TABLE II

RATE DATA OBTAINED AS A FUNCTION OF TEMPERATURE FOR THE REACTION OF VANADIUM(IV) WITH THE MANGANESE(III) COMPLEXES OF CyDTA AND EDTA

$Mn^{III}CyDTAH_2O^-$			$Mn^{III}EDTAH_2O^-$		
$10^{-2}k_0$, M^{-1} sec^{-1}	k_1, sec^{-1}	Temp, °C	$10^{-2}k_0$, M^{-1} sec^{-1}	k_1, sec^{-1}	Temp, °C
1.25	0.74	13.9	1.73	0.71	7.0
0.87	0.66	11.2	1.30	0.68	4.3
0.65	0.53	7.0	0.78	0.47	1.7
0.50	0.37	3.4			
0.40	0.29	1.7			

those for $Mn^{III}CyDTAH_2O^-$ under identical conditions may be indicative of two parallel paths (*i.e.*, a reaction proceeding either through a hydrolyzed vanadium or a hydrolyzed manganese). An alternate possibility is the steric effect of the bulky cyclohexane ring to hamper intermediate formation compared to the ethylene backbone in EDTA.

The ratio of the rate constants for the hydroxo and aquo pathways, k_{OH}/k_{H_2O}, at 1.7° and pH 2.10 was ~72 for the CyDTA complex and ~60 for the EDTA complex. These values are in accordance with the general observation of greater reactivity, 10^2 to 10^4, of a hydroxy-bridged path over a water-bridged path for inner-sphere electron-transfer reactions.[7,26-28] Such an enhancement in rate does not seem to occur for outer-sphere reactions. A comparison of reduction reactions of VO^{2+} with Cu^+, V^{2+}, Cr^{2+}, and Fe^{2+} illustrates the importance of dinuclear hydroxy-bridged species as intermediates.[29]

Vanadium(IV) is sufficiently labile to react by an inner-sphere mechanism[15,16] in agreement with oxidation-reduction studies.

All oxidation-reduction reaction rates of manganese(III) studied to date are within the estimated time scale for the rate of water exchange. Davies has suggested that the rate of water loss is rate determining even for the fastest reactions that have been observed.[9] In view of the large discrimination between hydroxide and water for the reactions studied, we propose that both $Mn^{III}CyDTAH_2O^-$ and $Mn^{III}EDTAH_2O^-$ are reacting by an inner-sphere mechanism. The situation for the reaction between hexaaquomanganese(III) and VO^{2+}, which shows only a slightly favored hydroxide pathway,[12] is still uncertain.

[26] A. Zwickel and H. Taube, *J. Amer. Chem. Soc.*, **81**, 1288 (1959).

[27] J. H. Espenson and O. J. Parker, *ibid.*, **90**, 3689 (1968).

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[29] K. Shaw and J. H. Espenson, *J. Amer. Chem. Soc.*, **90**, 6622 (1968).

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Structure and Reactivity in Octahedral Complexes. XIII. Trans-to-Cis Isomerizations and Hydrolysis Reactions of Some Chromium(III) Anionic Complexes[1]

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The kinetics of isomerization and hydrolysis reactions of some anionic complexes of chromium(III) have been investigated. The results obtained for the trans-to-cis isomerizations of $Cr(ox)_2(OH_2)_2^-$, $Cr(ox)_2(OH_2)OH^{2-}$, and $Cr(ox)_2(OH)_2^{3-}$ are interpreted in terms of one-ended dissociation of the oxalato ligand. In contrast, the similar malonato series reveals a breakdown in the kinetic pattern, which suggests a change in mechanism for the aquohydroxo and diaquo forms involving the primary dissociation of a water molecule. The hydrolysis of *trans*-$Cr(ox)_2(OAc)_2^{3-}$ occurs at a rate independent of pH in the range pH 2–11, with retention of geometrical configuration. The pH ranges related to the hydrolysis of the aquoacetato or the hydroxoacetato complexes are below 6.8 and above 10.8, respectively; the hydrolysis of the former is acid catalyzed. The final product of all these reactions is *cis*-$Cr(ox)_2(OH_2)_2^-$ or its conjugate bases. The mechanism of the hydrolysis is discussed in the light of the isomerization behavior of the related species above, of the activation parameters, and, in part, of the stereochemical results. A common feature is the tendency to a dissociation mechanism as a function of the overall negative charge of the complex.

Introduction

Most studies on the reactivity of octahedral complexes concern cationic species, especially those involving Co(III) as the transition metal. Much less information is available on anionic complexes.

In hydrolysis reactions cationic Co(III) complexes display a dissociative mechanism. In acid solution aquation takes place by a first-order process.[2] Although base hydrolysis of such complexes as $Co(NH_3)_5Cl^{2+}$ shows second-order kinetics, provided that acidic protons in the ligands are available, the mechanism still involves a dissociative path *via* the conjugate base.[2] A clear proof of a dissociative mechanism with this general type of complex was obtained when acidic protons were absent in the substrate structure; thus with $Co(dipy)_2(OAc)_2^+$, first-order kinetics were observed.[3] However, the existence of an associative mechanism is also well-established, particularly with the octahedral complexes of the second- and third-row metals, such as Rh(III) and Ir(III).[4]

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In reactions of anionic complexes, dissociation mechanisms are expected to be even more generally valid, since in the interaction of like charges, association phenomena are kept to a minimum. This appears to be the case with $Co(CN)_5X^{3-}$.[5] In view of a systematic investigation on anionic complexes, Cr(III) complexes seemed to be a good starting point because of the existence of some work concerning the properties of oxalato complexes. In several instances, such as ^{18}O exchange,[6] isomerization,[7] and racemization reactions,[8] mechanisms *via* a one-ended dissociation of an oxalato ligand have been proposed.

This paper deals with the kinetics of the hydrolysis of some *trans*-bis(oxalato)diacidochromate(III) anions and of the isomerization of *trans*-bis(oxalato)- and bis(malonato)diaquochromate(III) complexes and their conjugate bases.

Results and Discussion

In Table I, the significant spectral data (molar absorptivities and wavelengths of the absorption maxima) of all the compounds considered are collected. All the spectra show a similar pattern with two maxima in the regions 375–430 and 520–580 nm. The configurations of these complexes, as based on the spectral data and on the empirical rules holding for complexes with tetragonal symmetry of the type[9a,b] MA_4B_2, agree with the ones proposed by Werner on the basis of chemical behavior.[9c] The rates of isomerization were determined spectrophotometrically at wavelengths of 420 and 560 nm for the bis-oxalato and at 570 and 580 nm for the bis-malonato complexes. The hydrolysis reactions were followed at 410 and 560 nm. The first-order rate constants were calculated from the slope of the plot of log $(A_\infty - A)$ *vs.* t, where A is the absorbance at time t and A_∞ is the absorbance after the reaction is complete (normally after 6 half-lives, when side reactions are still negligible).

Table I

Spectral Data for Some Complex Ions of the Type $Cr(AA)_2XY^{n-}$

	ϵ (λ_{max})			
	Trans isomer		Cis isomer	
Complex ion	Band I	Band II	Band I	Band II
$Cr(ox)_2(OAc)_2^{3-}$	17.2 (410)	17.5 (540)	91.3 (415)	64.4 (575)
$Cr(ox)_2(OH_2)OAc^{2-}$	22.2 (410)	20.0 (545)		
$Cr(ox)_2(OH)_2^{3-}$	126 (410)	44.6 (580)	104 (410)	37 (585)
$Cr(ox)_2(OH_2)(OH)^{2-}$	48 (408)	44 (570)	77 (410)	51 (580)
$Cr(ox)_2(OH_2)_2^{-}$ [a]	34.4 (416)	32 (555)	68.5 (416)	51 (562)
$Cr(ox)_2(py)_2^{-}$	29.4 (375)	31.0 (517)		
$Cr(mal)_2(OH)_2^{3-}$	25 (430)	20 (580)	55 (415)	37 (580)
$Cr(mal)_2(OH_2)(OH)^{2-}$	41 (420)	26 (570)	48 (425)	43 (575)
$Cr(mal)_2(OH_2)_2^{-}$	22 (405)	21 (560)	41 (415)	51 (565)

[a] See ref 7a and G. E. Cummingham, R. W. Burley, and M. T. Friend, *Nature (London)*, **166,** 1103 (1952).

Isomerization Reactions. (a) ***trans*-Cr(ox)$_2$(OH$_2$)$_2^-$ and Its Conjugate Bases.**—First-order rate constants and activation parameters are reported in Table II.

Table II

Kinetic Data for the Isomerization Reactions of *trans*-$Cr(ox)_2(OH_2)_2^-$, *trans*-$Cr(mal)_2(OH_2)_2^-$, and Their Conjugate Bases, in Aqueous Solution at 25°

Complex	10^3k,[c] sec^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
$Cr(ox)_2(OH)_2^{3-}$	19.4[a]	13.8	−20.3
$Cr(ox)_2(OH_2)(OH)^{2-}$	2.0	14.6	−23.0
$Cr(ox)_2(OH_2)_2^{-}$ [b]	0.42	17.5	−15.3
$Cr(mal)_2(OH)_2^{3-}$	0.25	17.9	−15.1
$Cr(mal)_2(OH_2)(OH)^{2-}$	1.41	24.3	+9.9
$Cr(mal)_2(OH_2)_2^{-}$	0.0018[a]	31.8	+21.5

[a] Calculated from the activation parameters. [b] Taken from ref 7a. [c] For the k values at temperatures other than 25°, see the Experimental Section.

The isomerization of *trans*-$Cr(ox)_2(OH_2)_2^-$ was also studied in water–methanol mixtures (see Experimental Section). The plot of log k *vs.* $1/D$ shows an upward drift from linearity in the mixtures of low dielectric constant, which can be attributed to a preferential "adsorption" of water by the complex anion.[10] The isomerization of *trans*-$Cr(ox)_2(OH_2)_2^-$ and its conjugate bases proceeds with complete change to the corresponding cis isomers. Attention was given to the possible intervention of an olation process of *cis*-$Cr(ox)_2(OH_2)OH^{2-}$; it appears that this side reaction does not influence the isomerization because of its much slower rate.[11]

The main results can be summarized as follows: (i) the reactivity increases regularly as the charge changes from 1− to 3−; (ii) the reactivities are in the range 10^{-4}–10^{-2} sec^{-1}, *i.e.*, high enough to make metal–water bond breaking unlikely as the inner-sphere water is known to be firmly bound in chromium(III)–aquo complexes;[6d,12] (iii) the entropies of activation are fairly large and negative, as in most investigated reactions of the chromium–oxalate complexes;[6-8] they indicate an increase in solvation on going from the ground to the transition state; (iv) the reaction of *trans*-$Cr(ox)_2(OH_2)_2^-$ slows down as the dielectric constant of the solvent is decreased.

The above facts suggest a mechanism of the type shown in Figure 1. According to point (ii), the first step is the slow dissociation of one end of an oxalate ligand rather than the dissociation of a water molecule. Since this involves repulsion between like charges and the concentration of a negative unit charge on the free end of the ligand, the results (i) and (iii) above can be easily understood. Fast subsequent rearrangement of the pentacoordinate intermediate to a trigonal bipyramidal structure is likely because of stabilization of the

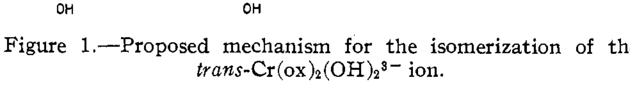

Figure 1.—Proposed mechanism for the isomerization of the *trans*-$Cr(ox)_2(OH)_2^{3-}$ ion.

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[5] R. Grassi, A. Haim, and W. K. Wilmarth, *Inorg. Chem.*, **6,** 237 (1967).

[6] (a) S. Sheel, D. T. Meloon, and G. M. Harris, *ibid.*, **1,** 170 (1962); (b) K. V. Krishnamurty and G. M. Harris, *Chem. Rev.*, **61,** 213 (1961); (c) C. A. Burton, J. H. Carter, D. R. Llewellyn, C. O'Connor, A. L. Odell, and S. Y. Yih, *J. Chem. Soc.*, 4615, 4622, 4627 (1964); (d) J. Aggett, I. Mawston, A. L. Odell, and B. E. Smith, *ibid., A*, 1413 (1968).

[7] (a) R. E. Hamm, *J. Amer. Chem. Soc.*, **75,** 609 (1953); (b) R. E. Hamm and R. H. Perkins, *ibid.*, **77,** 2083 (1955).

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[9] (a) Y. Shimura, *Bull. Chem. Soc. Jap.*, **25,** 49 (1952); (b) L. E. Orgel, *J. Chem. Phys.*, **23,** 1004 (1955); (c) A. Werner, *Ann.*, **406,** 261 (1914).

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[11] D. M. Grant and R. E. Hamm, *J. Amer. Chem. Soc.*, **78,** 3006 (1956).

[12] H. Taube and R. Plane, *J. Phys. Chem.*, **56,** 33 (1952).

π bonds of the hydroxo groups.[13] Finally, attack of the free end on the equatorial plane leads to the observed cis species.

(b) **trans-$Cr(mal)_2(OH_2)_2^-$ and Its Conjugate Bases.**—First-order rate constants and activation parameters for the isomerizations of these complexes are reported in Table II. The complete isomerization of *trans*-$Cr(mal)_2(OH)_2^{3-}$ could not be ascertained because of the decomposition of this complex ion (see Experimental Section). In order to study the complex species present in solution at the various pH values, the pK_a values for the first ionization of *cis*- and *trans*-$Cr(mal)_2(OH_2)_2^-$ were determined; they were found to be 7.80 and 7.90, respectively.

First we note that the data show a breakdown on going from the dihydroxo to the diaquo complex. While the former displays a negative $\Delta S^{\ddagger}$ value of the same magnitude as that observed for the dioxalato complexes, fairly large, positive $\Delta S^{\ddagger}$ values are given by both the hydroxoaquo and the diaquo complexes. In the second place, the reactivity order is not the same as is observed with the dioxalato series. The dihydroxo complex reacts more slowly than any of the dioxalato complexes and, in particular, much more slowly than *trans*-$Cr(ox)_2(OH)_2^{3-}$. This is probably a polar effect. On going from a 3− charge to a 1− charge, one would expect a steady decrease in rate. On the contrary, a rate increase was observed on going from a 3− to a 2− charge, and a very large decrease, on going from a 2− to a 1− charge. Finally, unlike the corresponding dioxalato complex, *trans*-$Cr(mal)_2(OH_2)_2^-$ shows no solvent effect, as though there were no essential difference in charge or charge distribution between the ground and transition state (see the Experimental Section for the data in water–methanol mixtures).

Combining the above evidence, we propose a change in mechanism as a likely explanation for the breakdown noted in the dimalonato series. In the case of the dihydroxo complex ion $Cr(mal)_2(OH)_2^{3-}$, where no water–metal bond breaking can occur, the reaction mechanism is assumed to be analogous to that postulated for the bis-oxalato complexes, *i.e.*, one involving the breaking of the chelating oxygen–metal bonds (Figure 1). In contrast, the isomerizations of diaquo and aquohydroxo complexes would involve the primary dissociation of a water molecule, followed by rearrangement of the pentacoordinated species and reinsertion of a water molecule (Figure 2).

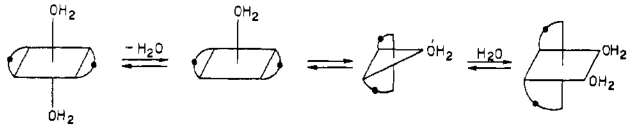

Figure 2.—Proposed mechanism for the isomerization of the *trans*-$Cr(mal)_2(OH_2)_2^-$ ion.

These two competing modes of isomerization are analogous to the isomerizations of $Co(en)_2(OH_2)_2^{3+}$ and $Co(en)_2(NH_3)OH_2^{3+}$ ions and their conjugate bases.[14,15] It is of interest to note that the isomerization rate ratio $Cr(mal)_2(OH_2)OH^{2-}$:$Cr(mal)_2(OH_2)_2^-$ is 777, a value very close to that observed for the ratio $Co(en)_2(OH_2)OH^{2+}$:$Co(en)_2(OH_2)_2^{3+}$ (735).[14] This is probably more than a fortuitous analogy and can be attributed to the labilizing effect of the hydroxo group.

Recently it has been suggested[16] that the isomerization of the bis(oxalato)diaquochromate(III) ion occurs by a twisting of the chromium–oxygen bonds, while that of bis(malonato)diaquochromate(III) might involve a total cleavage of the chromium–oxygen bonds; this hypothesis, although reasonable, is in contrast to the generally suggested reaction mechanism of oxalato complexes *via* one-end dissociation of the chelate ring;[6–8,17] it is difficult, however, to reconcile the above hypothesis with the observed strong change in the activation parameters.

Hydrolysis Reactions. (a) **trans-$Cr(ox)_2(OAc)_2^{3-}$.**—The substitution of the first acetato ligand in *trans*-$Cr(ox)_2(OAc)_2^{3-}$ was investigated in the $[H^+]$ range of 10^{-2}–10^{-11} *M* at 0°. In this range, the rate constant is essentially unaffected by the hydrogen ion concentration (Table III). Since the reaction is extremely rapid, no attempt was made to ascertain acid catalysis in more acidic solutions.

TABLE III

FIRST-ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF SOME COMPLEX ANIONS OF THE TYPE *trans*-$Cr(ox)_2A(OAc)^{n-}$ [a]

$Cr(ox)_2(OAc)_2^{3-}$		$Cr(ox)_2(OH_2)(OAc)^{2-}$ and $Cr(ox)_2(OH)(OAc)^{3-}$		
$[H^+]$, *M*	10^2k_{obsd}, sec^{-1} (0°)	$[H^+]$, *M*	10^2k_{obsd}, sec^{-1} (25°)	10^2k_{calcd}, sec^{-1}
1×10^{-2}	3.70	2.0	0.570	0.530
1×10^{-5}	3.30	1.7	0.448	0.456
1×10^{-8}	3.90	1.4	0.395	0.390
1×10^{-11}	4.02	1.0	0.289	0.290
		0.7	0.200	0.215
		0.4	0.131	0.140
		0.1	0.072	0.075
		1×10^{-2}	0.061	0.054
		1×10^{-3}	0.051	0.051
		1×10^{-4}	0.060	
		1×10^{-5}	0.065	
		1×10^{-8}	0.722	
		1×10^{-9}	2.540	
		1×10^{-10}	2.450	
		1×10^{-11}	2.890	
		1×10^{-12}	3.100	

[a] Activation parameters: *trans*-$Cr(ox)_2(OAc)(OH_2)^{2-}$ at pH 3, $\Delta H^{\ddagger} = 16.3$ kcal/mol and $\Delta S^{\ddagger} = -18.8$ eu; *trans*-$Cr(ox)_2(OAc)(OH)^{3-}$ at pH 11, $\Delta H^{\ddagger} = 8.4$ kcal/mol and $\Delta S^{\ddagger} = -38.8$ eu. For the *k* values at temperatures other than 25°, see the Experimental Section. The kinetic experiments were run in duplicate. The probable errors in *k*, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ were found to be 2%, 1 kcal/mol, and 2 eu, respectively.

(b) **trans-$Cr(ox)_2(OH_2)OAc^{2-}$.**—The reaction was investigated over a wider pH range than in the preceding case, the hydrogen ion concentration varying between 2 and 10^{-12} *M*. In the $[H^+]$ range from 2 to 10^{-5} *M* (Table III), the reaction is acid-catalyzed up to about 10^{-2} *M;* then it follows regular first-order kinetics. The acid catalysis law is

$$k_{obsd} = k_{H_2O} + k_{H^+}[H^+]$$

where $k_{H_2O} = 5.1 \times 10^{-4}$ sec^{-1} and $k_{H^+} = 2.4 \times 10^{-3}$ M^{-1} sec^{-1} at 25°. The first term in this equation is believed to correspond to the aquation of the original $Cr(ox)_2(OH_2)OAc^{2-}$ complex ion; the latter, to the

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(13) F. Basolo and R. G. Pearson, *J. Amer. Chem. Soc.*, **78**, 4878 (1956).

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(15) D. F. Martin and M. L. Tobe, *ibid.*, 1388 (1962).

(16) K. R. Ashley and K. Lane, *Inorg. Chem.*, **9**, 1795 (1970).

(17) A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc., London*, 388 (1962).

aquation of a protonated species therefrom, according to the process

$$\text{complex} + \text{H}^+ \rightleftharpoons (\text{complex,H}^+)$$

$$(\text{complex,H}^+) + \text{H}_2\text{O} \xrightarrow{k_{\text{H}^+}} \text{products}$$

A priori, the protonation site can be either an ox ligand or an AcO ligand. In weakly basic solution the first-order rate constant increases quite sharply as the [H$^+$] decreases; it reaches a value of 2.54 × 10^{-2} sec^{-1} at [H$^+$] = 10^{-9} *M* and 25° and then remains practically constant up to [H$^+$] = 10^{-12} *M*. These data are also reported in Table III.

The pK_a value of $Cr(ox)_2(OH_2)OAc^{2-}$ as a weak acid is assumed to be close to (and probably somewhat less than) 8.8, which is the value[11] for the second ionization of $Cr(ox)_2(OH_2)_2^-$. This means that the complex is expected to be essentially in the aquo form at pH values below 6.8 and in the hydroxo form above 10.8. Both in moderately acidic solutions and in sufficiently basic solutions, first-order kinetics were observed; changes in the rate constant at intermediate pH values were due to the presence of two species at equilibrium undergoing hydrolysis.

The specific rate of hydrolysis of the hydroxo form is about 50 times as great as the specific rate of hydrolysis of the aquo form. This is probably a charge effect and suggests a dissociative mechanism. The reactivity of the diacetato complex $Cr(ox)_2(OAc)_2^{3-}$ is similar to that of the hydroxoacetato complex $Cr(ox)_2(OH)OAc^{3-}$, the specific rates at 0° being 3.7 × 10^{-2} and 0.67 × 10^{-2} sec^{-1}, respectively. Here the structural effect is small because the OAc and OH ligands are of similar polar type and no charge variation is involved. In contrast, in the acid hydrolysis of *trans*-$Rh(ox)_2ACl^{n-}$, where an associative mechanism was assumed, no essential reactivity change was noticed for A = Cl or OH_2, although the charge on these complexes differs by one unit.[4]

It is of interest to compare the activation parameters for the hydrolysis of *trans*-$Cr(ox)_2(OH)OAc^{3-}$ and *trans*-$Cr(ox)_2(OH_2)OAc^{2-}$ with those for *trans*-$Cr(ox)_2(py)_2^-$ (to be dealt with further on). On going from the first complex to the third, the activation enthalpy increases, while the activation entropy becomes more negative. The trend in the $\Delta H^\ddagger$ values may be due to a decrease in the electrostatic repulsion between the complex anion and the outgoing ligand. The trend in the $\Delta S^\ddagger$ values can be traced back to solvation changes on going from the ground to the transition state. Let us consider a dissociative process as described by

$$Cr(ox)_2AX^{n-} \longrightarrow Cr(ox)_2A^{p-}\cdots X^{q-} \longrightarrow \text{products} \quad (p + q = n) \qquad (1)$$

For A = X = pyridine, $q = 0$ and the solvation is weakly affected by dissociation of the ligand; the $\Delta S^\ddagger$ value, +10.3 eu, is accordingly fairly high and positive. In contrast, for A = OH_2 or OH and X = OAc^-, $q = 1$ and one unit charge is more concentrated in the transition state than in the ground state; this would explain the low, negative $\Delta S^\ddagger$ values, differing from each other depending on the overall charge of the system (A = OH_2, −18.8 eu; A = OH, −38.8 eu).

(c) **Stereochemistry.**—Complete retention of geometrical configuration was observed in both acid and base hydrolysis of the *trans*-diacetato complex. Since ring-opening and ring-closure phenomena *via* one-ended dissociation of the chelating ligand (ox) have been found in $Cr(ox)_3^{3-}$ and related complex ions and are now proposed for the isomerization reactions of all the dioxalato complexes examined (see preceding section), a similar process is possible in all the hydrolysis reactions. However, retention of configuration may be explained on the basis of the high reactivity displayed by the above substrate. This probably makes the chelating ox ligand unable to undergo one-ended dissociation as a primary step, if an intervening process competes with it. Such a process may involve the participation of a water molecule in the early stage of the dissociation of an acetato ligand, as shown in Figure 3 (I_d-type mechanism).

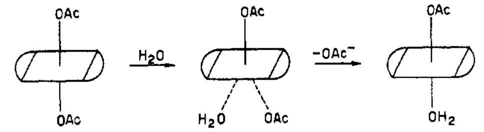

Figure 3.—Proposed mechanism for the hydrolysis of the *trans*-$Cr(ox)_2(OAc)_2^{3-}$ ion.

It may be worth noting that the observed independence of the stereochemical result of the H$^+$ concentration would rule out any incursion of carbonyl–oxygen bond-breaking, which is known to require acid- and base-catalysis in organic esters and has been in fact ascertained only for very high OH$^-$ concentrations in octahedral complexes.[18]

The hydrolysis of both *trans*-$Cr(ox)_2(OAc)OH_2^{2-}$ and *trans*-$Cr(ox)_2(OAc)OH^{3-}$ occurs with the formation of *cis*-$Cr(ox)_2(OH_2)_2^-$ and *cis*-$Cr(ox)_2(OH)_2^{3-}$. In order to ascertain whether the stereochemical change occurs during or after the hydrolysis step, expressions were derived for the total absorbance of the reaction solution in the alternative hypotheses

$$\text{trans acetato} \xrightarrow{k} \text{cis product} \qquad (2)$$

$$\text{trans acetato} \xrightarrow{k_1} \text{trans product} \qquad (3a)$$

$$\text{trans product} \xrightarrow{k_2} \text{cis product} \qquad (3b)$$

Such expressions for the acid hydrolysis were as follows: for eq 2

$$A = \epsilon_{\text{trans OAc}}C_0e^{-kt} + \epsilon_{\text{cis OH}_2}C_0(1 - e^{-kt})$$

For eq 3

$$A = \epsilon_{\text{trans OAc}}C_0e^{-k_1t} + \epsilon_{\text{trans OH}_2}C_0\left(\frac{1 - e^{-k_1t}}{1 + e^{-k_2t}}\right) + \epsilon_{\text{cis OH}_2}C_0\left(\frac{1 - e^{-k_1t}}{1 + e^{-k_2t}}\right)e^{-k_2t}$$

where $\epsilon_{\text{trans OAc}}$, $\epsilon_{\text{cis OH}_2}$, and $\epsilon_{\text{trans OH}_2}$ are the molar extinction coefficients for *trans*-$Cr(ox)_2(OH_2)OAc^{2-}$ and *cis*- and *trans*-$Cr(ox)_2(OH_2)_2^-$, respectively, C_0 is the initial concentration of the complex, k is the observed first-order rate constant for the hydrolysis reaction with isomerization, k_1 is the first-order rate constant for the hydrolysis of *trans*-$Cr(ox)_2(OH_2)OAc^{2-}$ to *trans*-$Cr(ox)_2(OH_2)_2^-$, and k_2 is the first-order rate constant for the trans-to-cis isomerization of $Cr(ox)_2(OH_2)_2^-$. Similar expressions were used for the base hydrolysis.

In the first instance (eq 2) the k value was calculated and compared with the observed overall rate constant.

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[18] H. Taube and R. B. Jordan, *J. Amer. Chem. Soc.*, **86**, 3890 (1964).

In the second instance, the calculated value for k_1 was compared with the observed isomerization rate constant (k_2), as reported in the preceding section. In both acid and base hydrolysis, the calculated values were of the same order of magnitude as the observed values (Table IV). Thus, there was no indication from this approach as to which alternative path might be the preferred one. While we leave this question open in the case of the acid hydrolysis, path 3 is probably more likely than path 2 in base hydrolysis, since the hydroxoacetato complex is nearly as reactive as the diacetato complex. A stereochemical course similar to that shown in Figure 3 is then possible in the latter case.

TABLE IV

CALCULATED AND OBSERVED RATE CONSTANTS FOR THE ALTERNATIVE STEREOCHEMICAL PATHS, EQ 2 AND 3

Path	Rate constants, sec^{-1}	
	Calcd	Obsd
Acid hydrolysis		
Eq 2	5.2×10^{-4}	5.1×10^{-4} [a]
Eq 3	8.8×10^{-4}	4.2×10^{-4} [b]
Base hydrolysis		
Eq 2	2.80×10^{-2}	3.0×10^{-2} [a]
Eq 3	1.75×10^{-2}	1.94×10^{-2} [b]

[a] Taken from Table III. [b] Taken from Table II.

(d) ***trans*-Cr(ox)$_2$(py)$_2^-$.**—The hydrolysis of *trans*-Cr(ox)$_2$(py)$_2^-$ was studied spectrophotometrically at 560 nm in the [H$^+$] range from 2 to 10^{-3} M. The rate constants were obtained from the following equation derived for two consecutive first-order reactions[19]

$$A_t - A_\infty = a_1e^{-k_1t} + a_2e^{-k_2t} \qquad (4)$$

The rate constants and the activation parameters for the hydrolysis of the dipyridino complexes are reported in Table V. In order to check the validity of this method, the ratio of the rate constants of the two consecutive reactions was calculated by the "time ratio method."[19] The stereochemical course of the individual reactions was not investigated; however, from the overall hydrolysis of *trans*-Cr(ox)$_2$(py)$_2^-$, only *cis*-Cr(ox)$_2$(OH$_2$)$_2^-$ appears to be formed.

TABLE V

FIRST-ORDER RATE CONSTANTS FOR THE HYDROLYSIS OF *trans*-Cr(ox)$_2$(py)$_2^-$ (k_1) AND Cr(ox)$_2$(OH$_2$)py$^-$ (k_2) AT 46.3° [a]

[H$^+$], M	10^4k_1, sec^{-1}	10^4k_2, sec^{-1}	[H$^+$], M	10^4k_1, sec^{-1}	10^4k_2, sec^{-1}
2.08	20	11.4	0.02	4.1	2.61
0.10	4.8	2.75	0.01	3.9	2.70

[a] Activation parameters for *trans*-Cr(ox)$_2$(py)$_2^-$ at pH 1.7: $\Delta H^\ddagger = 27.7$ kcal/mol and $\Delta S^\ddagger = 10.3$ eu. For the k_1 values at temperatures other than 46.3°, see the Experimental Section.

Experimental Section

Materials.—The following compounds were prepared according to known procedures: *trans*-Na$_3$[Cr(ox)$_2$(OAc)$_2$]·4H$_2$O, *cis*-Na$_3$[Cr(ox)$_2$(OAc)$_2$]·5H$_2$O, *trans*- and *cis*-Ba[Cr(ox)$_2$(OH$_2$)OAc]·7H$_2$O, *trans*-Na$_2$[Cr(ox)$_2$(OH$_2$)OAc]·4H$_2$O, *trans*-Na[Cr(ox)$_2$(OH$_2$)$_2$]·5H$_2$O, *cis*-K[Cr(ox)$_2$(OH$_2$)$_2$]·2H$_2$O, *trans*-Na[Cr(ox)$_2$(py)$_2$]·H$_2$O, and *cis*- and *trans*-K[Cr(mal)$_2$(OH$_2$)$_2$]·3H$_2$O.[7b,9c,20] The purity of each salt was checked by elemental analysis for Cr, C, and H.

Spectrophotometric Measurements.—Absorption spectra in the visible region were obtained with a Beckman Model DU spectrophotometer, using 10-mm silica cells, thermostated at the chosen temperature. Solutions of the complexes were *ca.* 2×10^{-2} M.

Potentiometric Measurements.—The values of the first dissociation constants of *cis*- and *trans*-Cr(mal)$_2$(OH$_2$)$_2^-$ were determined at 25° by a potentiometric method, using a Radiometer Copenhagen pH meter, Model PHM 22r, with conventional external glass and saturated calomel electrodes, the ionic strength being 0.1 M (NaClO$_4$).

Isomerization Rate Measurements.—The solutions (5 ml) for the kinetic runs were prepared from a calculated amount of the complex in HClO$_4$ solution (10^{-2}–10^{-4} M). For the diaquo complexes, the pH of the solution (measured with the pH meter) was in the range 2–4.5. The solutions of the aquohydroxo and dihydroxo complexes were obtained by adding 1.1 and 2.8 equiv, respectively, of a 0.1 N NaOH solution to a solution of the complex in CO$_2$-free water. All the solutions were precooled to 0° to slow down the reactions in the time passing between the mixing of the reagents and the immersion in the thermostat (*ca.* 45 sec); the latter was chosen as zero time. The reaction was followed spectrophotometrically by recording the change in absorbance at fixed wavelengths of 3-ml samples at given time intervals. In the case of the aquohydroxo and the dihydroxo complexes, the samples were first quenched with 2 ml of a 1 M HClO$_4$ solution, not only because we wished to reduce the rate of the reaction but also because the *trans*- and *cis*-diaquo complexes show greater differences in molar absorptivities than their conjugate bases. Blank experiments showed that acidification does not affect the isomeric composition of the mixture. The completion of the reaction was checked by comparing the spectrum of the reaction solution at infinite time to that of a solution of an authentic specimen of the corresponding cis complex.

Whereas the course of the isomerization of *trans*-Cr(ox)$_2$(OH)$_2^{3-}$ was not affected by any decomposition of the complex, in the reaction of *trans*-Cr(mal)$_2$(OH)$_2^{3-}$ the absorbance first rose without attaining the calculated value for the complete formation of *cis*-Cr(mal)$_2$(OH)$_2^{3-}$; then it slowly decreased. This behavior was shown to be due to the decomposition of the cis complex, by blank experiments. The rate constants were obtained from the spectral measurements relative to the first percentage of the reaction (20–25%) and from an A_∞ value calculated on the basis of the known molar extinction coefficients of *cis*-Cr(mal)$_2$(OH)$_2^{3-}$. The validity of this procedure was confirmed by the fact that the rate constant was found to be independent of the initial complex concentration and the Arrhenius equation was obeyed.

The dependence of the rate of isomerization of *trans*-Cr(ox)$_2$(OH$_2$)$_2^-$ and *trans*-Cr(mal)$_2$(OH$_2$)$_2^-$ on the dielectric constant of the medium was determined by dissolving the complexes in the appropriate aqueous solution of HClO$_4$ (10^{-2} M) or methanol (Erba RS), by the procedure described above. The values of the dielectric constants of the solvents were taken from the literature.[10] The first-order rate constant, 10^4k (sec^{-1}) at 25°, were as follows (per cent MeOH in parentheses): *trans*-Cr(ox)$_2$(OH$_2$)$_2^-$, 4.19 (0%), 3.0 (15%), 1.90 (30%), 0.75 (60%), 0.23 (90%); *trans*-Cr(mal)$_2$(OH$_2$)$_2^-$, 0.018 (0%), 0.07 (90% at 46.3°).

The isomerization rate constants (10^5k, sec^{-1}) at diverse temperatures (given in parentheses as °C) are as follows, except for those in Table II: *trans*-Cr(ox)$_2$(OH$_2$)OH^{2-}, 110 (18.0), 355 (32.0); *trans*-Cr(ox)$_2$(OH)$_2^{3-}$, 195 (1.0), 447 (9.5), 742 (15.5), 1420 (22.0); *trans*-Cr(mal)$_2$(OH$_2$)$_2^-$, 3.98 (45.8), 17.0 (55.0), 72.5 (65.0); *trans*-Cr(mal)$_2$(OH$_2$)(OH)$^{2-}$, 46.8 (17.5), 340 (32.0); *trans*-Cr(mal)$_2$(OH)$_2^{3-}$, 4.47 (8.5), 9.12 (15.0), 14.8 (19.0).

Hydrolysis Rate Measurements.—Kinetic runs were made using a Beckman Model DU spectrophotometer, the temperature being regulated to within ±0.1°. For the rapid reactions a Beckman Model DB spectrophotometer, equipped with a Sargent recording apparatus, was used in order to permit continuous recording of the absorbance during the reaction. The required amount of the complex was weighed into a 5-ml volumetric flask, together with the calculated amount of NaClO$_4$, and a solution of HClO$_4$ of the desired concentration, precooled at 0°, was added. After mixing, the reaction solution was immediately transferred to the cell and this time was taken as zero time. The solutions of HClO$_4$ were prepared by dilution of a titrated solution of HClO$_4$ (2.046 M) and checked by potentiometric titration with a CO$_2$-free solution of sodium hydroxide. For the base hydrolysis, buffer solutions of H$_3$BO$_3$–NaOH or Na$_2$B$_4$O$_7$–H$_3$BO$_3$ mixtures at given pH values were prepared according to a given

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(19) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Wiley, New York, N. Y., 1961, pp 166–171.

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

procedure.[21] The final spectra of the hydrolysis products were found to be unaffected by the presence of the buffer ions. To determine the stereochemical course of the hydrolysis reactions, *trans*-$Na_3[Cr(ox)_2(OAc)_2]$ was dissolved in a solution (10^{-2} M) of $HClO_4$ at 0°; after 5 min (100% of the first reaction) the recorded spectrum of the solution was found to be identical, in both molar absorptivities and λ_{max} values, with that of an authentic specimen of *trans*-$Na_2[Cr(ox)_2(OH_2)OAc]$. This result was confirmed by the quantitative isolation of *trans*-$Ba[Cr(ox)_2(OH_2)OAc]$, as obtained on precipitation of the latter from the reaction solution of *trans*-$Na_3[Cr(ox)_2(OAc)_2]$ with a CH_3COOH–$Ba(OAc)_2$ mixture.

In the case of base hydrolysis, the complex in the reaction solution was first converted into the aquo form by acidification. The spectra of the acidified solutions of the complete acid and base hydrolysis products of *trans*-$Cr(ox)_2(OAc)_2{}^{3-}$ were found to be identical with that of the *cis*-$Cr(ox)_2(OH_2)_2{}^{-}$ complex. The spectra of the solutions of *trans*-$Cr(ox)_2(OH_2)OAc^{2-}$ on acid hydrolysis ($2\ M \geq [H^+] \geq 1 \times 10^{-5}\ M$) were found to be identical with that of *cis*-$Cr(ox)_2(OH_2)_2{}^{-}$. Under basic conditions ($1 \times 10^{-11}\ M \geq [H^+] \geq 1 \times 10^{-9}\ M$), the spectra were identical with those of *cis*-$Cr(ox)_2(OH)_2{}^{3-}$, and this result was confirmed by conversion of *cis*-$Cr(ox)_2(OH)_2{}^{3-}$, as produced during the reaction, into the corresponding diaquo form. The hydrolysis of *cis*-$Na_3[Cr(ox)_2(OAc)_2]$ and *cis*-$Na_2[Cr(ox)_2(OH_2)OAc]$ did not proceed with the formation of well-defined reaction products, in accordance with the early findings of Werner.[9c]

The hydrolysis rate constants (10^4k, sec^{-1}) at diverse temperatures (given in parentheses as °C) are as follows, except for those in Tables III and V: *trans*-$Cr(ox)_2(OAc)(OH_2)^{2-}$ at pH 3, 2.15 (16.0), 2.76 (18.5), 9.85 (30.5); *trans*-$Cr(ox)_2(OAc)(OH)^{3-}$ at pH 11, 160 (14.0), 231 (21.0); *trans*-$Cr(ox)_2(py)_2{}^{-}$, 0.98 (35.6), 13.8 (56.0).

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[21] H. T. S. Britton, "Hydrogen Ions," Chapman and Hall, London, 1965, p 361.

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Substitution Reactions of Oxalato Complex Ions. X. The Kinetics and Mechanism of Electron Transfer between the Chromium(II) Aquo Cation and Some Aquooxalatochromium(III) Complex Ions

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Electron transfer in the system $Cr(C_2O_4)(H_2O)_4{}^+$–$Cr_{aq}{}^{2+}$ occurs with no net chemical change but can be observed by use of chromium-51 labeling. The reaction is first order in each species and is independent of acid concentration up to 2.0 M $HClO_4$. At 25° and $I = 2.0\ M$, the values of k, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are 0.13 M^{-1} sec^{-1}, 11 kcal/mol, and −26 cal/deg mol, respectively. In contrast, the reaction between *cis*-$Cr(C_2O_4)_2(H_2O)_2{}^-$ and $Cr_{aq}{}^{2+}$ is first order in acid concentration as well as in each of the other two reactants. Electron transfer is accompanied by transfer of a single oxalate ligand so that in effect catalyzed aquation of the Cr(III) complex occurs. At 25°, $I = 2.0\ M$, and $[H^+] = 1.0\ M$, the values of k, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ are 0.04 M^{-2} sec^{-1}, 12 kcal/mol, and −24 cal/deg mol, respectively. Mechanisms involving an intermediate with oxalate doubly bridged between the two chromium ions provide a satisfactory explanation of the observations.

Introduction

The aqueous solution chemistry of the chromium(III) oxalato complex ions of the type $[Cr(C_2O_4)_n(H_2O)_{6-2n}]^{3-2n}$ has been extensively investigated, with much of the recent attention focused on the kinetics of anation,[1-3] aquation,[4-6] isomerization,[7-9] and oxygen exchange.[10,11] All of these reactions are relatively slow, attesting to the considerable resistance of either the water or the oxalate ligand to displacement from a chromium(III) ion coordination site. However, early oxygen-18 studies of the water-exchange reaction of the $Cr(H_2O)_6{}^{3+}$ ion demonstrated an appreciable accelerating influence by chromium(II) aquo cation. Thus, the reaction

$$Cr(H_2O)_6{}^{3+} + Cr_{aq}{}^{2+} + H_2{}^{18}O \rightleftharpoons Cr(H_2O)_5(H_2{}^{18}O)^{3+} + Cr_{aq}{}^{2+} + H_2O \qquad (1)$$

has a half-time of 2.1 hr at 27° in 0.33 M $HClO_4$ and with chromium(III) and chromium(II) concentrations of 1.05 and 0.16 M, respectively, while in the absence of chromium(II) but with other conditions nearly identical a 35-hr half-time is observed.[12] Furthermore, the second-order rate constant for reaction 1, deduced on the assumption of first-order catalysis by $Cr_{aq}{}^{2+}$, is 4.7×10^{-4} M^{-1} sec^{-1}. This is almost identical with the rate constant for electron transfer according to the reaction

$$^{51}Cr_{aq}{}^{3+} + Cr_{aq}{}^{2+} \rightleftharpoons Cr_{aq}{}^{3+} + {}^{51}Cr_{aq}{}^{2+} \qquad (2)$$

for which the value can be calculated to be 4.5×10^{-4} M^{-1} sec^{-1} under similar conditions on the basis of recorded data.[13] This comparison indicates that chromium(II)-catalyzed water exchange as symbolized by eq 1 probably occurs by a ligand–bridge electron-transfer mechanism of the type now so familiar for many inor-

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