intermediate. Protonation which occurs at O_b first (because O_a is internal) would be expected to weaken the $V-O_b$ bond and make dissociation more probable as is observed.

Finally, in the acidic region, pH >4, the initial rate constant for exchange increases dramatically. However, linear McKay graphs are not obtained indicating either (a) more than one kind of oxygen in the ion or (b) a chemical change with time. Experimentally the apparent rate of exchange decreases with time which makes (b) rather unlikely since it is difficult to suggest how the known depolymerization toward $VO_2^+(aq)$ could lower the rate of exchange of the remaining V_{10} entity. Postulate (a) seems more likely. The change in rate is due to nonequality of oxygens in the structure. The "outer" oxygens are more susceptible to an increase in rate due to protonation, while the "inner" oxygen rate is unperturbed by the acidic environment.

Summary

An interpretation of the ^{18}O exchange and base dissociation kinetics of $V_{10}O_{28}^{6-}$ has been made which postulates that decavanadate ion has an intrinsic rate of unwrapping to a partially bonded intermediate which is common to both the exchange and decomposition reactions. Closure of the partially bonded intermediate leads to oxygen exchange while rupture of the remaining bond leads to decomposition to smaller units. It is suggested that if the ion opens in only one way, the cyclic V_4 unit appears to be the most likely "half-bonded" unit to explain the exchange behavior.

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Registry No. $V_{10}O_{28}^{6-}$, 12397-12-5; ^{18}O, 14797-71-8; $V_2O_7^{4-}$, 22466-30-4; H^+, 12408-02-5.

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Volumes of Activation for Isomerization and Acid-Catalyzed Aquation Reactions of Diaquobis(oxalato)- and Diaquobis(malonato)chromium(III) Complexes from High-Pressure Studies in Solution

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The effect of high pressure on the rates of isomerization in aqueous perchlorate solutions of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ and *trans*-$[Cr(mal)_2(OH_2)_2]^-$ (ox^{2-} = oxalate; mal^{2-} = malonate) has been evaluated. The isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ at pH 3.15 exhibits a volume of activation ($\Delta V^{\ddagger}$) of -16.6 cm^3 mol^{-1} with a compressibility coefficient of activation ($\Delta\beta^{\ddagger}$) of -1.8 cm^3 mol^{-1} kbar^{-1} which is shown to be consistent with isomerization through one-ended dissociation of an oxalato ligand. For the isomerization of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ at pH 3.0, $\Delta V^{\ddagger}$ is $+8.9$ cm^3 mol^{-1} with no measurable $\Delta\beta^{\ddagger}$, consistent with a mechanism via dissociative interchange of an aquo ligand. Enthalpies and entropies of activation evaluated for these systems are consistent with these separate mechanisms. The effect of high pressure on the acid-catalyzed aquation of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ and *cis*-$[Cr(mal)_2(OH_2)_2]^-$ in perchloric acid solutions has also been determined. Volumes of activation are $\Delta V^{\ddagger} = +1.7$ cm^3 mol^{-1} for *cis*-$[Cr(ox)_2(OH_2)_2]^-$ and $\Delta V^{\ddagger} = +2.4$ cm^3 mol^{-1} for *cis*-$[Cr(mal)_2(OH_2)_2]^-$ and are consistent with one mechanism operating for both aquation reactions. A mechanism involving direct proton attack at a coordinated carboxylate and subsequent dissociative release of the protonated acid is most consistent with the determined volumes of activation. Enthalpies and entropies of activation were evaluated for each system; the negative $\Delta S^{\ddagger}$ observed for both reactions is also consistent with a common mechanistic pathway.

Introduction

Extensive investigations of the isomerization kinetics of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ (ox^{2-} = oxalate dianion = $^-OOC-COO^-$) have been reported in the chemical literature.[1-14] The isomerization may be represented as equilibrium reaction 1

$$\text{trans} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{cis} \qquad (1)$$

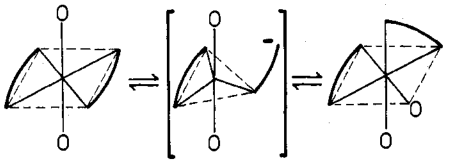
in which $k_f \gg k_b$. The mechanism of the reaction has been interpreted by several authors in terms of a transition state involving a five-coordinate intermediate formed by one-ended dissociation of a bidentate oxalate. The variation of the isomerization rate with solvent,[13] the catalysis of the reaction by added ions,[9] and $H_2{}^{17}O$ ligand-exchange data[7,11] provide strong evidence to support this mechanism. The negative entropy of activation for isomerization has been interpreted in terms of either association of cations with the free end of the unidentate oxalate generated in the transition state[12] or, alternatively, a decrease in entropy of the solvent in the vicinity of the oxalate.[15]

Studies of the isomerization kinetics of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ (mal^{2-} = malonate dianion = $^-OOC{-}CH_2{-}COO^-$) have not been as extensive, and the mechanism is less clearly defined.[16-18] The slower rate of isomerization observed, unlike the oxalate analogue, is not catalyzed by added ions.[17] Recently, Casula and co-workers have interpreted the mechanism in terms of a five-coordinate intermediate which involves loss of coordinated water.[16] The entropy of activation for the malonate complex ($\Delta S^{\ddagger} = +90$ J K^{-1} mol^{-1})[16] differs markedly from the value for the oxalate complex ($\Delta S^{\ddagger} = -64$ J K^{-1} mol^{-1}),[2] indicating a different mechanism may be operating.

Previously Conze, Steiger, and Kelm have determined the volume of activation ($\Delta V^{\ddagger}$) for the trans–cis isomerization of $[Cr(ox)_2(OH_2)_2]^-$ from high-pressure rate measurements in solution.[14] They argued that the volume of activation ($\Delta V^{\ddagger} = -16$ cm^3 mol^{-1}) supports the proposed mechanism of one-ended oxalate dissociation. It is apparent that the measurement of $\Delta V^{\ddagger}$ for the malonate complex may likewise provide evidence to support the different mechanism for this complex proposed by Casula and co-workers.[16]

The application of high-pressure studies to the elucidation of inorganic reaction mechanisms has been recently reviewed by Stranks.[19] Using appropriate models, it is possible to predict the expected sign and size of the volume of activation for different isomerization mechanisms.

The proposed mechanism for isomerization of *trans*-$[Cr(diacido)(OH_2)_2]^-$ complexes via one-ended acid dissociation of the acido ligand may be represented as in eq 2, where the dangling ligand carries a formal charge.



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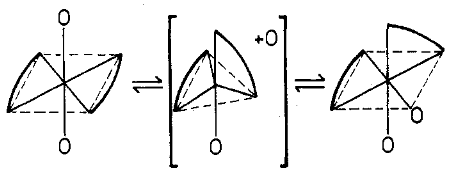
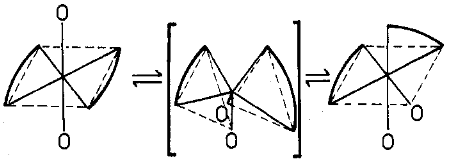


(3)

The transition state in eq 2 remains five-coordinate with an intrinsic volume equivalent to that of its six-coordinate precursor,[19] except for the additional volume contribution from the dangling ligand generated by one-ended release of the bidentate ligand. For a charged ligand, however, the solvent surrounding the newly implanted charge will suffer electrostriction of a magnitude exceeding any volume increase from the intrinsic volume of the ligand. Hence one-ended dissociation of a charged ligand should yield a negative volume of activation. A detailed analysis of the predicted $\Delta V^{\ddagger}$ has been incorporated subsequently in the Discussion.

An alternate mechanism by which isomerization can occur involves release of a coordinated aquo ligand in forming a five-coordinate intermediate, as represented in eq 3. Internal rearrangement within the complex to form a five-coordinate intermediate subsequent to the initial dissociation of a ligand will cause a negligible volume change, since it can be assumed to occur to a first approximation without any bond lengthening or further ligand dissociation. Release of a neutrally charged water molecule, however, will introduce a positive contribution to the volume of activation, arising from the intrinsic volume of the ligand. Complete dissociative release of a water molecule into the second coordination sphere would involve in the upper limit a positive volume contribution due to the intrinsic molar volume of water of +15 cm^3 mol^{-1}.[19] It is apparent that the two mechanisms discussed above should be associated with distinctly different volumes of activation.

In addition to the two previously proposed mechanisms, it is possible to consider two additional possible mechanisms. An internal-twist mechanism (eq 4) involving only bond angle changes should exhibit a negligible volume change in forming the transition state, with $\Delta V^{\ddagger} \simeq 0$, analogous to the twist mechanism discussed previously for racemization of certain chromium(III) complexes.[20] An associative (I_a) mechanism (eq 5) involves movement of a water molecule from the second coordination sphere to the first coordination sphere in forming a seven-coordinate transition state. Assuming to a first approximation no increase in the intrinsic volume of the seven-coordinate intermediate, a negative volume change is expected, which in the upper limit would approach the intrinsic volume of a solvent water molecule in the second coordination sphere of −15 cm^3 mol^{-1}. By comparison, $H_2{}^{18}O$ exchange with $Cr(OH_2)_6{}^{3+}$ exhibits a value $\Delta V^{\ddagger} = -9$ cm^3 mol^{-1} and an I_a mechanism has been invoked in this case.



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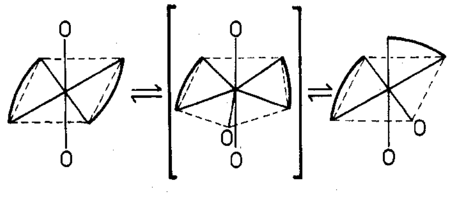


(5)

Acid-catalyzed aquation reactions of *cis*-$[Cr(ox)_2(OH_2)_2]^-$[21] and *cis*-$[Cr(mal)_2(OH_2)_2]^-$[17,22-24] have been studied in addition to trans → cis isomerization reactions in recent years. Aquation of both complexes is dependent on $[H^+]$, and the overall reaction

$$cis\text{-}[Cr(aa)_2(OH_2)_2]^- \xrightarrow[H_2O]{H^+} [Cr(aa)(OH_2)_4]^+ + aaH_2 \qquad (6)$$

(aa = ox^{2-}, mal^{2-}) has been interpreted in terms of a mechanism involving a rapid protonation preequilibrium followed by rate-determining water attack on the protonated intermediate.[17] The slower loss of aa from $Cr(aa)(OH_2)_4{}^+$ does not interfere with reaction 6[21,22] and this subsequent reaction step was not studied here.

Volumes of activation for reactions involving aquation of unidentate leaving groups[25,26] and chelated diimines[27] have proved valuable in defining mechanisms. While volumes of activation for substitution reactions of hexaaquochromium(III) by oxalate have been determined,[28] no data on aquation reactions of chromium(III) complexes of bidentate diacido ligands at high pressures have been reported. From comparison of predicted volumes of activation derived from consideration of mechanistic sequences analogous to those previously proposed with experimentally determined volumes of activation, evidence for a particular mechanism may be forthcoming. A detailed analysis of this comparison is deferred to the Discussion.

We report here the rates of reaction at various pressures for the isomerization reaction *trans*-$[Cr(mal)_2(OH_2)_2]^-$ → *cis*-$[Cr(mal)_2(OH_2)_2]^-$ for the first time, together with redetermined rates for the analogous *trans*-$[Cr(ox)_2(OH_2)_2]^-$ → *cis*-$[Cr(ox)_2(OH_2)_2]^-$ isomerization at elevated pressures.

Table I. Visible Absorption Maxima of Chromium(III) Diacido Complexes[a,b]

Complex	λ_{max}, nm	ϵ, M^{-1} cm^{-1}
trans-$[Cr(mal)_2(OH_2)_2]^-$	560 (560)	20.1 (21)
	404 (405)	21.4 (22)
cis-$[Cr(mal)_2(OH_2)_2]^-$	565 (565)	51.5 (51)
	415 (415)	42.1 (41)
trans-$[Cr(ox)_2(OH_2)_2]^-$	555 (555)	16.1 (15)
	413 (416)	20.5 (19)
cis-$[Cr(ox)_2(OH_2)_2]^-$	563 (562)	55.7 (50)
	414 (416)	74.4 (74)

[a] Comparable data from ref 2 and 16 are presented in parentheses. [b] Measured in 0.1 M $HClO_4$ at 10 °C; $\mu = 1.0$ M ($NaClO_4$).

In addition, rates of reaction at elevated pressures for the acid-catalyzed aquation reactions of *cis*-$[Cr(aa)_2(OH_2)_2]^-$ (aa = ox^{2-}, mal^{2-}) have been determined for the first time. Temperature variation of the rates of isomerization and dissociation under conditions identical with those of the high-pressure studies are also reported to allow comparison of volumes and entropies of activation.

Experimental Section

Preparation of Complexes. The trans and cis isomers of potassium bis(oxalato)diaquochromate(III) were prepared by the methods of Werner[29] as adapted by Palmer.[30] Anal. Calcd for $K[Cr(C_2O_4)_2(OH_2)_2]\cdot 3H_2O$: Cr, 14.56; C, 13.43; H, 2.82. Found for trans isomer: Cr, 14.67; C, 13.53; H, 2.59. Found for cis isomer: Cr, 14.64; C, 13.16; H, 2.69.

The trans and cis isomers of potassium bis(malonato)diaquochromate(III) were prepared essentially by the methods of Chang.[23] Anal. Calcd for $K[Cr(C_3H_2O_4)_2(OH_2)_2]\cdot 3H_2O$: Cr, 13.50; C, 18.69; H, 3.66. Found for trans isomer: Cr, 13.62; C, 18.70; H, 3.37. Found for cis isomer: Cr, 13.40; C, 19.14; H, 2.92.

Carbon and hydrogen analyses were performed by the Australian Microanalytical Service, Melbourne. Chromium was determined by oxidation to Cr(VI) with sodium perborate, followed by spectrophotometric analysis of the resulting CrO_4^{2-} (ϵ_{375} 4815 L mol^{-1} cm^{-1}).[31]

Visible absorption spectra of the chromium(III) complexes (Table I) compare favorably with previously reported data.

Kinetic Studies. The rates of isomerization and dissociation at high pressures were determined by monitoring absorbance changes at 410 nm using a Varian 635D spectrophotometer incorporating a high-pressure cell in which the reaction solution was pressurized up to 1724 bar. Temperature within the high-pressure cell block was maintained to within ±0.1 °C by thermostated water circulation.

Rate constants (k_p) were evaluated using least-squares analysis via the Guggenheim method. Volumes and, where appropriate, compressibilities of activation were determined using the expression[19]

$$-RT(\partial \ln k_p/\partial P)_T = \Delta V^{\ddagger} \tag{7}$$

from plots of ln k_p vs. P. Where the volume of activation itself exhibits a pressure dependence, a quadratic expression

$$\ln k_p = \ln k_0 + bP + cP^2 \tag{8}$$

adequately describes the reaction.[32] The volume of activation at any pressure is then

$$\Delta V^{\ddagger}{}_p = bRT - 2RTcP \tag{9}$$

and the volume of activation at zero pressure is

$$\Delta V^{\ddagger} = -bRT \tag{10}$$

with the compressibility coefficient of activation defined by

$$\Delta\beta^{\ddagger} = -(\partial \Delta V^{\ddagger}/\partial P)_T = 2RTc \tag{11}$$

Volumes and compressibilities of activation were determined by means of first-, second-, or third-order polynomial regressions on the data using a computer to determine the best fit.

Table II. Rates of Isomerization of Chromium(III) Diacido Complexes at Various High Pressures

P, bar	10^3k_p, s^{-1}	P, bar	10^3k_p, s^{-1}
	trans-$[Cr(ox)_2(OH_2)_2]^-$ [a]		
1	1.07 ± 0.08 (6)[b]	1024	2.04 ± 0.10 (5)
345	1.36 ± 0.05 (4)	1380	2.48 ± 0.08 (5)
690	1.65 ± 0.04 (6)	1724	3.01 ± 0.02 (3)
	trans-$[Cr(mal)_2(OH_2)_2]^-$ [c]		
1	2.09 ± 0.06 (4)[b]	1034	1.53 ± 0.07 (6)
345	1.87 ± 0.08 (8)	1380	1.32 ± 0.03 (3)
690	1.66 ± 0.05 (5)	1724	1.22 ± 0.04 (4)

[a] $T = 30$ °C, pH 3.15, $\mu = 1.0$ M ($NaClO_4$). [b] Standard deviations and number of independent measurements at each pressure (in parentheses) are given. [c] $T = 65$ °C, pH 3.00, $\mu = 1.0$ M ($NaClO_4$).

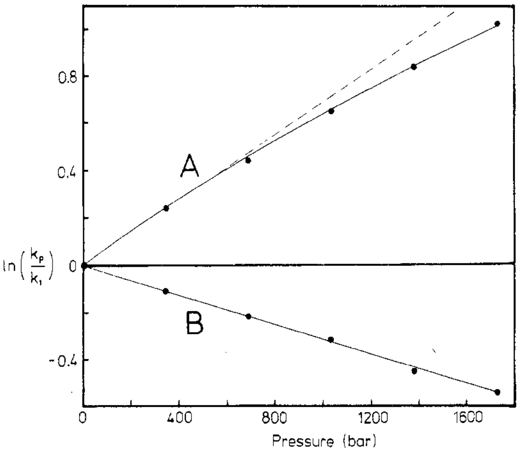


Figure 1. Pressure variation of rate coefficients for isomerization of $[Cr(ox)_2(OH_2)_2]^-$ (A) and $[Cr(mal)_2(OH_2)_2]^-$ (B) in aqueous solution.

The rates of isomerization and dissociation at room pressure and various temperatures were determined by monitoring absorbance changes at 410 nm using a Cary 17 spectrophotometer fitted with a thermostated cell compartment in which the temperature was controlled to ±0.1 °C by water circulation. Rate constants (k_{obsd}) were evaluated as above.

Measurements of pH were performed using a Radiometer PHM62 meter and a Radiometer GK2401C combined electrode. Analytical reagent grade sodium perchlorate and perchloric acid were used without further purification to control ionic strength and acidity, respectively.

Results

High-Pressure Isomerization. The rate of isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ at pH 3.15 showed a marked acceleration upon the application of high pressures. In contrast, the isomerization of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ at pH 3.00 showed a retardation upon the application of pressure.

Table II summarizes mean values of the rate coefficients determined at different pressures. While the data for the malonato complex can be adequately accommodated via the simple relationship in eq 7, a slight pressure dependence of the volume of activation itself is observed over the pressure range used in the case of the oxalato complex. This is apparent from Figure 1, where ln (k_p/k_1) is a linear function of the applied pressure in the case of the malonato complex, but slight curvature is exhibited for the oxalato complex. Volumes of activation and, where appropriate, compressibilities of activation deduced from the data together with their standard deviations calculated via a normal least-squares routine are included in Table IV.

Variable-Temperature Isomerization. The rate of isomerization at room pressure in solution was measured for each complex at five different temperatures over a temperature

Table III. Rates of Isomerization of Chromium(III) Diacido Complexes at Room Pressure and Various Temperatures

trans-$[Cr(ox)_2(OH_2)_2]^-$

T, °C	10^3k_{obsd},[a] s^{-1}	10^3k_{obsd},[b] s^{-1}
25.0	0.61 ± 0.03 (4)[c]	0.66 ± 0.04 (5)[c]
30.0	1.00 ± 0.01 (3)	1.06 ± 0.06 (6)
35.0	1.57 ± 0.04 (3)	1.71 ± 0.04 (4)
39.7	2.40 ± 0.03 (4)	2.72 ± 0.04 (4)
45.0	4.30 ± 0.03 (4)	4.62 ± 0.06 (5)

trans-$[Cr(mal)_2(OH_2)_2]^-$

T, °C	10^3k_{obsd},[d] s^{-1}
58.4	0.71 ± 0.02 (3)[c]
63.6	1.40 ± 0.04 (4)
64.3	1.72 ± 0.05 (5)
69.0	3.18 ± 0.06 (4)
75.0	6.50 ± 0.04 (4)

[a] pH 3.15, μ = 1.0 M ($NaClO_4$). [b] pH 5.17, μ = 1.0 M ($NaClO_4$). [c] Standard deviations and number of independent measurements at each temperature (in parentheses) are given. [d] pH 3.00, μ = 1.0 M ($NaClO_4$).

Table IV. Activation Parameters for Isomerization of Chromium(III) Diacido Complexes

Complex	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} $kbar^{-1}$	Ref
trans-$[Cr(ox)_2(OH_2)_2]^-$	73.2 ± 2	−61 ± 5	−16.6 ± 0.5	−1.8 ± 0.6	*a*
	74.1 ± 1.4	−58 ± 3			*b*
	73.2	−64			*c*
trans-$[Cr(mal)_2(OH_2)_2]^-$	126.4 ± 3	+74 ± 5	+8.9 ± 0.3	0	*d*
	127.6	+73			*e*

[a] This work; pH 3.15. [b] This work; pH 5.17. [c] Data from ref 2. [d] This work; pH 3.00. [e] Data from ref 18.

range of approximately 20 °C. For the complex *trans*-$[Cr(ox)_2(OH_2)_2]^-$, rates were measured at pH 3.15 and 5.17, and for *trans*-$[Cr(mal)_2(OH_2)_2]^-$, at pH 3.00. The mean values of the rate coefficients determined at different temperatures are summarized in Table III.

The activation energy (E_a) and enthalpy of activation ($\Delta H^{\ddagger}$) for racemization of each complex were deduced from plots of ln k_{obsd} vs. $1/T$, and the entropy of activation ($\Delta S^{\ddagger}$) was calculated subsequently from E_a and the racemization rate in the usual manner. Values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, together with standard deviations calculated via a standard least-squares routine, are collected in Table IV. Data from previous studies are included for comparative purposes.

The rate of isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ at pH 3.15 is in the region where acid catalysis is minimal[2,17] and the data collected at pH 5.17 indicated that the sensitivity to base catalysis is small at least up to this pH. For *trans*-$[Cr(mal)_2(OH_2)_2]^-$, the pH of 3.00 chosen for study is again in the region where acid- and base-catalysis effects are minimal. The distinctly slower rate of isomerization in the malonato complex is reflected in a higher energy of activation.

High-Pressure Aquation. The rate of aquation of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ in 3.0 M $HClO_4$ showed a slight retardation upon the application of high pressures. A similar slight retardation at high pressure was observed for the rate of aquation of *cis*-$[Cr(mal)_2(OH_2)_2]^-$ in 0.5 M $HClO_4$.

Table V summarizes mean values of the rate coefficients determined at different pressures. The data can be accommodated adequately by the simple expression in equation 7. No pressure dependence of the volume of activation itself can be detected in either case, due to the small variation of the observed aquation rate with pressure. Volumes of activation deduced from the data are included in Table VII.

Table V. Rates of Aquation of Chromium(III) Diacido Complexes at High Pressures

cis-$[Cr(ox)_2(OH_2)_2]^-$

P, bar	10^3k_p,[a] s^{-1}
1	1.15 ± 0.02 (2)[b]
690	1.12 ± 0.01 (3)
1380	1.10 ± 0.02 (4)

cis-$[Cr(mal)_2(OH_2)_2]^-$

P, bar	10^3k_p,[c] s^{-1}
1	6.26 ± 0.12 (6)
690	5.72 ± 0.16 (6)
1380	5.53 ± 0.14 (5)

[a] T = 45 °C, 3 M $HClO_4$. [b] Standard deviations and number of independent measurements at each pressure (in parentheses) are given. [c] T = 65 °C; 0.5 M $HClO_4$, μ = 1.0 M ($NaClO_4$).

Table VI. Rates of Aquation of Chromium(III) Diacido Complexes at Room Pressure and Various Temperatures

cis-$[Cr(ox)_2(OH_2)_2]^-$

T, °C	10^4k_{obsd},[a] s^{-1}	T, °C	10^4k_{obsd},[a] s^{-1}
30.0	0.17 ± 0.02 (3)[b]	45.0	1.15 ± 0.02 (2)
35.0	0.33 ± 0.01 (2)	50.0	2.06 ± 0.04 (3)
40.0	0.61 ± 0.02 (2)		

cis-$[Cr(mal)_2(OH_2)_2]^-$

T, °C	10^4k_{obsd},[c] s^{-1}	T, °C	10^4k_{obsd},[c] s^{-1}
35.0	1.12 ± 0.05 (3)	50.0	5.58 ± 0.07 (4)
40.0	2.00 ± 0.06 (3)	55.0	9.87 ± 0.08 (5)
45.0	3.51 ± 0.08 (4)		

[a] 3.0 M $HClO_4$ solution. [b] Standard deviations and number of independent measurements at each temperature (in parentheses) are given. [c] 0.5 M $HClO_4$ solution, μ = 1.0 M ($NaClO_4$).

Table VII. Activation Parameters for Aquation of Chromium(III) Diacido Complexes

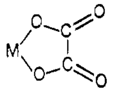
Complex	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	Ref
cis-$[Cr(ox)_2(OH_2)_2]^-$	99.0 ± 0.5	−10 ± 1	+1.7 ± 0.7	*a*
	100.0	−19		*b*
cis-$[Cr(mal)_2(OH_2)_2]^-$	87.8 ± 1.5	−35 ± 4	+2.4 ± 0.6	*c*
	84.5	−32		*d*
	91.2	−19		*e*

[a] This work; 3.0 M $HClO_4$ solution. [b] Data from ref 21. [c] This work; 0.5 M $HClO_4$ solution, μ = 1.0 M ($NaClO_4$). [d] Data from ref 22. [e] Data from ref 17.

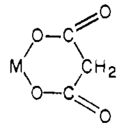
Variable-Temperature Aquation. The rate of aquation at room pressure in solution was measured for each complex at five different temperatures over a temperature range of approximately 20 °C. The aquation reaction of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ was followed in 3.0 M $HClO_4$ and that of *cis*-$[Cr(mal)_2(OH_2)_2]^-$ in 0.5 M $HClO_4$ with the ionic strength adjusted to 1.0 M with $NaClO_4$. The mean values of the rate coefficients determined at different temperatures are summarized in Table VI. Activation parameters, calculated as described above, are collected in Table VII. Data from previous studies are included for comparative purposes.

Discussion

Isomerization Reactions. The complexes *trans*-$[Cr(ox)_2(OH_2)_2]^-$ and *trans*-$[Cr(mal)_2(OH_2)_2]^-$ differ structurally principally in the size of the chelate ring, with oxalate forming a five-membered chelate ring (I) and malonate a six-membered chelate ring (II). Evidence from x-ray structural data of chromium(III) complexes containing bidentate oxalato and malonato ligands indicates that both chelate rings deviate only slightly from planarity,[33-35] with malonato showing the greater deviation toward a flattened boat conformation.[35]



I



II

The oxalate chelate ring exhibits a markedly compressed intraligand (O–Cr–O) angle of 82.7° in $[Cr(en)(ox)_2]^-$ [33] and 83° in $[Cr(ox)_3]^{3-}$.[34] This bond angle is greater than that for a trigonal-prismatic structure of 81.8°, but an intramolecular twist mechanism via such an intermediate cannot be excluded on the basis of structural characteristics provided sufficient ligand flexibility exists. The malonate chelate ring in $[Cr(mal)_3]^{3-}$ exhibits a less strained intraligand angle of 92.4°, and this complex shows much less trigonal distortion than the $[Cr(ox)_3]^{3-}$ complex.[35] On the basis of the structural data, the chelated oxalato ligand might be considered more susceptible to a one-ended dissociation than the chelated malonato ligand as a mechanism for relieving ring strain in the former chelate, although this does not point conclusively to a mechanistic differentiation.

Isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$. Evidence for a one-ended dissociation mechanism for isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ comes from kinetic studies[2–18] of isomerization and ligand exchange. The rate of isomerization has been shown to be 150 times faster than aquo ligand exchange and 3000 times faster than oxalato oxygen exchange of ^{17}O-enriched complex ligands with solvent water.[11] This suggests that the ring opening and closing process, if it occurs, is faster than the oxygen exchange. The possibility of a solvent water molecule occupying the vacated site in a five-coordinate intermediate is also eliminated since this should lead to oxygen exchange for each ring opening. In the same manner an associative mechanism via a seven-coordinate intermediate formed by entry of a solvent water molecule into the coordination sphere is ruled out by the slow aquo ligand exchange data.

Isomerization and oxygen exchange are both subject to acid catalysis, the rate of isomerization being first order in hydrogen ion concentration.[5] The rate of isomerization is also accelerated by a range of metal ions.[5] Both the proton and metal ions are presumed to directly promote chromium–oxygen bond fission of one end of the oxalato chelate to yield a one-ended oxalato intermediate. A fully intramolecular twist mechanism has been estimated to involve an unrealistically high activation energy,[36] and although consistent with isotopic oxygen exchange, data are not consistent with the observations of cation and proton catalysis. In methanol–water mixtures, the rate of isomerization decreases as the protic nature and dielectric constant of the solvent decreases,[16] consistent with destabilization of the free carboxylate ion generated by one-ended dissociation.

The negative entropy of activation reported for the isomerization process has been interpreted in terms of an association of cations in the solution with the free carboxylate generated by one-ended dissociation[12] or, alternatively, as a decrease in the entropy of the solvent in the vicinity of the newly implanted carboxylate arising from electrostrictive effects.[15] It is apparent from this body of evidence that isomerization of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ can be considered to occur via a one-ended dissociative mechanism.

In terms of the predicted volume of activation for one-ended oxalato dissociation, an estimate can be made as follows.

The dissociation could lead to a carboxylate group of unit charge implanted in the solvent some 400–560 pm from the chromium center, depending on the amount of rotation about the O–C and C–C oxalato bonds (structure I). The distance the dissociated carboxylate must extend into the solvent in order to act as an independent charge exercising its own electrostrictive effect upon the solvent is not readily estimated and the maximum separation from the parent chromium ion is not necessarily implied. The volume change associated with implanting a free carboxylate group in water can be taken to be that for the ionization of carboxylic acids, which exhibit values of $\Delta V°$ in the range of -14.2 to $-9.0\ cm^3\ mol^{-1}$.[37,38] A mean electrostrictive volume effect of $-12.5\ cm^3\ mol^{-1}$ for the generation of the carboxylate anion in the solvent water can then be estimated.[20]

In addition to this electrostrictive effect, the volume increase accompanying the release of the oxalato ligand into the solvent must also be estimated. In the initial chelate, both C=O groups are already sufficiently far from the chromium center to be in direct contact with the solvent, which would be expected to adjust continuously to motion of these groups during dissociation. The only net volume change should thus be due to the release of the O atom coordinated to the chromium center, which can be calculated to be $+1.0\ cm^3\ mol^{-1}$ for an O atom of radius 74 pm released into the solvent. The net volume effect of releasing a free carboxylate anion is thus estimated to be $-12.5 + 1.0 = -11.5\ cm^3\ mol^{-1}$.

Release of a carboxylate ion with one formal charge reduces the formal charge on the remaining five-coordinate parent from -1 to 0. The simple Born treatment of ions in a uniform dielectric would predict[19] a change in electrostriction proportional to Z^2/r for ions of charge Z and radius r. Since both parent and intermediate might be considered to have comparable radii of the order of 400 pm, this treatment would predict a reduced electrostrictive effect in the five-coordinate intermediate and thus a substantial volume increase. However, there is strong experimental evidence that the formal Born approach breaks down for large complex ions. Acidity constants for a range of aquometal cations are found experimentally to have $\Delta V°$ in the range -1.2 to $-3.8\ cm^3\ mol^{-1}$,[39,40] as against the prediction of the Born treatment of $\Delta V°$ of approximately $+25\ cm^3\ mol^{-1}$. The indication is that electrostatic effects of large complex ions are determined not by formal charge but by specific interactions of solvent and peripheral ligand atoms, also illustrated by the hydrodynamic properties of $Fe(phen)_3^{2+}$, $Fe(bpy)_3^{2+}$, and $(Co(en)_2(OH_2))_3Co^{6+}$ in water.[41] From this evidence, it is appropriate to assume no significant volume change on reducing the formal charge on the chromium center.

Thus a final predicted volume of activation of approximately $-11.5\ cm^3\ mol^{-1}$ for a one-ended dissociative mechanism of *trans*-$[Cr(ox)_2(OH_2)_2]^-$ is obtained from this analysis, compared to the observed value of $\Delta V^{\ddagger} = -16.6\ cm^3\ mol^{-1}$. This value is the same within experimental error as that previously reported by Kelm and co-workers[14] of $-16\ cm^3\ mol^{-1}$. The larger negative value of $\Delta V^{\ddagger}$ observed compared with prediction may arise from some contraction of the secondary hydration sphere to accommodate the more open transition state, leading to a negative volume contribution. The sensitivity of the reaction to solvent is consistent with such a secondary mechanistic process.

The dominance of electrostrictive effects about the newly implanted carboxylate center of the five-coordinate intermediate is also consistent with the negative entropy of activation ($\Delta S^{\ddagger} = -61\ J\ K^{-1}\ mol^{-1}$) observed, in terms of a decrease in entropy of the solvent in the vicinity of the newly implanted charge center. An apparent curvature of the volume of activation itself is observed, with the compressibility of activation $\Delta\beta^{\ddagger}$ estimated to be approximately $-1.8\ cm^3\ mol^{-1}\ kbar^{-1}$. Water in the first hydration sphere about an ion has been estimated to have a distinctly lower molar volume and compressibility than water in the bulk solvent.[19] Bulk water exhibits a compressibility coefficient $\beta = 0.84\ cm^3\ mol^{-1}\ kbar^{-1}$, whereas the compressibility coefficient of water in the electrostricted zone of an ion of unit charge is likely[42] to be of the order of $\beta = 0.10$ cm^3 mol^{-1} kbar^{-1}. When a single water molecule is transferred from the bulk to the region of a carboxylate anion, then $\Delta\beta = 0.10 - 0.84 = -0.74$ cm^3 mol^{-1} kbar^{-1}. The experimental value $\Delta\beta^\ddagger = -1.8 \pm 0.6$ cm^3 mol^{-1} kbar^{-1} thus suggests that about two water molecules are drawn into the region of the carboxylate anion as it is formed in the dissociative process under discussion. Implantation of a new charge center and consequent solvent electrostriction should therefore be reflected in both a negative volume and a negative compressibility of activation, leading to an expectation of curvature in the plot of ln k_p vs. P. The observation of some curvature in the experimental graph (Figure 1) for this reaction in which electrostriction is assumed to be the dominant contributor to the volume of activation is therefore consistent with a one-ended dissociative mechanism involving a charged dangling ligand.

Isomerization of *trans*-$[Cr(mal)_2(OH_2)_2]^-$. Isomerization of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ occurs at a rate 350 times slower than that for *trans*-$[Cr(ox)_2(OH_2)_2]^-$ at 25 °C.[16] No isotopic oxygen-exchange data are available for this reaction, although a rate in the range 10^{-6}–10^{-5} s^{-1} at 25 °C similar to that observed for other Cr(III) complexes would be compatible with a water-exchange mechanism.[17] Further, as distinct from the oxalato complex, the malonato complex does does not exhibit any significant dependence of the rate on the protic nature of the solvent and dielectric constant in methanol–water mixtures. A change from a negative $\Delta S^\ddagger$ for isomerization of *trans*-$[Cr(mal)_2(OH)_2]^{3-}$ to positive values of $\Delta S^\ddagger$ for isomerization of both *trans*-$[Cr(mal)_2(OH)(OH_2)]^{2-}$ and *trans*-$[Cr(mal)_2(OH_2)_2]^-$ has been reported and differs from a consistently negative $\Delta S^\ddagger$ for the analogous oxalato series.[16] The measured $\Delta S^\ddagger = +74$ J K^{-1} mol^{-1} for isomerization of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ is analogous to that measured for the isomerization of *trans*-$[Co(en)_2(SeO_3H)(OH_2)]^{2+}$ of $\Delta S^\ddagger = +53$ J K^{-1} mol^{-1}, which has been shown to proceed through an aquo ligand dissociative mechanism.[43] A change in mechanism from a one-ended dissociative mechanism for *trans*-$[Cr(ox)_2(OH_2)_2]^-$ to a dissociative mechanism involving aquo ligand release in the case of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ has been implied to occur on the basis of the limited experimental evidence available.

In terms of the predicted volume of activation for an aquo ligand dissociative mechanism, an estimate can be made in the following manner.

Aquo ligand dissociation is not accompanied by any change in formal charge of the metal ion, and re-formation of a six-coordinate species from the five-coordinate intermediate must occur without the possibility of entry of any other coordinating ligand except water into the sixth coordination site in aqueous solution. Since the hydrated complex ion is relatively incompressible, the effects of electrostriction are virtually constant throughout the course of the reaction. The volumes and compressibilities of water in the first and second coordination spheres about an ion have been estimated to be very similar, indicating that no appreciable pressure dependence of the volume of activation itself is expected. For an I_d mechanism, it has been established[42] that $\Delta\beta^\ddagger$ $(=\beta_{\text{hydr sphere}} - \beta_{\text{coord sphere}}) \ll 0.06$ cm^3 mol^{-1} kbar^{-1}, and hence for all practical purposes $\Delta\beta^\ddagger = 0$.

Arguments have been developed that the five-coordinate intermediate should define the same intrinsic volume as a six-coordinate complex, and hence no volume contribution from this source need be considered.[19] Therefore, the expected $\Delta V^\ddagger$ for complete dissociative release of aquo ligand into the second coordination sphere should be no more than the molar volume of water of +15 cm^3 mol^{-1}. By a similar argument, an associative interchange mechanism would involve a negative $\Delta V^\ddagger$ of no more than −15 cm^3 mol^{-1}.

For water exchange in *trans*-$[Co(en)_2(OH_2)_2]^{3+}$, assigned a dissociative (D) mechanism of aquo ligand release, $\Delta V^\ddagger = +14.3$ cm^3 mol^{-1} has been observed.[43] In complexes in which an I_d dissociative interchange mechanism has been assigned, such as for the trans → cis isomerization reactions of $[Co(en)_2(SeO_3)(OH_2)]^+$ and $[Co(en)_2(SeO_3H)(OH_2)]^{2+}$, measured values of $\Delta V^\ddagger$ were +7.6 and +8.0 cm^3 mol^{-1}, respectively, with no appreciable curvature being observed.[44] These volumes are more consistent with substantial metal–oxygen bond stretching of the aquo ligand rather than complete dissociation. It is anticipated that a volume of activation of the order of +8 cm^3 mol^{-1} would therefore be consistent with an aquo ligand dissociation I_d mechanism. The measured $\Delta V^\ddagger = +8.9$ cm^3 mol^{-1} with no observed curvature for the isomerization of *trans*-$[Cr(mal)_2(OH_2)_2]^-$ is therefore in agreement with the proposed mechanism.

Acid-Catalyzed Aquation Reactions. Both *cis*-$[Cr(ox)_2(OH_2)_2]^-$ and *cis*-$[Cr(mal)_2(OH_2)_2]^-$ have been shown to exhibit rates of aquation dependent on $[H^+]$ in perchloric acid solutions.[17,21] The dissociation of the malonato complex occurs approximately 20 times faster at 45 °C than that of the oxalato complex and exhibits a lower enthalpy of activation.[17] This observation is not consistent with the greater ring strain in the oxalato complex indicated by x-ray structure determinations[33-35] which could be expected to facilitate metal–oxygen bond breaking in the chelated ligand and may indicate that ring opening is not the rate-determining step. Entropies of activation are negative for both reactions and hence do not indicate significantly different mechanisms for the two reactions.

The aquation in both complexes in acid solution has been proposed to proceed via a pathway involving a rapid preequilibrium and formation of an intermediate with a unidentate coordinated diacid and subsequent rate-determining dissociative release of that ligand.[17,21,22] This process can be represented by the sequence

$$\textit{cis}\text{-}[Cr(aa)_2(OH_2)_2]^- \underset{\text{fast}}{\overset{H^+,\, H_2O}{\rightleftharpoons}} [Cr(aa)(aaH)(OH_2)_3]^0$$

$$[Cr(aa)(aaH)(OH_2)_3] \xrightarrow{H^+,\, H_2O} [Cr(aa)(OH_2)_4]^+ + HaaH$$

where aa represents the unprotonated diacid oxalato or malonato. The protonated intermediate $[Cr(aa)(aaH)(OH_2)_3]$ has been identified for both oxalate and malonate complexes and found to form very rapidly in acidic solution,[45] consistent with rapid proton preequilibrium. The faster rate of aquation of the malonato complex compared with that of the oxalato complex has been attributed to the greater basicity of the malonate ion favoring the proton preequilibrium step in the proposed mechanism.[17]

The negative entropies of activation for both reactions have been interpreted as indicating participation of a molecule of water in the rate-determining step.[22] Previously, associative mechanisms for water exchange in $[Cr(OH_2)_6]^{3+}$ and for chromium(III)–oxalato formation reactions have been indicated by the negative $\Delta V^\ddagger$ values measured. Reaction of the unidentate intermediate either by an associative mechanism involving entry of a water molecule into the first coordination sphere in the transition state or, alternatively, by a dissociative mechanism involving release of the charged unidentate carboxylate ion into the bulk solvent in forming the transition state should be associated with negative $\Delta V^\ddagger$ values, by analogy to similar isomerization mechanisms discussed earlier. The determined $\Delta V^\ddagger = +1.7$ cm^3 mol^{-1} for acid-catalyzed aquation of *cis*-$[Cr(ox)_2(OH_2)_2]^-$ and $\Delta V^\ddagger = +2.4$ cm^3 mol^{-1} for acid-catalyzed aquation of *cis*-$[Cr(mal)_2(OH_2)_2]^-$ are not consistent with either of these two processes as the rate-determining pathway, although it is apparent that both most likely proceed through the same mechanism.

Direct proton attack at the coordinated unidentate carboxylate of the intermediate and subsequent dissociative release of the neutral protonated carboxylate into the bulk solvent is more consistent with the small positive volume of activation measured. Such a process can be rationalized in the following manner.

Contributions to the overall volume of activation both from an equilibrium protonation (ΔV_{prot}) and from the dissociative release of the protonated acid (ΔV_{diss}) can be considered. An estimate of ΔV_{prot} can be made by considering the experimentally determined acidity constants for a range of aquometal cations,[39,40] where for the process

$$M(OH_2)_6{}^{n+} \rightleftharpoons M(OH_2)_5(OH)^{(n-1)+} + H_{aq}{}^+$$

the average $\Delta V^\ddagger$ is -2 cm^3 mol^{-1}. For the reverse equilibrium protonation process, an analogous $\Delta V^\ddagger$ of the opposite sign might be expected, and hence it is possible to assign $\Delta V_{\text{prot}} < +2$ cm^3 mol^{-1}. Dissociative release of the protonated unidentate carboxylate should involve no contribution from electrostriction since the leaving ligand is formally neutral but will involve a positive volume of activation arising from the implantation of the carboxylate arm into the solvent. Arguments have been presented earlier in the discussion which assign the ΔV for such a process to only the volume of the coordinated oxygen, and hence $\Delta V_{\text{diss}} = +1.0$ cm^3 mol^{-1} can be predicted. Overall, a $\Delta V^\ddagger$ of the order of $+3$ cm^3 mol^{-1} at the upper limit can be expected for a mechanism involving direct protonation of the coordinated carboxylate and subsequent dissociative release of the protonated acid to form a five-coordinate intermediate of the same intrinsic volume as its six-coordinate precursor. The small positive values of $\Delta V^\ddagger$ measured for both acid-catalyzed aquations are consistent with this one mechanism.

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Registry No. *trans*-$[Cr(ox)_2(OH_2)_2]^-$, 18954-99-9; *trans*-$[Cr(mal)_2(OH_2)_2]^-$, 29770-09-0; *cis*-$[Cr(ox)_2(OH_2)_2]^-$, 15489-30-2; *cis*-$[Cr(mal)_2(OH_2)_2]^-$, 18485-09-1.

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