more important than for the cobalt series. Such a proposal would not be inconsistent with the expected abilities of low-spin d^6 and d^3 ions to form a bond with an incoming nucleophile. However, the rate differences for aquation are much smaller than for base hydrolysis and they could possibly arise from variations in other factors.

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The *trans–cis* Isomerization of Bis(malonato)diaquochromate(III)

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The rate of isomerization of *trans*-bis(malonato)diaquochromate(III) has been studied at 40, 50, 60, and 70° in aqueous solution at a constant ionic strength of 1.0 *F* ($NaClO_4$) and at pH 3. The rate law is $-d[trans\text{-}Cr(C_3H_2O_4)_2(OH_2)_2^-]/dt = k \cdot [trans\text{-}Cr(C_3H_2O_4)_2(OH_2)_2^-]$, where $k = 2.66 \times 10^{-5}$, 1.02×10^{-4}, 5.09×10^{-4}, and 1.95×10^{-3} sec^{-1} at 40, 50, 60, and 70°, respectively. The activation parameters for the isomerization are $\Delta H^* = 30.5 \pm 0.5$ kcal/mol and $\Delta S^* = 17.6 \pm 1.4$ cal/deg mol, where the associated uncertainties are standard deviations. The visible spectra of solutions of $Cr(C_3H_2O_4)_2(OH_2)_2^-$ at equilibrium with respect to the *trans–cis* isomerization were found to be identical within experimental error from 40 to 70° and to correspond to within 5% at 560 and 418 nm of that of a solution of pure *cis* isomer. This indicated that the *trans–cis* isomerization is greater than 95% complete in this temperature range.

Introduction

Few studies have been made of the isomerization reactions of chromate(III) complexes. The *trans–cis* isomerization of *trans*-bis(oxalato)diaquochromate(III) has been studied by several different groups.[1] Hamm and Perkins reported the preparation of the *cis* and *trans* isomers of potassium bis(malonato)diaquochromate(III) but did not study the kinetics of the isomerization reaction.[2] This paper reports the results of the investigation of the kinetics of the isomerization of *trans*-bis(malonato)diaquochromate(III) at pH 3. Comparisons with the bis(oxalato)diaquochromate(III) isomerization are made.

Experimental Section

Reagents.—All commercial chemicals were of reagent grade and were used without further purification, except as specified below. Hexaaquochromium(III) perchlorate was prepared by the procedure of Plane and Phipps.[3] The uv–visible spectrum of the product obtained compared favorably with that reported by Plane and Laswick.[4]

Potassium *trans*-bis(malonato)diaquochromate(III) was prepared in a manner similar to that described by Hamm and Perkins.[2] The product was recrystallized twice from water. *Anal.* Calcd for $K[Cr(C_3H_2O_4)_2(OH_2)_2]\cdot 3H_2O$: Cr, 13.49; C, 18.62; H, 2.59. Found: Cr, 13.2; C, 20.01; H, 2.97. The analysis for chromium, as chromate(VI), was performed spectrophotometrically. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc.

The purity of the potassium *trans*-bis(malonato)diaquochromate(III) was established by using ion-exchange chromatography. The following procedure was used. A 25.0-ml solution containing 0.1444 g of the compound, which had isomerized at 25°, was run into a Dowex 50W-X8, 100–200 mesh, Na^+-form, cation-exchange column. The column was washed with 50 ml of water. A narrow purple band remained at the top of the column, indicating the presence of a positively charged chromium(III) species in the mixture. All of the effluent from the cation-exchange column was run into a Dowex 1-X8, 200–400 mesh, NO_3^--form, anion-exchange column. A purple band formed at the top of the column, and no chromium species remained in the effluent after passing through the column. Both columns were jacketed and cooled to 1° with circulating water. The cation-exchange column was eluted with 0.10 *F* sodium nitrate. The narrow band did not separate upon elution. This implied a 1+ species.[5] The effluent was analyzed for chromium as described above. This species, which probably was malonatotetraaquochromium(III), contained 2.03% of the recovered chromium. The anion-exchange column was eluted first with 0.10 *F* sodium nitrate. Two bands developed. One remained at the top of the column and the other was eluted. This behavior implied that the species which was removed was 1− charged and it was bis(malonato)diaquochromate(III).[5] By chromium analysis, this species was determined to be 93.7% of the recovered chromium. The second band was eluted with 1.0 *F* sodium nitrate, implying a 3− species which probably was tris(malonato)chromate(III).[5] This species was 4.24% of the total recovered chromium. Of the chromium taken 99.97% was recovered.

A sample of the *trans* isomer which had not isomerized was analyzed in the same manner. This analysis gave 1.56% 1+ species, 96.4% bis(malonato)diaquochromate(III), and 2.32% 3− species. Since this sample of potassium *trans*-bis(malonato)diaquochromate(III) had already been recrystallized twice

(1) (a) R. E. Hamm, *J. Amer. Chem. Soc.*, **75**, 609 (1953); (b) G. E. Cunningham, R. W. Burley, and M. T. Friend, *Nature*, **169**, 1103 (1952); (c) H. L. Schlaefer, H. Gausmann, and W. T. Tausch, *Z. Phys. Chem.* (Frankfurt am Main), **34**, 113 (1962); (d) H. L. Schlaefer, *Angew. Chem.*, **73**, 545 (1961); (e) R. E. Hamm and K. R. Ashley, *Inorg. Chem.*, **4**, 1120 (1965).

(2) R. E. Hamm and R. H. Perkins, *J. Amer. Chem. Soc.*, **77**, 2083 (1955).

(3) R. A. Plane and A. L. Phipps, *ibid.*, **79**, 2458 (1957).

(4) R. A. Plane and J. A. Laswick, *ibid.*, **81**, 3564 (1959).

(5) In this laboratory, under these same conditions, it has been found that 0.10 *F* sodium nitrate will elute *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ from anion-exchange resin or $Cr(C_2O_4)(OH_2)_4^+$ from cation-exchange resin and that 1.0 *F* sodium nitrate will elute $Cr(C_2O_4)_3^{3-}$.

and since the reaction studied did not necessitate a purer sample, no further purification steps were taken.

The sodium perchlorate stock solution was prepared and analyzed as previously reported.[1e]

Procedure.—The stability of the *trans*-bis(malonato)diaquochromate(III) with respect to aquation during the isomerization reaction was established in the following manner. A solution containing only nitric acid at the desired concentration was thermostated at a chosen temperature. Enough *trans*-bis(malonato)diaquochromate(III) was added so that the concentration was 0.01 *F*. Periodically, aliquots were withdrawn and quenched in liquid nitrogen. The samples were analyzed for negatively charged chromium(III) species and for positively and/or neutrally charged chromium(III) species. This was performed using anion-exchange chromatography techniques. The columns were cooled to 1°. An aliquot was run into a Dowex 1-X2, 20–50 mesh, NO_3^--form, anion-exchange column. The column was washed with several bed volumes of water. This effluent, which contained positively and/or neutrally charged chromium(III) species, was analyzed for chromium as previously described. The negatively charged chromium(III) species were eluted with 1.0 *F* sodium nitrate and the amount of chromium was determined as before.

The experiments designed to separate the *trans* and *cis* isomers were done using a Dowex 1-X8, 200–400 mesh, NO_3^--form, anion-exchange resin. Preliminary experiments employed a 1.0 cm × 22 cm column. Later experiments used a 1.0 cm × 70 cm column. The experiments were performed in a cold room at 1°. The following general procedure was used.

A 0.20-g sample in 5 ml of water was run into the column and washed with about 5 ml of water. The column was eluted with the desired concentration of sodium nitrate at pH 3 at a flow rate of about 5 ml/hr. Fractions of the desired volume, usually 2.4 ml, were collected using a fraction collector. The spectra of the fractions from 300 to 700 nm were taken and the fractions were analyzed for chromium as previously described.

The visible absorption spectra between 700 and 300 nm of the *cis* and *trans* isomers were determined in solutions which were 0.010 *F* in complex and 1.00×10^{-3} *F* in perchloric acid. The ionic strength was 1.00 *F* ($NaClO_4$). The spectrum of the *trans* complex was obtained at 25° immediately after dissolving the complex. No appreciable isomerization occurred during the time of the measurement. The spectra of the *cis* isomer were determined at temperatures of 40, 50, 60, and 70° after a time corresponding to 10 half-lives of the isomerization reaction (as determined from preliminary kinetic studies). All absorption spectra were taken using a Cary Model 15 equipped with a constant-temperature block allowing temperature control to within ±0.1°.

The rates of isomerization were determined spectrophotometrically using a Beckman DU-2 at wavelengths of 410 and 560 nm between 40 and 70°. Temperature control was within ±0.1° of the desired temperature. The ionic strength of the solutions was 1.00 *F* ($NaClO_4$) and the pH was adjusted using perchloric acid. The pH was determined with a Beckman Research Model pH meter using a general-purpose glass electrode and a calomel reference electrode which contained 4.0 *F* sodium chloride instead of saturated potassium chloride. The complex concentration was 0.015 *F*. The first-order rate constant was taken from the slope of the $\ln (A_\infty - A)$ *vs.* *t* plot, where *A* is the absorbance at time *t* and A_∞ is the absorbance after isomerization had occurred.

Results

The stability of *trans*-bis(malonato)diaquochromate(III) to aquation as a function of temperature and pH is reported in Table I. The temperatures of 40 and 70° represent the limits of the investigated temperature range. The reaction time in half-lives ($t_{1/2}$) refers to the $t_{1/2}$ for isomerization of the complex. In the last two columns are reported the per cent of the plus and/or neutrally charged species and the per cent of the negatively charged species. The percentages are based on total chromium recovered. The *trans* isomer used contained 1.6% plus charged species and 98.4% negatively charged species. One can see that at both 40 and 70° and at pH 3 and 4 there is less than 5% aquation at 5 half-lives. However, at pH 2, there is appreciable aquation. At 70°, even within $0.5t_{1/2}$ there is greater than 5% aquation.

TABLE I
STABILITY TO AQUATION OF *trans*-$Cr(C_3H_2O_4)_2(OH_2)_2^-$ [a]

pH	$t_r/t_{1/2}$ [b]	% Cr(III) [c] species positively and/or neutrally charged	% Cr(III) [c] species negatively charged
		70°	
4.1 [d]	12.4	Trace	100
3.0 [d]	1.0	2.4	97.6
	2.0	3.1	96.9
	3.0	3.3	96.7
	4.0	3.4	96.6
	5.0	3.9	96.1
	10.6	5.4	94.6
2.0 [d]	6.0	28.1	71.9
2.0 [e]	0.5	6.3	93.7
	1.0	8.4	91.6
	5.0	17.7	82.3
	10.0	26.8	73.2
	15.0	31.7	68.3
	20.0	35.5	64.5
		40°	
4.1 [d]	5.9	3.17	96.8
	12.0	3.48	96.5
	16.7	3.44	96.6
3.0 [d]	5.9	3.09	96.9
	12.0	5.10	94.9
	16.7	5.56	94.4
2.0 [d]	5.9	12.9	87.1
	12.0	23.9	76.1
	16.7	25.9	74.1

[a] Unbuffered solutions with no added electrolyte except HNO_3. [b] Time that sample reacted (t_r) divided by half-life of isomerization reaction ($t_{1/2}$). [c] Analysis of the *trans* isomer gave 1.6% plus and/or neutrally charged species and 98.4% negatively charged species. [d] Total complex concentration was 0.01 *F*. [e] Total complex concentration was 0.02 *F*.

Preliminary anion-exchange experiments indicated that the *trans* and *cis* isomers possibly could be separated. Figure 1 is a plot of $A/l[Cr]_t$ *vs.* fraction number, where *A* is the absorbance at 560 nm, *l* is the path length of the cells, and $[Cr]_t$ is total chromium concentration. These results were obtained using 0.05 *F* sodium nitrate as the eluent. Similar but less definitive results were obtained when 0.20 *F* sodium nitrate was used as the eluent.

When a sample of *cis* isomer which was formed by allowing the *trans* isomer to isomerize at 70° was put onto the column and eluted with 0.05 *F* sodium nitrate, only one band formed. The sample was on the column for about 3 days. Twenty-four fractions which contained chromium were collected. A plot of $A/l[Cr]_t$

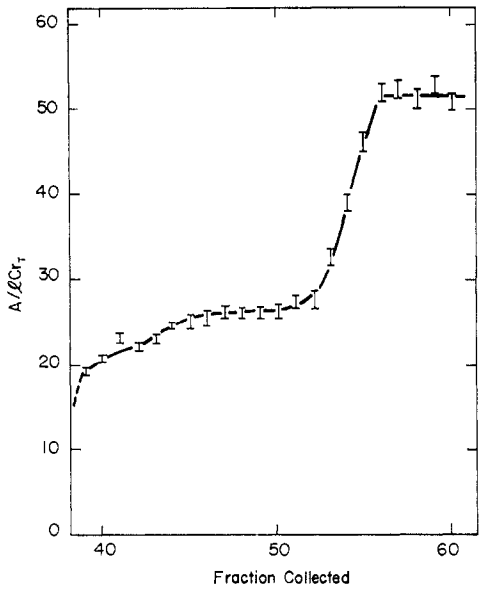

Figure 1.—Plot of $A/l[\mathrm{Cr}]_t$ *vs.* fraction collected for the anion-exchange separation of *cis*- and *trans*-$Cr(C_3H_2O_4)_2(OH_2)_2^-$ at 1°. Each fraction is about 2.4 ml.

vs. fraction number was a line with a slight positive slope. The average value of $A/l[\mathrm{Cr}]_t$ at 560 nm for the first seven fractions was 49.1 M^{-1} cm^{-1}, for the second seven fractions it was 52.9 M^{-1} cm^{-1}, and for the last seven fractions it was 55.5 M^{-1} cm^{-1}. At 417 nm the average values of $A/l[\mathrm{Cr}]_t$ for the first, second, and third seven fractions were 43.1, 45.0, and 47.5 M^{-1} cm^{-1}, respectively.

The equilibrium spectra of isomerized samples of *trans*-bis(malonato)diaquochromate(III) were measured at 40, 50, 60, and 70° at pH 3 and μ = 1.00 F ($NaClO_4$). The spectra at the different temperatures were the same within experimental error. The deviations from the mean appeared to be random and no trend was noted. Table II lists the molar absorptivities for the *trans* and *cis* isomers.

TABLE II
MOLAR ABSORPTIVITIES OF *cis*- AND *trans*-$Cr(C_3H_2O_4)_2(OH_2)_2^-$

	λ_{max},[e] nm	λ_{max},[e] nm
cis-$Cr(C_3H_2O)_2(OH_2)_2^-$	565 (49.4)[a]	415 (41.0)[a]
	566 (49.9)[d]	417 (41.4)[d]
trans-$Cr(C_3H_2O_4)_2(OH_2)_2^-$	560 (27.6)[b]	405 (26.2)[b]
	560 (21.5)[c]	405 (21.7)[c]
	560 (19.6)[d]	404 (21.0)[d]

[a] Average of values for 40, 50, 60, and 70°; pH 3.0; μ = 1.00 F ($NaClO_4$). [b] pH 3.0; μ = 1.00 F ($NaClO_4$); 25°. [c] pH 3.0; μ = 0.05 F ($NaNO_3$); 20°; average of first four fractions from ion-exchange separation. [d] S. C. Chang, *J. Inorg. Nucl. Chem.*, **30**, 945 (1968). [e] Values in parentheses are molar absorptivities (M^{-1} cm^{-1}).

In Table III are reported the first-order rate constants for the isomerization reaction. The activation parameters associated with the rate constants at each wavelength were determined by least-squares analysis of the data. The values of the activation parameters derived from the simultaneous consideration of the rate constants at both wavelengths are ΔH^* = 30.48 ± 0.45 kcal/mol and ΔS^* = 17.60 ± 1.38 cal/deg mol. The associated uncertainties are standard deviations.

TABLE III
FIRST-ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE *trans–cis* ISOMERIZATION OF $Cr(C_3H_2O_4)_2(OH_2)_2^-$ [a]

		k,[b] sec^{-1}	
Temp, °C	pH	λ 410 nm	λ 560 nm
40	3.0	(2.67 ± 0.06) × 10^{-5}	(2.65 ± 0.05) × 10^{-5}
50	3.0	(1.11 ± 0.07) × 10^{-4}	(1.04 ± 0.07) × 10^{-4}
	4.0	(0.96 ± 0.06) × 10^{-4}	(0.95 ± 0.06) × 10^{-4}
60	3.0	(5.16 ± 0.16) × 10^{-4}	(5.03 ± 0.19) × 10^{-4}
70	3.0	...	(1.95 ± 0.08) × 01^{-3}
ΔH^*, kcal/mol		30.53 ± 0.80	30.53 ± 0.70
ΔS^*, cal/deg mol		17.79 ± 2.47	17.75 ± 1.84

[a] Unbuffered solutions with $HClO_4$ and $NaClO_4$. μ = 1.00 F. Complex concentration was 0.015 F. [b] Associated uncertainties are standard deviations.

Discussion

Benerjea and Chatterjee have investigated the acid-assisted aquation of *cis*-bis(malonato)diaquochromate(III)[6] and tris(malonato)chromate(III)[7] and have found that the products are malonatotetraaquochromium(III) and *cis*-bis(malonato)diaquochromate(III), respectively. The second-order rate constants for aquation at 40° and μ = 2.00 F ($NaClO_4$) were 1.90 × 10^{-3} and 3.94 × 10^{-3} M^{-1} sec^{-1}, respectively. At pH 3, the observed rate constants would be 1.90 × 10^{-6} and 3.94 × 10^{-6} sec^{-1}, respectively. The rate constant for isomerization at 40° was 2.67 × 10^{-5} sec^{-1}. Assuming that aquation is independent of ionic strength, one would anticipate that in the time of isomerization from 18 to 35% of the $Cr(C_3H_2O_4)_2(OH_2)_2^-$ would aquate at pH 3. This is not observed. The reason for this is apparent when one realizes that at this pH complete aquation does not occur and that an equilibrium exists. The data reported by Benerjea and Chatterjee[6] were for pH 1.0 and lower. As the pH is decreased, the equilibrium will be shifted toward the aquated product. At pH 2 the amount of aquation has increased significantly.

The initial impression upon examining Figure 1 is that the *trans* and *cis* isomers can be separated using anion-exchange column techniques. However, this is not totally correct. There is a slight but real increase in $A/l[\mathrm{Cr}]_t$ from fraction 39 to fraction 50, which implies that there is more than one species in these fractions. Also, the plots of log A *vs.* λ, where λ is the wavelength, for the first 11 fractions are not superimposable. If there were only one species in these fractions, these plots would be superimposable.[8] However, the plots of log A *vs.* λ for fractions 39–42 are superimposable. Moreover, the $A/l[\mathrm{Cr}]_t$ values are almost the same within error. The values of the molar absorptivity at 560 and 405 nm are 21.5 and 21.7 M^{-1} cm^{-1}, respectively. Since this species was easier to

(6) D. Benerjea and C. Chatterjee, *J. Inorg. Nucl. Chem.*, **29**, 2387 (1967).
(7) D. Benerjea and C. Chatterjee, *ibid.*, **30**, 3354 (1968).
(8) H. H. Willard, L. L. Merritt, and J. A. Dean, "Instrumental Methods of Analysis," 4th ed, Van Nostrand, Princeton, N. J., 1965, p 80.

elute and since the molar absorptivities were the lower, this species is considered to be the *trans* isomer. This is consistent with the reported separation of other *cis* and *trans* isomers.[9]

In Table II are reported three different sets of values for the molar absorptivity of *trans*-bis(malonato)-diaquochromate(III). The smallest set of values are the previously reported ones.[10] The *trans* isomer was prepared in essentially the same manner as prepared in this work. The middle values are the ones obtained from the chromatographic separation of the isomers. The larger values are the ones obtained when the solid *trans* isomer was dissolved in 1.00 F ($NaClO_4$) at pH 3 at 25°. Identical results were obtained from a second preparation of the *trans* isomer. Using the published values of malonatotetraaquochromium(III)[11] and tris-(malonato)chromate(III)[10] and the purity values for the *trans* isomer reported in the Experimental Section, the calculated molar absorptivities for the *trans* isomer at 560 and 405 nm are about 25.9 and 24.7 M^{-1} cm^{-1}, respectively. These values are still larger than those obtained from the chromatographically separated isomer. Assuming that this increased molar absorptivity is due to *cis*-isomer impurity, there is 16% *cis* isomer mixed in with the *trans* isomer. Almost identical results were obtained for a second preparation of the *trans* isomer. Since the *trans* isomer crystallized in the presence of a large excess of *cis* isomers it is not surprising that it is contaminated with *cis* isomer. However, the discrepancy between the molar absorptivities reported previously and the values reported here is unexplainable.

Fractions 56–60 have almost constant $A/l[Cr]_t$. Also the log A *vs.* λ plots are superimposable. The molar absorptivities at 565 and 417 nm are 51.3 and 40.6 M^{-1} cm^{-1}, respectively. This species is considered to be the *cis* isomer because of its higher molar absorptivity and elution behavior. These values are consistent with the previously reported values.[10]

The results from the chromatography of a solution which had isomerized at 70° are somewhat interesting. The last third of the fractions had $A/l[Cr]_t$ values at 417 and 560 nm which were appreciably higher than those expected for the *cis* isomer. Even the middle third of the fractions had $A/l[Cr]_t$ values greater than anticipated for a *cis* isomer. The first third of the fractions had $A/l[Cr]_t$ values which were lower than expected at 560 nm but which were larger than expected at 417 nm. At this time, no completely acceptable explanation can be offered for this. However, a tentative suggestion can be made.

The eluent used was 0.05 F sodium nitrate at the natural pH of water, which was about pH 7. The value of the first pK_a of *cis*-$Cr(C_2O_4)_2(OH_2)_2^-$ is about 7.0.[12] Assuming that the first pK_a of *cis*-$Cr(C_3H_2O_4)_2(OH_2)_2^-$ is also about 7.0, this would mean that in the sodium nitrate solution there would be present a small amount of *cis*-$Cr(C_3H_2O_4)_2OH(OH_2)^{2-}$. If the $Cr(C_3H_2O_4)_2(OH_2)_2^-$ were adsorbed on ion-exchange resin and water were continually passed through the resin, the amount of *cis*-$Cr(C_3H_2O_4)_2OH(OH_2)^{2-}$ would increase. It is known that *cis*-$Cr(C_2O_4)_2OH(OH_2)^{2-}$ dimerizes with an observed rate constant equal to 2.8×10^{-6} sec^{-1} at $\mu = 0.1$ at 25°.[12a] At $\mu = 2.10$, the observed rate constant is 18×10^{-6} sec^{-1}. It seems reasonable to suspect that $Cr(C_3H_2O_4)_2OH(OH_2)^{2-}$ would also dimerize and that the ion-exchange resin might increase the rate of this reaction since the ionic strength in the resin is very high.[13] If the dimer or the hydroxy species had a larger molar absorptivity than the *cis* isomer, then the increased $A/l[Cr]_t$ values are readily explained. In subsequent experiments, the pH of the eluent was adjusted to pH 3.

These results imply that the *cis* and *trans* isomers are separated on the column but that the *trans* isomer undergoes isomerization to the *cis* isomer. This results in a contamination by the *cis* isomer of the first fractions. This does not occur in the last fractions which contain only the *cis* isomer.

Since the *trans* isomer can be partly separated from the *cis* isomer, the chromotography of the solution which had isomerized at 70° also gives information concerning the *trans–cis* equilibrium. Assuming that at 560 nm the molar absorptivity of the *cis* isomer is 51.3 M^{-1} cm^{-1} and that of the *trans* isomer is 21.5 M^{-1} cm^{-1}, the first fraction contains 13.7% *trans* isomer and the second fraction contains 5.4% *trans* isomer. This is less than 0.5% of the total chromium recovered. Thus, based on this, isomerization is virtually complete.

The absorption spectrum at equilibrium is, within experimental error, the same at 40, 50, 60, and 70°. Assuming that at equilibrium 5% of the chromium(III) exists as $Cr(C_3H_2O_2)(OH_2)_4^+$ (see Table I), the remainder is a mixture of the *cis* and *trans* isomers of $Cr(C_3H_2O_2)_2(OH_2)_2^-$, and using the corresponding molar absorptivities at 560 nm, there is about 4% *trans* isomer present at equilibrium. This is consistent with the chromotography results. This means that the only reaction observed was the *trans–cis* isomerization.

The isomerization of bis(malonato)diaquochromate-(III) is much slower than the similar reaction for bis-(oxalato)diaquochromate(III). The ΔH^* for isomerization of bis(oxalato)diaquochromate(III) is 17.9 ± 1.2 kcal/mol[1e] compared to 30.5 ± 0.5 kcal/mol for bis(malonato)diaquochromate(III). The ΔS^* values for isomerization of the two complexes are −13 ± 4[1e] and +17.6 ± 1.4 cal/deg mol, respectively.

There are two reasonable extreme situations to account for the difference in activation parameters. One situation would be that the activated complexes for the two reactions are similar but that the difference in

(9) D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, **83**, 4152 (1961).

(10) J. C. Chang, *J. Inorg. Nucl. Chem.*, **30**, 945 (1968).

(11) D. H. Huchital and H. Taube, *J. Amer. Chem. Soc.*, **87**, 5371 (1965).

(12) (a) D. M. Grant and R. E. Hamm, *ibid.*, **78**, 3006 (1956). The first pK_a is reported to be 6.4. (b) H. Kelm and G. M. Harris, *Inorg. Chem.*, **6**, 706 (1967). The first pK_a is reported to be 7.1.

(13) H. A. Dean, "Chemical Separation Methods," Van Nostrand Reinhold, New York, N. Y., 1969, p 92.

ΔH^* and ΔS^* arises from the difference in ΔH_f° and ΔS_f° of the two *trans* complexes. The difference in ΔH_f° is reasonable if one examines models of the two complexes.

In bis(oxalato)diaquochromate(III), the chelate ring is five membered. It is possible, and reasonable, that there is less strain in the six-membered ring than there is in the five-membered ring. This would tend to make the malonate complex more stable. If this is the case, and assuming similar activated complexes, then it would require less energy to lengthen or break the chromium–oxygen bond in bis(oxalato)diaquochromate(III).

The difference in entropies of activation should arise mostly from differences in solvation of the *trans* isomers since the assumption is that the two activated complexes are similar. However, it is somewhat difficult to imagine how this difference in ΔS^* arises since the *trans* isomers are very similar.

It has been reported that isomerization occurs in bis(oxalato)diaquochromate(III) without $H_2{}^{18}O$ exchange.[14] Thus, if there is actually total chromium–oxygen bond cleavage in bis(oxalato)diaquochromate(III), then the rechelation of the oxalate ligand must occur before water entry. It seems more reasonable to assume that isomerization occurs by a twisting of the chromium–oxygen bonds rather than actual bond cleavage.

The second extreme situation might be that ΔH_f° and ΔS_f° for the two complexes are similar but that the large differences in ΔH^* and ΔS^* occur because of the differences in the activated complexes. The very high ΔH^* of isomerization for bis(malonato)diaquochromate(III) might imply that there is total chromium–oxygen bond cleavage for the reaction.

(14) J. Agget, I. Mawston, A. L. Odell, and B. E. Smith, *J. Chem. Soc. A*, 1413 (1968).

This model is partially supported in view of the reported activation parameters for water exchange in $Cr(H_2O)_6^{3+}$. The ΔH^* is 24 ± 2 kcal/mol and ΔS^* is +2.5 cal/deg mol.[15] The large ΔH^* has been since interpreted to imply a dissociatively activated reaction; *i.e.*, bond breaking is more important than bond making.[16] Even if there is great apparent difference between $Cr(H_2O)_6^{3+}$ and *trans*-$Cr(C_3H_2O_4)_2(OH_2)_2^-$, there should be some validity to the comparison, particularly in view of the similarity of the ΔH^* values for water exchange and the isomerization of the malonate complex. Consequently, there may be less bond breaking in the isomerization of bis(oxalato)diaquochromate(III) than in the isomerization of bis(malonato)diaquochromate(III).

Such a model has the additional advantage that the large differences in ΔS^* can be readily explained, as well as the difference in sign. If it is assumed that the chromium–oxygen bond is totally broken in the isomerization of the malonate complex, an increase in entropy in going to the activated complex should result. If the chromium–oxygen bond in the oxalate complex is not cleaved and if a twist mechanism is operative, then a decrease in entropy in going to the activated state is expected. This is what is observed.

Until the relative stabilities of the *trans* isomers are known, either explanation is acceptable. In fact, the actual situation is probably a combination of differences in the ΔG° of the *trans* complexes and in the ΔG^* of activated complexes.

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