_{a_1}	pK_{a_2}	ref
cis-$Cr(C_2O_4)_2(H_2O)_2^-$	7.1	9.3	*a*
trans-$Cr(C_2O_4)_2(H_2O)_2^-$	5.97	9.64	*b*
cis-$Cr(H_2NC_2H_2NH_2)_2(H_2O)_2^{3+}$	4.80	7.20	*c*
trans-$Cr(H_2NC_2H_4NH_2)_2(H_2O)_2^{3+}$	4.08	7.5	*c*
cis-$Cr(NH_3)_4(H_2O)_2^{3+}$	5.1	7.4	*d*
trans-$Cr(NH_3)_4(H_2O)_2^{3+}$	4.2		*d*

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The supposition that the hydroxy oxygen–chromium bond strength is increased, or at least made more kinetically inert, is supported by the observation that in two different labile chromium porphyrin complexes the ligation of the dihydroxy complexes has not been observed.[1,7]

These results and conclusions are at odds with the previously reported ones.[13] One can see from Figure 1 that it would be impossible to measure accurately the isomerization of only *trans*-$Cr(C_2O_4)_2(OH)H_2O^{2-}$ by adding 1.1 equiv of NaOH. Also, it was noted that, above a pH of about 12, a second, consecutive reaction occurred and then precipitation began. This second reaction was indeed slower than the isomerization, but it did begin within 100 s of the completion of the isomerization reaction. This is probably dimerization of *cis*-$Cr(C_2O_4)_2(OH)_2^{3-}$.[19]

The isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ has been reported to occur with values of ΔH^* and ΔS^* of +30.5 ± 0.8 kcal/mol and +17.8 ± 2.5 cal/(deg mol), respectively.[20] These values, when compared to the values for isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$, were taken to imply that the isomerization of *trans*-$Cr(C_3H_2O_4)_2(H_2O)_2^-$ occurred with substantial lengthening or cleavage of the malonate oxygen–chromium bond. No kinetic results at higher pH values were reported.

The present study clearly shows that the hydroxy ligand labilizes the isomerization of *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ and that the source of this effect is a substantial increase in ΔS^*. However, upon examination of other examples of labilization by the hydroxy ligand, it is found that the values of the activation parameters do not vary in any systematic manner. Clearly, the systems are more complicated than first supposed.

Superficially, it would appear that there is no comparison between the mechanisms of ligation and isomerization. However, both reactions require the lengthening or possible breaking of a bond. Hence, there are similarities.

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The aquation of *cis*-$Cr(C_2O_4)_2(N_3)(OH)^{3-}$ is 2.3×10^4 times faster than that of the corresponding *cis*-$Cr(C_2O_4)_2(N_3)(H_2O)^{2-}$ at 25 °C.[4] This is a result of an increase in ΔS^* from −18.1 to +24.6 cal/(deg mol) and in ΔH^* from +18.4 to +26.2 kcal/mol. These activation parameters imply that the mechanism changed from associative activation to dissociative activation for the aquation reaction.

This contrasts the results for the aquation of *trans*-$Cr(C_2O_4)_2(CH_3COO)H_2O^{2-}$ and for that of the corresponding hydroxy complex.[13] In this system, there is a 60-fold increase in the rate constant. The value of ΔH^* changes from +16.3 to +8.4 kcal/mol and that of ΔS^* from −18.8 to −38.8 cal/(deg mol). This difference in the direction of change of the values of the activation parameters is very hard to rationalize. It might be that the CH_3COO^- ligand is involved in extensive hydrogen bonding in the activated complex.

The labilization of ligation of $Cr(H_2O)_5(OH)^{2+}$ compared to that of $Cr(H_2O)_6^{3+}$ is documented.[5,6] It was concluded that the ligation reactions of $Cr(H_2O)_5(OH)^{2+}$ were more dissociative than those of $Cr(H_2O)_6^{3+}$ and that the coordinated hydroxide stabilized the transition state.

In the aquation reaction of $Cr(H_2O)_5X^{n+}$, where X is Cl^-,[21] Br^-,[22] I^-,[21] N_3^-,[23] NO_3^-,[24] SO_4^{2-},[25] and α-hydroxyalkyl,[26] there is a term in the rate law that is inverse first order in $[H^+]$ and that becomes predominant at higher pH values. Presumably, this term is due to the reaction of $Cr(H_2O)_4(OH)X^+$. However, the rate law is incompletely defined, and hence, no comparisons can be made.

The ligation of $CrTPPS(OH)H_2O^{4-}$ by NCS^-, pyridine, and imidazole is 6100, 350, and 21 times faster than that of $CrTPPS(H_2O)_2^{3-}$ at 25 °C, respectively.[1,27,28] However, the lability of the hydroxy complex compared to that of the aquo complex is not reflected in a monotonic change of the activation parameters. The change in the value of ΔH^* from the aquo to the hydroxy complex, $\Delta(\Delta H^*)$, is −0.1, −13.0, and −4.0 kcal/mol, respectively. The change in the values of $\Delta(\Delta S^*)$ is +16.9, −25.8, and −5.7 cal/(deg mol), respectively. In the ligation reaction of $CrTMpyP(H_2O)_2^{5+}$ by NCS^- this increase is 5880 times.[5,28] However, the reasons for this lability in these two complexes are totally different. In the $CrTPPS(H_2O)_2^{3-}$ system the lability is due to a constant ΔH^* (+16.7 ± 0.1 kcal/mol) and a substantial positive increase in ΔS^* (from −12.8 to +4.1 cal/(deg mol)) whereas in the $CrTMpyP(H_2O)_2^{5+}$ system ΔH^* decreases from +19.8 to +14.6 kcal/mol and ΔS^* decreases from −5.5 to −7.2 cal/(deg mol). These changes are difficult to explain.

A viable explanation of these observations awaits additional work.

Registry No. *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$, 18954-99-9; *trans*-$Cr(C_2O_4)_2(OH)(H_2O)^{2-}$, 36444-11-8; *trans*-$Cr(C_2O_4)_2(OH)_2^{3-}$, 36444-10-7.

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(28) $TPPS^{6-}$ = *meso*-tetrakis(*p*-sulfonatophenyl)porphyrinate. $TMpyP^{2+}$ = *meso*-tetrakis(*N*-methylpyridium-4-yl)porphyrin.

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Rate and Mechanism of Ligand Exchange of Tris(acetylacetonato)scandium(III) in Acetonitrile

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Tris(acetylaceotnato)scandium(III) undergoes ligand exchange with the enolate form of acetylacetone in CD_3CN at 30–74 °C. The observed first-order rate constant, obtained by the ^1H NMR method, is expressed by $k_0 = k_1'[\text{enol}] + k_2'$ at [complex] $\simeq$ 0.05 M, [Hacac] = 0.19 − 0.58 M, and $[H_2O]$ = 0.026–0.26 M; $k_1' = 52 \pm 3\ M^{-1}\ s^{-1}$ and $k_2' = 1.5 \pm 0.9\ s^{-1}$ at 56 °C. No water catalysis was observed. The k_2' term is minor in the concentration region. The ΔH^* and ΔS^* values for k_1' are 36 ± 5 kJ mol^{-1} and −105 ± 16 J K^{-1} mol^{-1}, respectively. The deuterium isotope effect $k_1'(H)/k_1'(D)$ was significant (ca. 5). The I_a mechanism is assigned to the rate-determining formation of an intermediate containing a one-ended $acac^-$ and a unidentate Hacac in the enol form.

Introduction

Very little information is available for ligand substitution of tervalent scandium complexes. Only the rate of anation of murexide to the "aqua" complex in aqueous solution (pH 4) was reported by Geier ($4.8 \times 10^7\ M^{-1}\ s^{-1}$ at 12 °C).[2] However, there is some uncertainty in the hydration number of the tervalent ion, which is readily hydrolyzed and dimerized.[3] There have been no kinetic data for verified $[Sc(H_2O)_6]^{3+}$. In trimethyl phosphate (TMP), there is the ion $[Sc(TMP)_6]^{3+}$,[4] for which a valuable result on the rate of the ligand exchange was obtained.[4,5a,b] The A or I_a mechanism was proposed from ΔH^*, ΔS^*, and ΔV^* values.[5b] However, it is uncertain whether the mechanism and the lability are general for $Sc^{III}O_6$-type complexes, since the ligand is rather bulky and the related information on $[M^{III}(TMP)_6]^{3+}$ is restricted to Al^{III}, Ga^{III}, and In^{III}.[5c] It would be essential for an understanding of the kinetic nature of Sc^{III} to compare Sc^{III} with various M^{III}, including transition-metal ions, for a single complex.

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