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Kinetics of Dissociation of the Chromium(II) Acetate Dimer

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The complex tetra-μ-acetato-dichromium(II) reacts in acetate buffer media with ethylenediaminetetraacetic acid and other polydentate ligands to form monomeric chromium(II) complexes and with various oxidants to form chromium(III). Ligand replacement reactions and oxidations by $Co(NH_3)_5Cl^{2+}$ and $Co(C_2O_4)_3^{3-}$ conform to the rate law $-d[Cr_2(OAc)_4]/dt = k_D[Cr_2(OAc)_4]$ all with the same rate constant and activation parameters. Other slower oxidations conform to the rate law $-2d[Cr_2(OAc)_4]/dt = k_A[Cr_2(OAc)_4]^{1/2}[\text{oxidant}]$ where $k_A = k_M K_D^{1/2}$; K_D is interpreted as the dissociation constant of the equilibrium $Cr_2(OAc)_4 \rightleftharpoons 2Cr(OAc)_2$ and k_M varies with the nature of the oxidant. At 25° and ionic strength 1.0 *M* ($NaClO_4$) we find $k_D = 505 \pm 50$ sec^{-1}, $\Delta H_D^{\ddagger} = 14.3$ kcal mol^{-1} and $\Delta S_D^{\ddagger} \approx 3$ cal K^{-1} mol^{-1}; for $Co(edta)^-$, $k_A = 2.9 \times 10^2$ $M^{-1/2}$ sec^{-1}, $\Delta H_A^{\ddagger} = 9.6$ kcal mol^{-1}, and $\Delta S_A^{\ddagger} = -15$ cal K^{-1} mol^{-1}; for $Co(NH_3)_5OH^{2+}$ at 5°, $k_A = 1.7 \times 10^4$ $M^{-1/2}$ sec^{-1}. The rate constant k_D is ascribed to a unimolecular dissociation of the binuclear Cr^{II} complex and its magnitude is rationalized in terms of a simple crystal field model.

It is well known[1] that the aquochromium(II) ion is exceptionally labile toward substitution and solvent exchange, in comparison with neighboring ions of the same valency in the first transition series. This behavior is apparently related to that of copper(II) and has been rationalized in terms of a Jahn–Teller distortion in the structure of the $Cr(H_2O)_6^{2+}$ ion.[1] It therefore appeared of particular interest when a chance observation[2] led to the discovery that the well-known binuclear acetato complex of chromium(II) could undergo ligand substitution reactions (eq 2) at rates within the range measurable by the stopped-flow method. Prior to this work, the only mechanistic studies involving the chromous acetate dimer had been concerned with the kinetics of electron transfer:[6,7] these demonstrated the existence of a reversible equilibrium between binuclear and mononuclear acetatochromium(II) complexes. Extension of the earlier work to a wider variety of oxidizing agents has now shown that both the electron-transfer and the ligand substitution data can be fitted into a common mechanistic scheme, with two characteristic types of kinetic behavior depending upon which of the two steps is rate determining.[8] In summary, we find that reactions with oxidants such as $Cr(NH_3)_5Cl^{2+}$, $Cr(NH_3)_5Br^{2+}$, $Co(NH_3)_5OH_2^{3+}$ and $Co(edta)^-$, corresponding to the general stoichiometric eq 1, obey the rate law 3a, each with characteristic rate and activation parameters, but reactions with the oxidants $Co(C_2O_4)_3^{3-}$ and $Co(NH_3)_5Cl^{2+}$ and with EDTA, corresponding to eq 1 or 2 as the case may be, obey rate law 3b, all with the same rate and activation parameters.[9] The single mechanism, eq 13 and 14 below,[10] will accommodate both sets of data. The rate of reaction, *R*, may be defined alternatively as $R = d[P]/dt$, where P stands for the product Cr^{III} or $Cr^{II}X$, or as $R = -2d[Cr_2(OAc)_4]/dt$ when there is net consumption of the chromium(II) dimer.

$$^{1}/_{2}Cr_2(OAc)_4 + X \rightarrow Cr^{III} \qquad (1)$$

$$^{1}/_{2}Cr_2(OAc)_4 + X \rightarrow Cr^{II}X \qquad (2)$$

$$R = -\frac{d[X]}{dt} = k_A[Cr_2(OAc)_4]^{1/2}[X] \qquad (3a)$$

$$R = -\frac{d[X]}{dt} = 2k_B[Cr_2(OAc)_4][X]^0 \qquad (3b)$$

Experimental Section

Chromium(II) perchlorate solutions were prepared by electrolytic reduction of hexaaquochromium(III) perchlorate (K & K Laboratories Inc.) at a mercury cathode and diluted with the requisite amount of sodium perchlorate. Chromium(II) concentration was determined by injecting aliquots, under nitrogen, into excess acidified iron(III) sulfate solution and back-titrating the iron(II) with permanganate. Free hydrogen ion was determined by pH titration with sodium bicarbonate, likewise under nitrogen.

All transfer operations were carried out in an atmosphere of nitrogen scrubbed free of oxygen by passage through 0.1 *M* chromium(II) solution. Solutions were stored in all-glass apparatus with PTFE stopcocks.

Sodium perchlorate and **sodium acetate** solutions were prepared by neutralizing sodium hydroxide solution (AnalaR grade, supplied in volumetric ampoules) with AnalaR perchloric and acetic acids.

Sodium tris(oxalato)cobaltate(III) was prepared by the method used by Bunton et al.[11] for the preparation of the potassium salt. The equivalent quantity of sodium oxalate was used in place of potassium oxalate and about twice as much ethanol was used at the precipitation stage, owing to the greater solubility of the sodium salt. Anal. Calcd for $Na_3Co(C_2O_4)_3 \cdot 3.5H_2O$: C, 15.8; H, 1.5. Found: C, 15.6; H, 1.2.

Aquopentaamminecobalt(III) Perchlorate. Carbonatopentaamminecobalt(III) nitrate, $Co(NH_3)_5CO_3 \cdot NO_3$, was prepared following Brauer[12] and warmed with a slight excess of perchloric acid. The product was recrystallized twice from water with the addition of a few drops of dilute perchloric acid.

Other reagents were of AnalaR grade where obtainable and taken from freshly opened bottles. Deionized water was used in all experiments.

Kinetic Measurements. The Aminco-Morrow stopped-flow apparatus was used, with the cell compartment modified for improved temperature control. In the standard form of this apparatus, the PTFE drive syringes are mounted in an aluminum block with passages for circulating liquid from an external thermostat but the mixing chamber is mounted on the back-plate and has no temperature control. In the modified form of the apparatus the mixing chamber is located at the center of a second fabricated aluminum cooling block, measuring 6 × 8 × 9 cm with a light passage of approximately 1 cm^2. The solutions are led from the drive syringes through PTFE tubes, ca. 2 mm external diameter, embedded in closely fitting channels within the cooling block, the length and internal diameter being such that the volume of solution held within the tubes at any time is greater than the amount passed through the cell compartment during a kinetic measurement. The two blocks are fed in parallel from a Grant LB4 thermostat bath using a peristaltic pump and wide-diameter (1 cm) Tygon or neoprene tubing. With a total flow rate of 3.5 l. min^{-1} the difference in temperature between the bath and the returning water did not exceed 0.2°. The temperature within the apparatus, monitored by means of a ferrous–constantan thermocouple placed in a small air space between the mixing chamber and the surrounding block, was found to be correct to within ±0.1° after equilibrating for 30 min. A temperature dependence study of the dehydration of H_2CO_3 gave results in satisfactory agreement with the literature[13] over the temperature range 4–25°.

The standard Aminco 10-mm path mixing chamber was used, but with Perspex windows in place of quartz.

The reactions reported here are rapid, some of them approaching the limits of possible measurement by this apparatus, and care was taken to exclude possible spurious effects. The dead time of the apparatus is approximately 4 msec, estimated by comparing the initial observed optical density in a $Cr_2(OAc)_4$ + EDTA reaction with that of a corresponding $Cr_2(OAc)_4$ solution in the absence of EDTA. The half-lives of reactions upon which our rate law is based (i.e., reactions

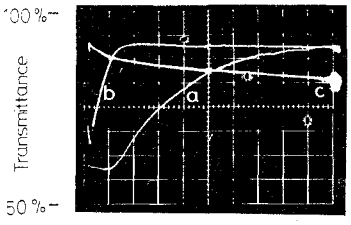


Figure 1. Oscilloscope traces for the reaction $Cr_2(OAc)_4$ + EDTA; $[Cr^{II}]_T = 8 \times 10^{-3}$ *M*, $[EDTA]_T = 12 \times 10^{-3}$ *M* initially; [NaOAc] = [HOAc] = 0.5 *M*; temperature 5°; ionic strength 1.0 *M* ($NaClO_4$); path length 10 mm; wavelength 440 nm: curve a, time scale 5 msec/horizontal division showing the initial rapid increase in transmittance; curve b, 50 msec/division; curve c, 5 sec/division, showing the subsequent slow decrease.

at or below 7.5°) are 2–3 times this value. For a reaction with a half-life equal to the dead time, observation begins only after 50% reaction. This does not invalidate the result, unless there are special effects arising from details of the mixing process. In practice all reactions with half-lives of 3 msec or less were found to be consistent with the rest, within experimental error (see, e.g., Figure 3), but they have been ignored when calculating the activation parameters.

As a further precaution against effects due to incomplete mixing, blank experiments were run with a colored nonreacting substance in one syringe and colorless solution in the other. With the colorless solution initially in the cell, no time-dependent effects were noted upon injection of the colored substance. These experiments were done with sodium acetate buffers of typical composition at temperatures down to 3°.

Treatment of Data. Output from the stopped-flow apparatus was displayed on a Tektronix R564B storage oscilloscope and photographed for permanent record. Data for analysis were taken from the photographs using the DMAC cartographic table. About 90 pairs of transmittance–time coordinates were obtained from each experiment and stored on punched paper tape. By a continuation of the same program the transmittance readings were converted to absorbance and then to log ($A - A_\infty$) when required for treatment according to eq 5 below, and they were finally traced automatically with a graph plotter.

Results

1. Reaction with EDTA. It was established in preliminary experiments that when chromium(II) acetate dimer is allowed to react with an equivalent or a slight excess of EDTA, decomposition to the sky blue monomer is complete. Comparison of equilibrium data for the Cr^{2+}–EDTA system[14] and for typical mononuclear acetato complexes[15,16] of divalent metals also indicates that complexation of Cr^{2+} by the chelate ligand is complete

$$Cr_2(OAc)_4 + 2H_2edta^{2-} \rightarrow 2Cr(edta)^{2-} + 4HOAc \qquad (4)$$

The results of a typical kinetic experiment are shown in Figure 1. When chromous acetate solution (prepared just before use by injecting chromous perchlorate into deaerated acetate buffer solution) is mixed with EDTA in an otherwise identical buffer solution, a rapid but measurable decrease in absorbance is seen (curves a, b). On a slower time scale there is a subsequent increase in absorbance (curve c). The reactions appear to be, first, the decomposition of the dimer to form the mononuclear $Cr(edta)^{2-}$ and, second, oxidation by water or H^+ ion to give $Cr^{III}(edta)^-$. (Compare the absorption spectra of the three species, Figure 2.) The assignment of the first reaction was confirmed by a study of the wavelength dependence. For a series of five experiments in the range λ 450–530 nm, the overall decrease in absorbance ($A_0 - A_\infty$) was greatest at 490 nm, corresponding to the maximum absorption of the dimer, while the specific rate of reaction remained the same within experimental error.

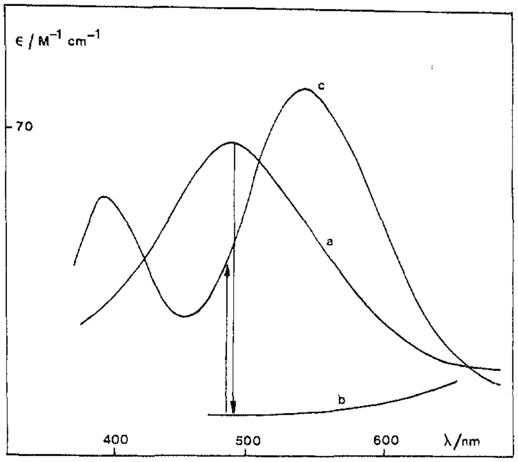


Figure 2. Visible absorption spectra: (a) chromium(II) in acetate buffer (the extinction coefficient is calculated per mole of $^1/_2Cr_2(OAc)_4$ for comparison with the mononuclear species); (b) the Cr^{II}-EDTA complex $Cr(edta)^{2-}$; (c) the Cr^{III}-EDTA complex $Cr(edta)^-$. The arrows correspond to the successive reactions shown in Figure 1.

The decrease in absorbance with time could be satisfactorily fitted to a pseudo-first-order rate law (eq 7), rate constants k_{obsd} being obtained from linear plots according to eq 6, where

$$A - A_\infty = (A_0 - A_\infty)e^{-k_{obsd}t} \qquad (5)$$

$$\log\left(\frac{A - A_\infty}{A_0 - A_\infty}\right) = -2.303k_{obsd}t \qquad (6)$$

A_0, A, and A_∞ denote the absorbances at the time of first observation, at time t, and at equilibrium. In view of the slow increase in A after the initial rapid decrease, A_∞ could not be read directly from the oscilloscope trace and the minimum absorbance was used instead. Plots according to eq 6 were satisfactorily linear for 2 or 3 half-lives but generally showed a downward curvature at longer time intervals. This is presumably a result of overestimating A_∞ but in view of the limited accuracy of data obtainable from the oscilloscope screen more detailed curve fitting was not considered worthwhile. The pseudo-first-order rate law 7 is confirmed by the lack of

$$-\frac{d}{dt}[Cr_2(OAc)_4] = k_{obsd}[Cr_2(OAc)_4] \qquad (7)$$

dependence of k_{obsd} on the initial chromium(II) concentration (Table I). Variations in EDTA concentration from 6.7 to 20 m*M*, in acetate concentration from 0.1 to 1.0 *M*, and in pH from 4.3 to 5.2 were all without effect on the specific rate (Table I) thus satisfying eq 3b. The temperature dependence is shown in Figure 3.

2. Reactions with Other Ligands. Experiments similar to the above were carried out using diethylenetriaminepentaacetic acid and *trans*-cyclohexane-1,2-diaminetetraacetic acid. Both were found to decompose the dimer to monomeric chromium(II) species under similar conditions and within experimental error the specific rates were the same as for the EDTA reaction, over the temperature range 5–15° (Figure 4).

Among other ligands studied, the following were found *not* to react appreciably with chromous acetate under the present conditions: nitrilotriacetic acid, ethylenediaminediacetic acid, *N*-methyliminodiacetic acid, citric acid, ethylenediamine, 2,2'-bipyridyl, glycolic acid, pyridine. These are listed in descending order of expected affinity for a given metal ion, at pH 4.9, as ascertained from published stability constants for Cu^{2+} and Co^{2+} complexes[16] and since nitrilotriacetic acid itself is notably less complexing than EDTA, no new feature is introduced by these negative results. The three ligands that do react with chromous acetate differ appreciably in their metal ion affinities, as shown by the following values of the logarithm of the equilibrium constant[16] $[CoL^{n-}]/[Co^{2+}][H_2L^{n-}]$, at pH 4.9 and 20°: EDTA,[9] 11.4; CYDTA,[9] 14.0; DTPA,[9] 14.8.

Table I. Reactions of Chromium(II) Acetate Dimer with EDTA and with Oxidizing Agents (X)[a]

$[Cr^{II}]_T$, mM	$[X]_T$, mM	$[OAc^-]$, M	k_B, sec^{-1}
	X = EDTA, T = 7.4°		
1.99	6.7	0.50	102
2.99	6.7	0.50	108
3.99	6.7	0.50	109
7.48	6.7	0.50	114
4.99	10.0	0.50	101
4.99	13.4	0.50	105
4.99	20.2	0.50	101
4.99	6.7	0.10	101
4.99	6.7	0.20	97
4.99	6.7	0.50	96
4.99	6.7	0.50	106
4.99	6.7	1.00	108
4.99	6.7	0.60	112[b]
4.99	6.7	0.40	103[c]
4.99	6.7	0.20	94[d]
4.99	6.7	0.20	111[e]
		Mean	104 ± 6
	X = Chloropentaamminecobalt(III), T = 10.5°		
4.04	10.0	0.50	129
5.38	10.0	0.50	134
6.73	10.0	0.50	130
8.04	10.0	0.50	130
2.69	7.5	0.50	121
2.69	10.0	0.50	128
2.69	15.0	0.50	130
		Mean	128 ± 4
	X = Tris(oxalato)cobaltate(III), T = 7.4°		
2.04	13.4	0.50	113
6.12	13.4	0.50	130
8.16	13.4	0.50	129
4.08	6.7	0.50	119
4.08	13.4	0.50	136
4.08	26.9	0.50	113
		Mean	123 ± 9

[a] Wavelength 490 nm; [HOAc] = $[OAc^-]$, except as indicated; ionic strength 1.0 M ($NaClO_4$); $[X]_T$ = total stoichiometric concentration of EDTA or oxidizing agent as the case may be. For temperature dependencies see Figure 3. $k_0 = k_{obsd}$ (cf. eq 3b). [b] [HOAc] = 0.10 M. [c] [HOAc] = 0.20 M. [d] [HOAc] = 0.40 M. [e] [HOAc] = 0.60 M.

The differences are enough to suggest that the similarity in rate constants k_B is mechanistically significant.

3. Chloropentaamminecobalt(III) Ion. It has been shown that this reaction is of the inner-sphere type with transfer of chloride ion from the cobalt to the chromium.[6] In the present study, reactions were followed at wavelength 490 nm, where $Cr_2(OAc)_4$ and $Co(NH_3)_5Cl^{2+}$ both contribute to the net decrease in absorbance with time. Satisfactorily linear first-order plots were obtained even though cobalt(III) was not in large excess over chromium(II), and variation of initial chromium(II) and cobalt(III) concentrations, through factors of 3 and 2 respectively, had no significant effect on the specific rate (Table I). Thus the rate law is first order in chromium(II) and zero-order in oxidizing agent (eq 3b, X = $Co^{III}(NH_3)_5Cl^{2+}$). At all temperatures studied, the observed rate constant is the same, within experimental error, as for the reactions with chelating ligands (Figure 3).

4. Tris(oxalato)cobaltate(III) Ion. Reactions with cobalt(III) in excess over chromium(II) gave the analogous rate law, first order in chromium(II) and zero order in cobalt(III) (Table I), and specific rates at different temperatures again agreed well with those for the ligand replacement reactions (Figure 3).

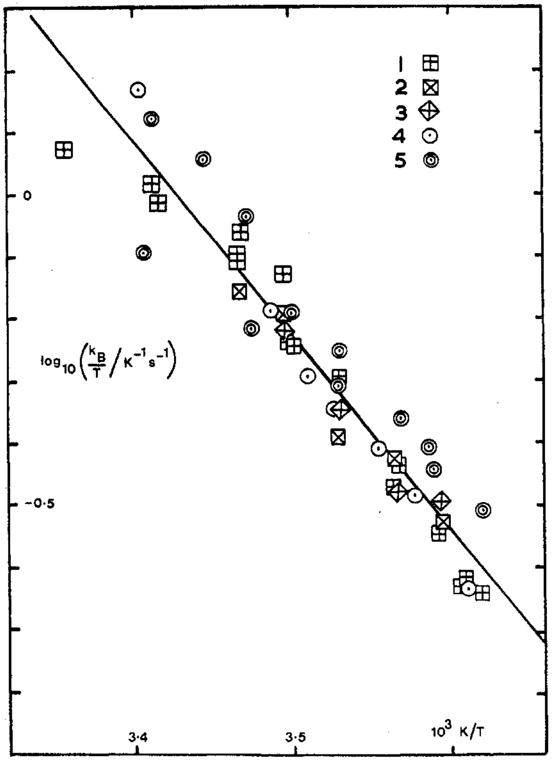


Figure 3. Temperature dependence of k_B (cf. eq 3b). Reagents: (1) EDTA, (2) DTPA, (3) CYDTA, (4) $Co(NH_3)_5Cl^{2+}$, (5) $Co(C_2O_4)_3^{3-}$. The straight line is a least-squares fit, excluding data for $T \geqslant 15°$.

Table II. Reactions of Chromous Acetate Dimer with Ethylenediaminetetraacetatocobalt(III) Ion[a]

T, °C	$[Cr^{II}]_0$, mM	$[Co^{III}]_0$, mM	k_{obsd}, sec^{-1}	k_A, $M^{-1/2}$ sec^{-1}
5.1	2.04	0.224	2.50	82
5.1	3.06	0.224	3.59	96
5.1	4.08	0.224	4.4	96
5.1	5.1	0.224	4.7	93
5.1	6.12	0.224	6.24	113
5.1	7.14	0.224	6.38	106
5.1	8.16	0.224	5.69	89
5.1	8.16	0.672	6.99	109
5.1	8.16	0.896	5.25	82
			Mean	96 ± 10
5.1	5.1	2.24	4.28[b]	85
8.3	5.1	2.24	5.19[b]	103
11.0	5.1	2.24	6.09[b]	122
14.5	5.1	2.24	6.78[b]	134
17.2	5.1	2.24	8.62[b]	171
20.4	5.1	2.24	10.22[b]	202
21.4	5.1	2.24	13.0[b]	257

[a] Wavelength 490 nm; [HOAc] = [NaOAc] = 0.50 M; ionic strength 1.0 M ($NaClO_4$) except as indicated. $k_A = 2^{1/2}k_{obsd}[Cr^{II}]_0^{-1/2}$ (cf. eq 3a). [b] Rate constant based on the first 2 half-lives of reaction.

5. Ethylenediaminetetraacetatocobalt(III) Ion, CoY^-. Reactions were carried out with chromium(II) in 10–40-fold excess and followed by the decrease in absorbance at 490 nm, where both reagents absorb strongly. In this case pseudo-first-order plots were obtained: specific rates k_{obsd} showed no significant variation with the initial cobalt(III) concentration but a marked chromium(II) dependence was observed (Table II) consistent with a half-order rate expression, eq 3a ($X^- = CoY^-$). The temperature dependence is shown in Figure 4; rate and activation parameters are listed in Table III.

6. Aquopentaamminecobalt(III) Ion ($RoOH_2^{3+}$).[9] With chromium(II) in three- to eightfold excess over cobalt(III), rates conformed closely to eq 3a ([X] = $[Co^{III}]_T$). A number of experiments were also performed at different reagent ratios, varying up to cobalt(III) in fourfold excess over chromium(II); rate constants obtained from the initial slopes of the log (A

Table III. Summary of Rate and Activation Parameters for the Reactions $Cr_2(OAc)_4$ + X in Acetate Buffer[a]

X	$k_0, M^{-1}\ sec^{-1}$	Ref	$k_A = k_M K_D^{1/2}$, $M^{-1/2}\ sec^{-1}$	$\Delta H_A^‡$, kcal mol^{-1}	$\Delta S_A^‡$, cal K^{-1} mol^{-1}	$k_M, M^{-1}\ sec^{-1}$	$k_B = k_D$ sec^{-1}	$\Delta H_D^‡$, kcal mol^{-1}	$\Delta S_D^‡$, cal K^{-1} mol^{-1}	Ref
EDTA	4×10^6 [h]	33					5.1×10^2	14.3	3	*i*
DTPA										
CYDTA										
$Co(C_2O_4)_3^{3-}$	4.0×10^6 [b]	30								
$Co(NH_3)_5Cl^{2+}$	2.6×10^6	31								
$Co(edta)^-$	1.6×10^5 [b]	30	2.9×10^2	9.6	−15	1.5×10^4 [g]				*i*
$RoOH^{2+}$	1.0×10^6 [d]	18	1.7×10^4 [d]							*i*
$RoOH^{2+}$ + $RoOH_2^{3+}$ (equilibrium mixture)	1.0×10^5 [e]	18	4.8×10^3 [f]	18.4[f]	+20[f]	2.4×10^5 [g]				*i*
$Cr(NH_3)_5Br^{2+}$	3.2×10^{-1}	32				5.0[c]				6, 7
$Cr(NH_3)_5Cl^{2+}$	3.0×10^{-2}	7				0.60				6, 7

[a] [HOAc] = [OAc^-] = 0.5 *M*; ionic strength 1.0 *M* ($NaClO_4$); temperature 25°. Rate constants k_0 are for the reactions Cr^{2+} + X; k_A, k_B, k_D, and k_M are defined by eq 3a, 3b, 13, and 14. [b] 20°. [c] 30°. [d] 5°. [e] Rate constant k_0' for the expression $-d \ln [Co^{III}]/dt = k_0'[Cr^{2+}]$, where $[Co^{III}]_T = [RoOH_2^{3+}] + [RoOH_2^{2+}]$, when $[H^+] = 2.5 \times 10^{-5}$ *M*. [f] Rate parameters k_A' etc. for the expression $-d \ln [Co^{III}]/dt = k_A'[Cr_2(OAc)_4]^{1/2}$, where $[Co^{III}]_T = [RoOH_2^{3+}] + [RoOH^{2+}]$. [g] Calculated from k_A and k_A', using K_D from ref 7. [h] Rate constant k_0 for the expression $-d \ln [Cr^{2+}]/dt = k_0[EDTA]_T$ from the rate law $-d \ln [Cr^{2+}]/dt = k[Hedta^{3-}]$ where $k = 8 \times 10^7\ M^{-1}\ sec^{-1}$. [i] This work.

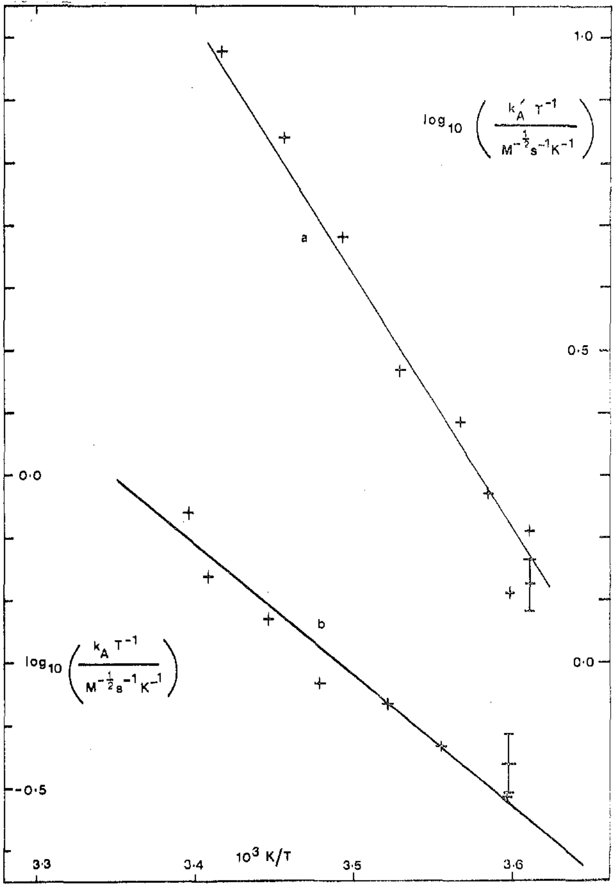


Figure 4. Temperature dependencies: (a) of k_A' (eq 9; cf. Table IV), right-hand vertical scale; (b) of k_A for the reaction CoY^- + $Cr_2(OAc)_4$, (cf. Table II), left-hand vertical scale.

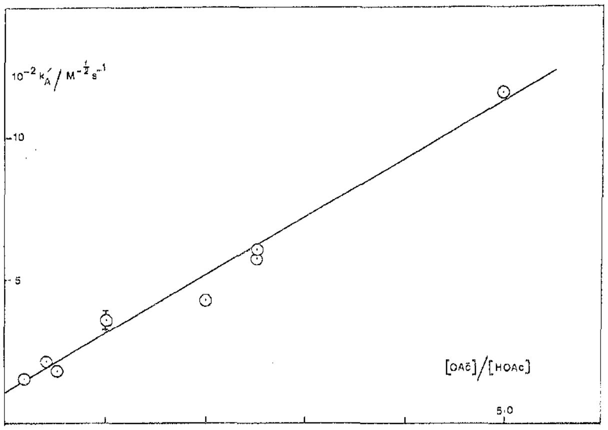


Figure 5. Hydrogen ion dependence of the $Cr_2(OAc)_4$ + $Co(NH_3)_5OH_2^{3+}$ reaction (cf. Table IV).

− A_∞) vs. time plots (see Table IV and footnotes) showed somewhat greater scatter than the first group. The temperature dependence is shown in Figure 4. Rates also varied with hydrogen ion activity {H} as controlled by the ratio of HOAc to OAc^- ion but showed no marked dependence on either reagent when these were varied separately. A plot of k_{obsd} vs. [OAc^-]/[HOAc] (Figure 5) suggests the two-term rate law

$$R = (k_A{}^0[RoOH_2{}^{3+}] + k_A{}^1[RoOH^{2+}])[Cr_2(OAc)_4]^{1/2} \quad (8)$$

$$= k_A'[Co^{III}]_T[Cr_2(OAc)_4]^{1/2} \quad (9)$$

where

$$k_A' = \frac{k_A{}^0 + k_A{}^1 K_a/\{H\}}{1 + K_a/\{H\}} \quad (10)$$

and K_a is the acid dissociation constant of $RoOH_2^{3+}$. Since the second term in the denominator is always small, this gives

$$k_A' \cong k_A{}^0 + (k_A{}^1 - k_A{}^0)K_a\{H\}^{-1}$$
$$= k_A{}^0 + (k_A{}^1 - k_A{}^0)\frac{K_a[OAc^-]}{K_a{}^*[HOAc]} \quad (11)$$

where $K_a{}^*$ is the acid dissociation constant of acetic acid. Taking $K_a = 3.0 \times 10^{-7}$ *M*[17] and $K_a{}^* = 2.5 \times 10^{-5}$ *M*[19] gives $k_A{}^0 = (1.1 \pm 0.4) \times 10^2\ M^{-1/2}\ sec^{-1}$ and $k_A{}^1 = 1.7 \times 10^4\ M^{-1/2}\ sec^{-1}$ at 5° and ionic strength 1.0 *M* ($NaClO_4$). The temperature dependence of k_A' is shown in Figure 4. The corresponding activation parameters are $\Delta H_A'^‡ = 18.4$ kcal mol^{-1} and $\Delta S_A'^‡ = 20$ cal K^{-1} mol^{-1}. Separate activation parameters for the $k_A{}^1$ and $k_A{}^0$ pathways cannot be calculated from these data, but the relatively large positive $\Delta H_A^‡$ presumably reflects the endothermic dissociation of $RoOH_2^{3+}$ (ΔH_a = 9.5 kcal mol^{-1}, ΔS_a = 5.0 cal K^{-1} mol^{-1} [17]).

7. **Reaction with Hydrogen Ion.** When solutions of the chromous acetate dimer in acetate buffer were mixed with excess perchloric acid in the stopped-flow apparatus, the red color was discharged within the time of mixing and no kinetic effects could be detected.

Table IV. Reactions of Chromous Acetate Dimer with Aquopentaamminecobalt(III) Ion[a]

T, °C	$[\mathrm{Cr^{II}}]_0$, mM	$[\mathrm{Co^{III}}]_0$, mM	k_{obsd}, sec^{-1}	$10^{-2}k_A'$, $M^{-1/2}$ sec^{-1}
4.0	3.45	1.0	14.2	3.4
4.0	4.6	1.0	16.4	3.4
4.0	5.7	1.0	21.9	4.1
4.0	6.9	1.0	21.1	3.5
4.0	8.05	1.0	25.5	4.0
				Mean 3.7 ± 0.3
5.0	6.9	1.0	9.5[b]	1.6
5.0	6.9	1.0	12.6[c]	2.2
5.0	6.9	1.0	11.0[d]	1.9
5.0	6.9	1.0	21.1	3.6
5.0	6.9	1.0	24.7[e]	4.3
5.0	6.9	1.0	35.9[f]	6.2
5.0	6.9	1.0	34.6[f]	6.0
5.0	6.9	1.0	67.9[g]	11.7
7.4	2.04	6.71	73[h]	6.9[i]
7.4	4.08	6.71	88[h]	11.9[i]
7.4	5.1	6.71	49[h]	7.4[i]
7.4	6.12	6.71	30[h]	5.0[i]
7.4	7.12	6.71	24[h]	4.0
7.4	5.1	20.0	88[h]	4.4[i]
7.4	5.1	12.0	66[h]	5.7[i]
7.4	5.1	3.0	45[h]	8.9
				Mean 6.8 ± 2.5
4.0	4.08	6.71	34[h]	4.5[i]
6.0	4.08	6.71	39[h]	5.2[i]
10.4	4.08	6.71	63[h]	8.3[i]
13.0	4.08	6.71	103[h]	13.7[i]
16.7	4.08	6.71	151[h]	20.0[i]
19.9	4.08	6.71	210[h]	

[a] Wavelength 490 nm; [HOAc] = [OAc$^-$] = 0.5 M except as indicated; ionic strength 1.0 M (NaClO$_4$). $k_A' = 2^{1/2}k_{\mathrm{obsd}}[\mathrm{Cr^{II}}]_T^{-1/2}$ (cf. eq 9), except where shown. [b] [OAc$^-$] = 0.1 M. [c] [OAc$^-$] = 0.2 M. [d] [HOAc] = 1.0 M. [e] [OAc$^-$] = 1.0 M. [f] [HOAc] = 0.2 M. [g] [HOAc] = 0.1 M. [h] Calculated from the initial part of the absorbance time curve: $k_{\mathrm{obsd}} = -(A_0 - A_\infty)^{-1}(\mathrm{d}A/\mathrm{d}t)_{t=0}$. [i] $10^{-2}k_A' = 10^{-2}2^{1/2}k_{\mathrm{obsd}}[\mathrm{Cr^{II}}]_0^{1/2}[\mathrm{Co^{III}}]^{-1}$.

8. Reactions under Pseudo-Zero-Order Conditions. For systems obeying eq 3b it is expected that if chromium(II) is initially in excess over the reagent X, the observed kinetics should tend to pseudo zero order (eq 12, $k^0 = 2k_B[\mathrm{Cr_2(OAc)_4}]$).

$$\frac{-\mathrm{d}[\mathrm{X}]}{\mathrm{d}t} = k^0 \qquad (12)$$

The solubility of chromous acetate is small however ($[\mathrm{Cr^{II}}]_T \geq 7$ mM at 5°) so that in order to test this prediction it is necessary to have an oxidizing agent which absorbs intensely enough to show a significant change in absorbance at still lower concentrations. The tris(oxalato)cobaltate(III) ion was found suitable, having $\epsilon_{\max} = 220\ M^{-1}\ \mathrm{cm}^{-1}$ at wavelength 440 nm. The result of a typical experiment with chromium in twofold excess over cobalt is shown in Figure 6. The transition from the initial rapid decrease in absorbance to the final value is appreciably more abrupt than in the case of pure pseudo-first-order kinetics. From the initial rate of change we estimate $k_B = 60$ sec^{-1} at 4.4°, in satisfactory agreement with the value $k_B = 70$ sec^{-1} interpolated from Figure 3. Similar results were obtained with iodine as oxidizing agent in the presence of excess iodide ion.

9. Other Oxidants. Preliminary experiments were carried out with a number of other oxidants under conditions similar to those above, i.e., [OAc$^-$] = [HOAc] = 0.5 M, $[\mathrm{Cr^{II}}]_T$ = 2–7 mM, [oxidant] = 1–2 mM initially except where otherwise stated, temperature 4–5°, and ionic strength 1.0 M (NaClO$_4$). The following were found to react "slowly" (i.e., the specific rate of disappearance of the oxidant was within the stopped-flow time scale but considerably lower than 70 sec^{-1} at 5°): $\mathrm{Hg^{2+}}$, $\mathrm{Fe_3O(OAc)_6^+}$, $\mathrm{ReCl_6^{2-}}$, $\mathrm{Co(en)_2CO_3^+}$, $\mathrm{Co(NO_2)_6^{3-}}$, $\mathrm{CrO_4^{2-}}$. The following reacted "rapidly" with specific rates ~70 sec^{-1} at 5°: $\mathrm{Fe(edta)^-}$, $\mathrm{IO_3^-}$, $\mathrm{MnO_4^-}$. An experiment with $\mathrm{PtCl_6^{2-}}$ in low concentration gave a pseudo-zero-order trace.

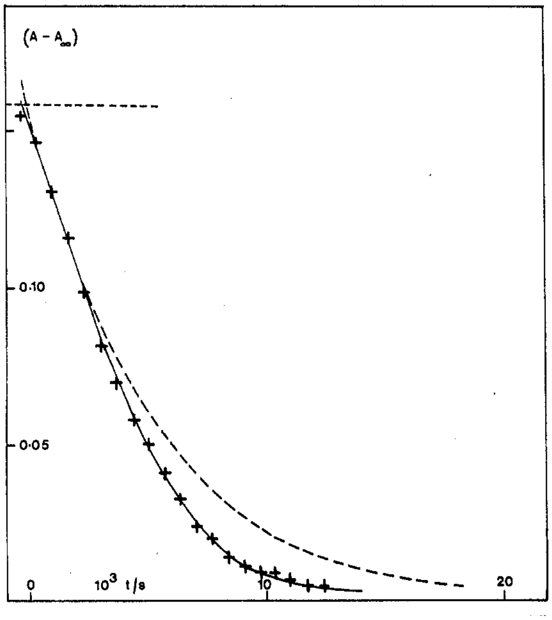


Figure 6. Absorbance–time curve showing partial zero-order behavior for the reaction $\mathrm{Cr_2(OAc)_4} + \mathrm{Co(C_2O_4)_3^{3-}}$, with chromium(II) in excess; $[\mathrm{Cr^{II}}]_T = 8 \times 10^{-3}\ M$, $[\mathrm{Co^{III}}] = 4 \times 10^{-3}\ M$ initially; [NaOAc] = [HOAc] = 0.5 M; temperature 5°; ionic strength 1.0 M (NaClO$_4$); path length 10 mm; wavelength 440 nm. The broken curve is an exponential curve calculated for the same initial and final absorbance and the same initial slope as the experimental curve.

Discussion

Rate constants and activation parameters for all of the reactions studied in this and the previous paper[7] are summarized in Table III. With the exception of the reaction with perchloric acid (paragraph 7 above), all of the observations are consistent with the following mechanism, where X stands for oxidant or chelating agent as the case may be and P for the reaction products[10]

$$\mathrm{Cr_2(OAc)_4} \underset{k_{-\mathrm{D}}}{\overset{k_\mathrm{D}}{\rightleftharpoons}} \mathrm{2Cr(OAc)_2} \tag{13}$$

$$\mathrm{Cr(OAc)_2} + \mathrm{X} \xrightarrow{k_\mathrm{M}} \mathrm{P} \tag{14}$$

A complete kinetic analysis of this mechanism is complicated but for our purpose it is sufficient to consider limiting cases as follows.

(a) If $k_{-\mathrm{D}}[\mathrm{Cr(OAc)_2}] >> k_\mathrm{M}[\mathrm{X}]$, the chromium(II) monomer is in equilibrium with the dimer and the general rate expression is

$$R = {}^1/_4 k_\mathrm{M} K_\mathrm{D}[-1 + (1 + 8[\mathrm{Cr^{II}}]_\mathrm{T}/K_\mathrm{D})^{1/2}][\mathrm{X}] \tag{15}$$

where R has been defined above, $K_\mathrm{D} = k_\mathrm{D}/k_{-\mathrm{D}}$, and $[\mathrm{Cr^{II}}]_\mathrm{T} = [\mathrm{Cr(OAc)_2}] + 2[\mathrm{Cr_2(OAc)_4}]$. This in turn assumes limiting forms at high and low total chromium(II) concentrations, namely

$$\begin{aligned} R &= k_\mathrm{M} K_\mathrm{D}{}^{1/2}[\mathrm{Cr_2(OAc)_4}]^{1/2}[\mathrm{X}] \\ &= k_\mathrm{M}(K_\mathrm{D}/2)^{1/2}[\mathrm{Cr^{II}}]_\mathrm{T}{}^{1/2}[\mathrm{X}] \end{aligned} \tag{16}$$

when $[\mathrm{Cr^{II}}]_\mathrm{T} >> K_\mathrm{D}/8$

$$R = k_\mathrm{M}[\mathrm{Cr(OAc)_2}][\mathrm{X}] = k_\mathrm{M}[\mathrm{Cr^{II}}]_\mathrm{T}[\mathrm{X}] \tag{17}$$

when $[\mathrm{Cr^{II}}] << K_\mathrm{D}/8$. Our empirical rate law 3a corresponds to the high-[chromium(II)] limit, with $k_\mathrm{A} = k_\mathrm{M}K_\mathrm{D}{}^{1/2}$. There is no doubt that at the acetate buffer concentrations used in these experiments and at the chromium(II) concentrations prevailing during the first 1 or 2 half-lives of each reaction the condition is fulfilled (typically, $[\mathrm{Cr^{II}}]_\mathrm{T} = 10^{-2}$ *M* compared with $K_\mathrm{D}/8 \geq 6 \times 10^{-5}$ *M*). In the more extensive studies referred to above[7] we have verified eq 15 and 17 as well.

(b) If $k_{-\mathrm{D}}[\mathrm{Cr(OAc)_2}] << k_\mathrm{M}[\mathrm{X}]$, the concentration of monomer is much less than the equilibrium value and we have

$$R = 2k_\mathrm{D}[\mathrm{Cr_2(OAc)_4}] \tag{18}$$

irrespective of the total chromium(II) concentration. This corresponds to the empirical rate law 3b with $k_\mathrm{B} = k_\mathrm{D}$.

It is evident then that under the conditions of our experiments the chelate ligands, the oxidants $\mathrm{Co(NH_3)_5Cl^{2+}}$ and $\mathrm{Co(C_2O_4)_3{}^{3-}}$, and possibly also $\mathrm{I_2}$ react with $\mathrm{Cr(OAc)_2}$ sufficiently rapidly to show rate law 18; but the milder oxidants $\mathrm{Cr(NH_3)_5Cl^{2+}}$,[7] $\mathrm{Cr(NH_3)_5Br^{2+}}$,[7] $\mathrm{Co(NH_3)_5OH_2{}^{3+}}$, and $\mathrm{Co(edta)^-}$ do not. Our experiments have not yielded values of k_M for all of these reagents, but in most cases we do have specific rates (k_O) for reactions of the same reagent with hexaaquochromium(II) ion. Of the six complexes listed in Table III the two which conform to eq 18 are those with the highest reactivity toward $\mathrm{Cr^{2+}}$. It is reasonable to suppose that they will also show the highest reactivity toward $\mathrm{Cr(OAc)_2}$ and this constitutes additional support for the proposed mechanism. Moreover, if we take $k_{-\mathrm{D}}[\mathrm{Cr(OAc)_2}] = k_\mathrm{D}K_\mathrm{D}{}^{-1/2}[\mathrm{Cr^{II}}]_\mathrm{T}{}^{1/2}$ with $K_\mathrm{D} = 5 \times 10^{-4}$ *M* and $k_\mathrm{D} = 500\ \mathrm{sec^{-1}}$ and take typical concentrations $[\mathrm{Cr^{II}}]_\mathrm{T} = 8$ m*M* and $[\mathrm{X}] = 10$ m*M*, then the critical value of k_M, above which we expect rate law 18, is of the order of $10^5\ M^{-1}\ \mathrm{sec^{-1}}$. Comparing the values of k_O for reagents in the two kinetic classes (Table III) this appears to be of reasonable magnitude.

It should be noted that the observed kinetic behavior is not solely a function of the nature of the reagent X; it involves also the concentration of X and may therefore change in the course of an experiment. For example if $\mathrm{Cr_2(OAc)_4}$ is initially in excess over X and if the kinetics initially conform to eq 18, then, as the reaction proceeds, the concentration of X must eventually sink below the limit corresponding to $k_{-\mathrm{D}}[\mathrm{Cr(OAc)_2}] \simeq k_\mathrm{M}[\mathrm{X}]$ and the rate law changes from zero order to first order in X (eq 15, 16, or 17, depending on the chromium(II) concentration). We have not been able to extend our measurements to lower X concentrations sufficiently to verify this in detail but we have observed some qualitative manifestations, as for example the terminal curvature in the plot of Figure 6.

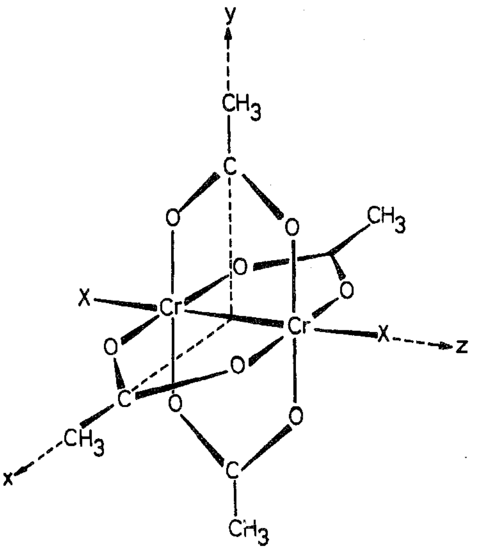


Figure 7. Molecular structure of chromium(II) acetate. In the solid the groups X may be $\mathrm{H_2O}$ or vacant sites; in aqueous solution they are presumed to be labile $\mathrm{H_2O}$ molecules, easily displaced by other nucleophiles.

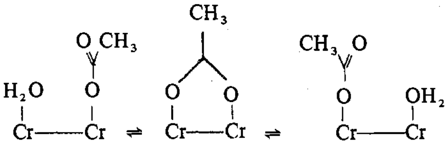
We turn now to consider the detailed mechanism of reaction 13. The structure of the chromium(II) acetate dimer has been established with certainty as far as the solid state is concerned. X-Ray diffraction studies[20] of the hydrated compound $\mathrm{Cr_2(OAc)_4{\cdot}2H_2O}$ have shown a binuclear structure (Figure 7) with short metal–metal bond distance, 2.36 Å. It seems certain that a similar structure persists in solution since the visible spectra observed in various solvents[6,21-23] resemble that of the solid[21] and the kinetic studies described above confirm the dimeric formula for the predominant species in solution.

A rate-determining attack by ligand or oxidant X is clearly ruled out by the rate law. An alternative which might be considered in the case of the chelate ligands, and perhaps also in the case of the $\mathrm{Co(C_2O_4)_3{}^{3-}}$ ion, is prior formation of an association complex (eq 19), for example, by attachment of X at one of the axial positions of the dimer molecule

$$\mathrm{Cr_2(OAc)_4 + H_2edta^{2-} \rightleftharpoons Cr_2(OAc)_4(H_2edta)^{2-} \rightarrow products} \tag{19}$$

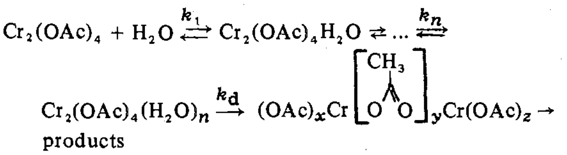
To fulfill the rate law with zero dependence on both EDTA and acetate ion, it would however be necessary to assume that the preequilibrium is completely displaced to the right but that under the same conditions in the absence of EDTA the axial position is not occupied by acetate ions (otherwise an inverse acetate ion dependence would appear). Since acetate ion is more basic than the free carboxyl groups in $\mathrm{H_2edta^{2-}}$,[16] these two conditions are unlikely to be fulfilled simultaneously. A unimolecular decomposition of the dimer is thus indicated. For the complete breakup of a complex like $\mathrm{Cr_2(OAc)_4}$ a network of reaction paths can be envisaged, but the rate law gives the important information that no acetate ion is completely separated from the molecule prior to the rate-determining step. It is also clear that fission of the metal–metal bond must be one of the later steps in the sequence since otherwise there would be simultaneous cleavage of two or more bonds. These considerations do not define the sequence of events absolutely, but they impose useful limitations.

It is possible that metal–oxygen bonds are repeatedly broken and re-formed during the lifetime of the metal–metal bond; so that in effect the acetate groups are "rocking" about their equilibrium positions (eq 20). Also it is reasonable to suppose



(20)

that the metal–metal bond would be progressively weakened by the opening of the rings, but once a ring is opened it seems unlikely that the breakage of the second metal–oxygen bond to release the acetate ion completely would weaken the metal–metal bond much further. Thus it seems likely that the rate-determining step is either ring opening by fission of a metal–oxygen bond or else the breakage of the metal–metal bond while one or more rings stand open. The sequence would then be as in (21), where $Cr_2(OAc)_4(H_2O)_n$ denotes a dimer



$$Cr_2(OAc)_4 + H_2O \underset{}{\overset{k_1}{\rightleftarrows}} Cr_2(OAc)_4H_2O \rightleftarrows \ldots \overset{k_n}{\rightleftarrows}$$
$$Cr_2(OAc)_4(H_2O)_n \xrightarrow{k_d} (OAc)_xCr\left[\begin{matrix}CH_3\\ O\;\;O\end{matrix}\right]_yCr(OAc)_z \rightarrow \text{products} \qquad (21)$$

molecule with n rings opened and $x + y + z = 4$. Nothing is known of the inherent strength of the Cr–Cr bond by which it would be possible to predict the activation energy of the k_d step; at the same time there is no report of any chromium(II) compound stable in polar solvents containing a metal–metal bond which is not reinforced with a cage of bridging ligands. For this reason we prefer at this stage to postulate one of the k_n steps, and most probably the first, as rate-determining. The rapid reaction with hydrogen ion is consistent with this, since acid catalysis has been demonstrated in other equations of metal acetate complexes.[24]

The value $k_D = 6 \times 10^2$ sec⁻¹ (at 25°) is in marked contrast with the specific rate $k \leq 10^9$ sec⁻¹ for water exchange on the uncomplexed chromium(II) ion, as determined by Merideth and Connick.[1a] Rates of substitution in complexes with predominantly ionic metal–ligand bonds are mainly determined by three factors: the charge, the ionic radius, and the additional stabilization due to partially filled d orbitals.[25] Excessively fast rates for $Cr^{2+}(aq)$ and $Cu^{2+}(aq)$ are attributed to a special mechanism involving rapid interchange of the long and short axes of the tetragonally distorted solvent shell.[1] In the chromous acetate dimer, tetragonal distortion is still present but interchange is prevented; hence, if our proposed mechanism is correct, the observed rate constant may be considered characteristic of replacement at the equatorial positions of the chromium(II) ion when the geometry is fixed. Moreover it is possible to offer a semiqualitative rationalization of the magnitude of k_D, in terms of an electron-pairing scheme in the dimer molecule. Labeling the axes x, y, and z as shown in Figure 7, the dimer may be supposed to have been generated by bringing together two monomeric units along the z axis. At infinite separation, the chromium(II) ions are high-spin $t_{2g}^3e_g^1$. The e_g orbital can be orientated along the z axis as a d_{z^2} orbital, and as the atoms approach, it will form bonding and antibonding σ-type molecular orbitals. The d_{xy}, d_{yz}, and d_{zx} orbitals also interact, but less strongly,[26] and in the complete dimer molecule, although all eight d electrons are coupled as evidenced by the diamagnetism,[27] the main contribution to bonding comes from one pair only. Thus the individual chromium atoms in the dimer can be compared to two atoms of t_{2g}^3 configurations, weakly coupled. The energies of the six t_{2g} electrons will be sensitive to distortions in the ligand environment in much the same way as the t_{2g} electrons of an isolated ion. Hence it can be expected that rates of substitution in the dimer will be similar to those of a monomeric complex of a d^3 ion of the same charge and radius as chromium(II), namely, vanadium(II). This appears to be the case since our values of k_D and $\Delta H_D^\ddagger$ are indeed comparable with the corresponding parameters for water exchange in $V(H_2O)_6^{2+}(aq)$ (90 sec⁻¹, 16.4 kcal mol⁻¹)[28] and for the reaction $[V(H_2O)_6^{2+}\cdot NCS^-] \rightarrow V(H_2O)_5NCS^+ + H_2O$ (ca. 100 sec⁻¹, 15.3 kcal mol⁻¹ [29]).

On the basis of this argument we conclude with the general prediction that, where a binuclear complex involves strong σ bonding, the kinetic behavior of the equatorial ligands will resemble that of ligands in mononuclear complexes of metals of the same valency, one place to the left in the periodic table. Thus we expect similarities in rate between $Rh_2(OAc)_4$ and Ru^{II} in some appropriate complex, between $Re_2Cl_8^{2-}$ and WCl_6^{3-}, between $Mn_2(CO)_{10}$ and $Cr(CO)_6$, and so on. On the other hand we do not make any corresponding predictions regarding $V_2(OOCC_6H_5)_6$ or $Cu_2(OAc)_4$ in spite of their having similar structures to $Cr_2(OAc)_4$, since in those cases the d_{z^2} orbitals are either empty or fully occupied and no strong σ bond exists.

In some cases the proposed comparison fails for lack of a suitable complex; e.g., there is no mononuclear Nb^{II} species to compare with $Mo_2(OAc)_4$. In such cases the following rather weaker prediction may be substituted: rates of replacement will be slower than in a corresponding mononuclear complex of the same metal ion but faster than in the corresponding complex of the same metal with the next higher oxidation number.

Acknowledgment. We are grateful to the Royal Society (London) and the Science Research Council for grants toward the purchase of equipment (SRC Grant B/SR/5039). The temperature-controlled cell housing in the stopped-flow apparatus was designed and built by Mr. H. W. Plumbley, Engineering Workshops, University of East Anglia. J.S.S. held an SRC Research Studentship.

Registry No. $Cr_2(OAc)_4$, 15020-15-2; CYDTA, 13291-61-7; $Co(EDTA)^-$, 15136-66-0; $Ro(H_2O)^{3+}$, 14403-82-8; EDTA, 60-00-4; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(C_2O_4)_3^{3-}$, 15053-34-6.

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(9) Throughout this paper we use the symbols $OAc^- = CH_3COO^-$, EDTA = ethylenediaminetetraacetic acid, edta^{4-} = anion of EDTA, DTPA = diethylenetriaminepentaacetic acid, CYDTA = *trans*-cyclohexane-1,2-diaminetetraacetic acid, and Ro = $Co(NH_3)_5$.

(10) The two water molecules in $Cr_2(OAc)_4\cdot 2H_2O$ are labile and easily replaced by other donor groups, and it is probable that at the higher acetate concentrations used in this work one or two acetate groups are attached. It makes no difference to any of the present arguments if the formulas $Cr_2(OAc)_4$, $Cr(OAc)_2$, etc. are replaced by $Cr_2(OAc)_6^{2-}$, $Cr(OAc)_3^-$, etc. The actual species denoted as dimer and monomer may in fact be equilibrium mixtures of these forms (cf. ref 6 and 7).

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Hydrogen Bonding. VI. Structural and Infrared Spectral Analysis of Lithium Hydroxide Monohydrate and Cesium and Rubidium Hydroxide Hydrates[1,2]

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The infrared spectrum of $LiOH{\cdot}H_2O$ shows, in addition to the stretching and bending modes of OH and H_2O groups, seven bands in the 1000–300-cm^{-1} region. Four of these bands give characteristic shifts upon deuterium substitution and confirm the presence of coordinated water and hydroxide ion in $LiOH{\cdot}H_2O$. On the basis of internal coordinate analysis of the coordinated water and hydroxide subunits of the crystal structure we may assign the various rocking and torsional vibrations of oxygen–hydrogen atoms and the lithium–oxygen lattice vibrations. Unlike other alkali metal hydroxide hydrates the water and hydroxide ions in $LiOH{\cdot}H_2O$ form discrete, planar, hydrogen-bonded $[(OH^-)_2(H_2O)_2]$ anionic units rather than extended chains. RbOH and CsOH also form stable mono- and hemihydrates, the infrared spectra of which contain the rocking and wagging modes of strongly hydrogen-bonded, coordinated water.

Introduction

We have been studying the infrared spectrum of coordinated water in the alkali metal hydroxide hydrates for two reasons. First, these compounds represent intermediate bonding states between the well-characterized clathrate type hydrates[4–6] or intermediate framework hydrates[7] and the tetramethylammonium hydroxide and fluoride monohydrates which we believe[8,9] contain discrete, tightly bound water–anion species as predicted by Jeffrey.[10] Second, by correlation of the infrared spectrum with known crystal structure for lithium hydroxide monohydrate, we hoped to gain insight into methods by which spectral data could be used to derive structural information on hydrates, such as the tetramethylammonium species mentioned above, for which single crystals for diffraction studies are difficult or impossible to prepare.

Although the infrared and Raman spectra of lithium hydroxide monohydrate have been reported in the literature many times,[11–15] no study has included the lower energy region of the spectrum, with the exception of a Raman effect study of lattice motions by Krishnamurti.[15] The region from 1000 to 400 cm^{-1} in the infrared spectrum of a hydrate is of particular interest, as this region asserts the presence of coordinated water and distinguishes it from water of crystallization.[16,17]

The general features of the crystal structure of lithium hydroxide monohydrate have been well established by X-ray diffraction studies;[18–21] these reports, however, did not consider the precise molecular bonding arrangements. We have previously[1] reported—based on our analysis of the data of Alcock—the identification of a discrete, planar, hydrogen-bonded subunit $[(OH^-)_2(H_2O)_2]$ in the crystal. This observation is confirmed by consideration of the recent neutron diffraction studies of Agron, Busing, and Levy[22,23] in which the hydrogen positions are precisely defined and the planar subunits can be clearly seen. The delineation of the spatial arrangements and electronic relationships of the atoms in a unit cell of lithium hydroxide monohydrate allows a clear interpretation of the infrared spectrum.

Experimental Section

Materials. Fisher lithium hydroxide monohydrate and Alfa Inorganics cesium and rubidium hydroxide monohydrates were used without further purification. The cesium and rubidium salts are extremely hygroscopic and were handled in the glove box. $LiOH{\cdot}H_2O$ neutralization equivalent: calcd, 41.95; found, 42.02. $CsOH{\cdot}H_2O$ neutralization equivalent: calcd, 167.92; found, 169.2. $RbOH{\cdot}H_2O$ neutralization equivalent: calcd, 120.49; found, 120.9.

Cesium and rubidium hemihydrates were prepared by heating the appropriate monohydrates at 114° and 0.01 Torr for 3 days over P_2O_5. Additional drying of these salts afforded no further dehydration. Rubidium hydroxide monohydrate melts at the temperature necessary to form the hemihydrate; the hemihydrate which crystallizes out of the sintered mass retains a slight excess of water. $CsOH{\cdot}{}^1/_2H_2O$ neutralization equivalent: calcd, 158.93; found, 158.72. $RbOH{\cdot}{}^1/_2H_2O$ neutralization equivalent: calcd, 111.49; found, 113.1.

Lithium, cesium, and rubidium deuteroxide monohydrates-d_2 were prepared by weighing samples of the appropriate monohydrate in a tared cell, injecting excess 99.7% D_2O through a rubber septum, and evaporating the solvent in vacuo. This process was repeated three times; on the third evaporation D_2O was removed until the weight of the cell indicated the theoretical amount for the deuteroxide monohydrate-d_2. In each case the deuteroxide monohydrate-d_2 was the first completely solid material obtained.

Measurements. Infrared spectra were recorded on a Beckman