Table I. Comparison of Apparent Deviations from Vegard's Law

Mol % VO_4 in prepn	Mol % VO_4 in solid soln (Aia[6])	Mol % VO_4 in solid soln (method b)
25	22.0	23.0
50	41.5	43.0
75	75.0	75.0

being the use of $(NH_4)_2HPO_4$. Examining his X-ray data, we find that they yield values for apparent deviations from Vegard's law close to our own. This can be seen from the values in Table I.

It is interesting to note that the particle habit of $YVO_4 \cdot YPO_4$ solid solutions follows that of the $YPO_4 \cdot {}^5/_3H_2O$ used in preparation. As shown in Figure 6, precipitated YVO_4 occurs as 0.1–1.0-μ platelets while YVO_4 made by solid-state reaction of oxides is a regular dodecahedron. Precipitated $YPO_4 \cdot {}^5/_3H_2O$ is acicular with many of the particles (2–6 μ) clustered from a central growth point to form a spiny sphere.[7] For high vanadate (>70–80% VO_4), the dodecahedrons prevail. For $(NH_4)_2HPO_4$-reacted particles, the particles are not uniform.

When $YPO_4 \cdot {}^5/_3H_2O$ is employed as a reactant, an acicular product results, for both high-phosphate and high-vanadate portions of the phase compositions (see Figure 6). Apparently, the phosphate acts as a reaction base for particle formation and the product is a pseudomorph. This is similar to a much better known case of pseudomorphism where the particle morphology of $CaHPO_4 \cdot 2H_2O$ (octagonal, square platelets, rectangular platelets, and acicular) is carried through the reacting $CaHPO_4$ to form pseudomorphic $Ca_5FCl(PO_4)_3$.

Registry No. YVO_4, 13566-12-6; YPO_4, 13990-54-0.

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Contribution from the School of Chemical Sciences,
University of East Anglia, University Plain, Norwich, NR4 7TJ, England

Kinetics of Chromium(III)–Chromium(II) Electron Transfer and Equilibria in the Chromium(II)–Acetate System

RODERICK D. CANNON* and JENNIFER S. STILLMAN

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The reactions $Cr(NH_3)_5X^{2+} + Cr^{II}$ in acetate buffer media (X = Cl, Br) obey the rate law $-d \ln [Cr(NH_3)_5X^{2+}]/dt = {}^1/_4 k_M{}^X K_D(-1 + (1 + 8[Cr^{II}]_T/K_D)^{1/2})$ where K_D is interpreted as the dissociation constant of the chromium(II) acetate dimer and $K_M{}^X$ as the specific rate of reaction of $Cr(NH_3)_5X^{2+}$ with chromium(II) monomer. At 25° in acetate buffer with $[OAc^-] = [HOAc] = 0.50\ M$ and ionic strength 1.0 M ($NaClO_4$), $K_D = (5.2 \pm 2) \times 10^{-4}\ M^{-1}$, $k_M{}^{Cl} = 0.60 \pm 0.2\ M^{-1}\ sec^{-1}$; at 25° with $[OAc^-] = [HOAc] = 0.10\ M$, $k_M{}^{Cl} = 0.34 \pm 0.1\ M^{-1}\ sec^{-1}$; at 30° with $[OAc^-] = [HOAc] = 0.10\ M$, $k_M{}^{Br} \simeq 5\ M^{-1}\ sec^{-1}$. Values of K_D and k_M for other acetate ion concentrations are tabulated. The dependences of $k_M{}^{Cl}$ and K_D upon acetate ion concentration are interpreted in terms of bimolecular electron-transfer steps $Cr(NH_3)Cl^{2+} + Cr(OAc)_n{}^{(2-n)+}$ with second-order specific rates k_n, where $0 \leq n \leq 3$, and equilibria defined by $K_n = [Cr(OAc)_n{}^{(2-n)+}]/[Cr(OAc)_{n-1}{}^{(3-n)+}][OAc^-]$ and $K_{D0} = [Cr(OAc)_2]^2/[Cr_2(OAc)_4]$. At 25° and ionic strength 1.0 M ($NaClO_4$), $k_0 = (3.0 \pm 0.2) \times 10^{-2}\ M^{-1}\ sec^{-1}$, $(k_1 - k_0)K_1 = (3.8 \pm 0.3)\ M^{-2}\ sec^{-1}$, $K_2 \approx 5\ M^{-1}$ and $K_{D0} = (4 \pm 1) \times 10^{-4}\ M$.

In an earlier study[1] of the reaction of chloropentaamminechromium(III) ion with chromium(II) in acetate media it was concluded that the effective reducing species were monomeric chromium(II) complexes present at low concentration in equilibrium with the chromous acetate dimer, and independent evidence of such equilibria was obtained from spectrophotometric measurements. It was not, however, possible to identify the chromium(II) complexes involved except to say that under the conditions used the average acetate: chromium ratio in the monomeric complexes was the same as that in the dimers. In view of the scarcity of data on chromium(II) complex equilibria and on mechanisms of reaction of metal–metal bonded species, we considered it worthwhile to undertake a further kinetic study under a wider range of conditions. From the new data we are now able to define the complexes involved in the electron-transfer processes and to estimate the stability of the chromium(II) acetate dimer.

Experimental Section

Preparation of Materials. Bromopentaamminechromium(III) bromide was prepared from rhodochromic chloride[2] as follows. The crude chloride salt was dissolved in hot water, treated with concentrated hydrobromic acid, and cooled in ice to obtain the corresponding bromide, which after being filtered off was heated with concentrated hydrobromic acid on the steam bath for 1 hr. The sparingly soluble product was washed with cold water and ethanol. Anal. Calcd for $Cr(NH_3)_5Br_3$: N, 18.6; H, 3.98. Found: N, 17.6, 18.0; H, 4.19, 4.03 (two samples). Attempts to obtain the perchlorate salt by the method previously used for the corresponding chloro complex led to extensive aquation; hence the bromide was used in all kinetic experiments. Chloropentaamminechromium(III) perchlorate was prepared and recrystallized from time to time as previously described.[1]

Chromium(II) perchlorate solutions were prepared by reduction of hexaaquochromium(III) perchlorate solutions both by zinc amalgam[1] and by electrolysis.[3] No difference in kinetic behavior could be detected between the two preparations. Storage and handling of the air-sensitive solutions are described elsewhere.[1]

Kinetic Measurements. For the slowest reactions a Hilger and Watts single-beam UVISPEK spectrophotometer was used with automatic cell changer allowing observation of up to three reactions at one time, a fourth cell being used as reference. Otherwise a Beckman DB spectrophotometer was used with a 10-in. chart recorder giving photometric accuracy better than ±0.2% transmission. Temperature control was achieved by two modifications: an aluminum box through which cooling water could be circulated was placed between the lamphouse and the cell compartment, and the latter was rebuilt with double walls for circulation of water from an external thermostat.

Data Treatment. Primary kinetic data obtained as pen-recorder

Table I. Specific Rates (Eq 6) for the Reaction $Cr(NH_3)_5Cl^{2+}$ + Cr^{2+} in Perchloric Acid Media[a]

$[H^+], M$	$[Na^+], M$	$[Li^+], M$	$10^4 k_{obsd}$, sec^{-1}	$10^2 k_0$,[b] M^{-1} sec^{-1}
1.00				5.13[c]
1.00			2.22	5.41
0.50	0.50		1.70	4.12
0.20	0.80		1.55	3.72
0.00	1.00			3.25[d]
0.50		0.50	1.61	
0.20		0.80	1.54	

[a] $[Cr^{III}] = 4 \times 10^{-3}$ M, $[Cr^{II}]_T = 3.96 \times 10^{-3}$ M, $[ClO_4^-] = 1.0$ M, temperature 25°. [b] $k_0 = (k_{obsd} - k_{aq})/[Cr^{II}]_T$ where $k_{aq} = 7.3 \times 10^{-6}$ sec^{-1}.[4] [c] Reference 4. [d] Extrapolated value.

traces of absorbance A vs. time t were transferred to punched tape by means of a DMAC cartographic table. Most reactions obeyed pseudo-first-order kinetics (eq 2) corresponding to the net chromium(II)-catalyzed conversion of pentaamminechromium(III) to acetatochromium(III)

$$Cr(NH_3)_5Cl^{2+} + Cr(OAc)_x{}^{(2-x)+} + 5HOAc \rightarrow Cr^{II} + Cr^{III}(OAc)_xCl^{(2-x)+} + 5OAc^- \tag{1}$$

Rate constants k_{obsd} were obtained from linear plots according to eq 3, where A_0, A, and A_∞ denote absorbances at times 0, t, ∞. An

$$A - A_\infty = (A_0 - A_\infty)\exp(-k_{obsd}t) \tag{2}$$

$$k_{obsd} = -d \ln (A - A_\infty)/dt \tag{3}$$

alternative treatment in more complicated cases is described below.

Results

1. $Cr(NH_3)_5Cl^{2+}$ + Cr^{2+} Reaction in Perchloric Acid Media. This reaction was briefly reinvestigated for comparison with later results. Reactions were followed at wavelength 502 nm and found to obey pseudo-first-order kinetics.

$$Cr(NH_3)_5Cl^{2+} + Cr^{2+} + 5H^+ \rightarrow Cr^{2+} + CrCl^{2+} + 5NH_4^+ \tag{4}$$

$$-d \ln [Cr(NH_3)_5Cl^{2+}]/dt = k_{obsd} \tag{5}$$

Previously, Ogard and Taube[4] showed that k_{obsd} includes a small contribution k_{aq} from the Cr^{II}-independent aquation reaction

$$k_{obsd} = k_{aq} + k_0[Cr^{2+}] \tag{6}$$

Values of k_0 calculated by means of eq 6 are listed in Table I. Our results agree satisfactorily with those of Ogard and Taube at $[H^+] = 1.0$ M, but unlike them, we find a significant decrease in rate as the H^+ concentration is lowered, when the ionic strength is maintained by means of sodium perchlorate. This is evidently a medium effect since it does not appear when lithium perchlorate is used. Extrapolating to $[H^+] = 0$ and $[Na^+] = 1.0$ M, we obtain $k_0 = (3.25 \pm 0.2) \times 10^{-2}$ M^{-1} sec^{-1} at 25°.

2. $Cr(NH_3)_5Cl^{2+}$ + Cr^{2+} Reaction. Chromium(II) Dependence in Excess Acetate Buffer. Reactions were followed at 590 nm. Pseudo-first-order kinetics were observed (Table II). A typical plot according to eq 2 was linear for 5 half-lives. Plots of k_{obsd} against $[Cr^{II}]_T$ and $[Cr^{II}]_T{}^{1/2}$ were found to be respectively concave and convex to the horizontal axis and this is consistent with a reaction involving a dimer–monomer equilibrium which at the lower chromium(II) concentrations is appreciably displaced from left to right

$$Cr^{II}{}_2 \overset{K_D}{\rightleftharpoons} 2Cr^{II}{}_1 \tag{7}$$

$$Cr(NH_3)_5Cl^{2+} + Cr^{II}{}_1 \xrightarrow{k_M} \text{products} \tag{8}$$

$$k_{obsd} = k_M[Cr^{II}{}_1] \tag{9a}$$

$$= {}^1\!/\!_4 k_M K_D(-1 + (1 + 8[Cr^{II}]_T/K_D)^{1/2} \tag{9b}$$

Table II. The Reaction $Cr(NH_3)_5Cl^{2+}$ + Cr^{II} in Acetate Buffer Media[a]

$10^3[Cr^{II}]_T, M$	$10^4 k_{obsd}$, sec^{-1}	$10^3[Cr^{II}]_T, M$	$10^4 k_{obsd}$, sec^{-1}
$[HOAc] = 0.20$ M, $[OAc^-] = 0.10$ M			
0.198	0.57	1.19	2.79
0.40	1.24	1.58	3.50
0.79	2.17	1.98	4.33
$[HOAc] = 0.60$ M, $[OAc^-] = 0.10$ M			
0.198	0.58	1.19	2.67
0.40	1.15	1.58	3.14
0.79	1.90	1.98	3.93
$[HOAc] = [OAc^-] = 0.20$ M			
0.198	0.81	1.19	2.78
0.40	1.34	1.58	3.37
0.59	1.97	1.98	3.99
0.79	2.20	2.97	5.46
$[HOAc] = [OAc^-] = 0.50$ M			
0.54	1.58	2.69	4.06
1.08	2.59	3.23	4.76
1.61	3.12	4.04	5.55
2.15	4.03		
$[HOAc] = [OAc^-] = 1.00$ M			
0.54	1.72	2.15	3.94
0.81	2.23	2.69	4.54
1.08	2.43	3.23	5.32
1.61	3.29	4.04	5.77

[a] $[Cr^{III}]_T = 3.98 \times 10^{-3}$ M, ionic strength 1.0 M ($NaClO_4$), temperature 25°.

In these expressions $[Cr^{II}{}_1]$ and $[Cr^{II}{}_2]$ denote total concentrations of all mono- and dinuclear chromium(II) species respectively, and $[Cr^{II}]_T$ denotes the total stoichiometric chromium(II) concentration $[Cr^{II}{}_1] + 2[Cr^{II}{}_2]$. The constants k_M and K_D are accordingly functions of $[OAc^-]$. Equation 9b takes a limiting form at high chromium(II) concentrations, i.e., when $[Cr^{II}]_T >> K_D/8$

$$k_{obsd} = k_M(K_D/2)^{1/2}[Cr^{II}]_T{}^{1/2} \tag{10}$$

$$= k_A[Cr^{II}{}_2]^{1/2} \tag{11}$$

where $k_A = k_M K_D{}^{1/2}$; and at low concentrations

$$k_{obsd} \cong k_M[Cr^{II}]_T = k_M[Cr^{II}{}_1] \tag{12}$$

Rearranging eq 9b we have

$$k_{obsd} = {}^1\!/\!_2 k_M K_D(k_M[Cr^{II}]_T k_{obsd}{}^{-1} - 1) \tag{13}$$

so that a plot of k_{obsd} against $[Cr^{II}]_T/k_{obsd}$ is expected to be linear with slope $k_A{}^2$. Typical plots are shown in Figure 1, with earlier data from ref 1 included for comparison. The new data extend to lower chromium(II) concentrations than the old and are believed to be more accurate. Straight lines have been fitted to the data by least-squares procedures and the results are summarized in Table III. Limits of error quoted for k_A are based on two standard errors of estimate of the slope. Limits for k_M and K_D are more difficult to define and the values given are visual estimates from the graphs. It seems unlikely that the variations in either k_M or K_D on going from 0.5 to 1.0 M acetate ion are experimentally significant.

3. $Cr(NH_3)_5Br^{2+}$ + Cr^{II} Reaction. Chromium(II) Dependence in Excess Acetate Buffer. This reaction is more rapid than that of the corresponding chloro complex and it was hoped thereby to extend measurements to still lower chromium(II) concentrations without the necessity of longer reaction times. However it was not found possible to work with $[Cr^{II}]_T < 1 \times 10^{-4}$ M and there was somewhat greater scatter of results. Specific rates k_{obsd} (Table IV) again conformed to eq 13 and the corresponding rate parameters are shown in Table III.

4. $Cr(NH_3)_5Cl^{2+}$ + Cr^{II} Reaction. Acetate Ion Dependence.

Table III. Summary of Kinetic Data for Reactions $Cr(NH_3)_5X^{2+} + Cr^{II}$ in Acetate Buffer[a]

X	T, °C	$[OAc^-]$, M	$[HOAc]$, M	$10^2k_A = 10^2k_MK_D^{1/2}$, $M^{1/2}$ sec^{-1}	10^4K_D, M	k_M, M^{-1} sec^{-1}
Cl	25	0.10	0.10	1.98 ± 0.30	33 ± 10	0.34 ± 0.1
Cl	25	0.10	0.60			
Cl	25	0.20	0.20	1.68 ± 0.17	11 ± 3	0.51 ± 0.15
Cl	25	0.50	0.50	1.37 ± 0.19	5.2 ± 2	0.60 ± 0.2
Cl	25	1.00	1.00	1.50 ± 0.18	7.2 ± 2	0.56 ± 0.15
Br	30	0.10	0.10	15.9 ± 2.5	10 ± 10	~5
Br	30	0.20	0.20	15.3 ± 1.7	4 ± 3	~4

[a] Ionic strength 1.0 M ($NaClO_4$).

Table IV. The Reaction $Cr(NH_3)_5Br^{2+} + Cr^{II}$ in Acetate Buffer[a]

$10^3[Cr^{II}]_T$, M	10^3k_{obsd}, sec^{-1}	$10^3[Cr^{II}]_T$, M	10^3k_{obsd}, sec^{-1}
	$[HOAc] = [OAc^-] = 0.10$ M		
0.21	0.78	1.59	3.85
0.42	1.48	1.70	3.45
0.59	1.89	2.07	3.98
0.85	1.98	2.37	5.02
0.89	2.24	1.98	4.31
1.18	2.75	2.13	4.08
1.28	2.66	2.96	4.62
1.48	2.88		
	$[HOAc] = [OAc^-] = 0.20$ M		
0.107	0.65	1.38	3.82
0.21	1.07	1.48	3.47
0.40	1.32	1.59	3.84
0.59	1.80	1.78	3.85
0.79	2.11	1.70	3.36
0.79	2.37	1.70	3.66
0.85	2.42	1.98	4.39
0.89	2.43	2.07	4.25
0.99	2.94	2.13	4.37
1.18	2.98	2.37	4.62
1.19	3.62	2.37	4.25

[a] $[Cr^{III}]_T = 3.96 \times 10^{-3}$ M, temperature 30°, ionic strength 1.0 M ($NaClO_4$).

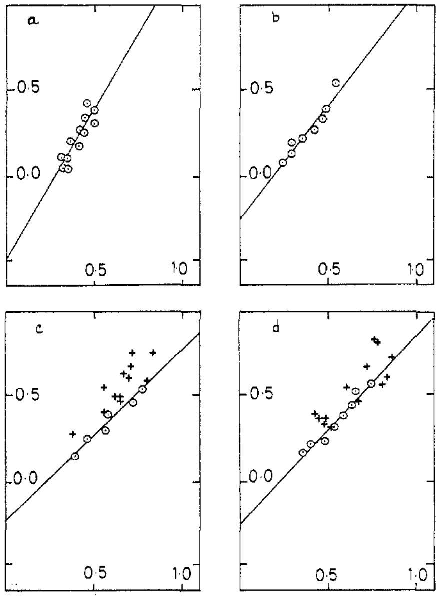

Figure 1. Data of Table II plotted according to eq 13: vertical axes, 10^3k_{obsd}/sec^{-1}; horizontal axes, $10^{-1}k_{obsd}^{-1}$ $[Cr^{II}]_T$/M sec. $[HOAc] = [OAc^-] = 0.1$ M (a), 0.2 M (b), 0.5 M (c), 1.0 M (d). + points are from ref 1; others, from this work.

A series of experiments was carried out with no acetate ion present initially but with various excess concentrations of acetic acid (Table V). These showed significant deviations from pseudo-first-order kinetics, the specific rate tending to increase as reaction progressed (Figure 2). This is conveniently illustrated in Figure 3 where the rate of change of absorbance (obtained from the original $A(t)$ trace by taking $\Delta A/\Delta t$ over appropriate time intervals) has been used to calculate the specific rate

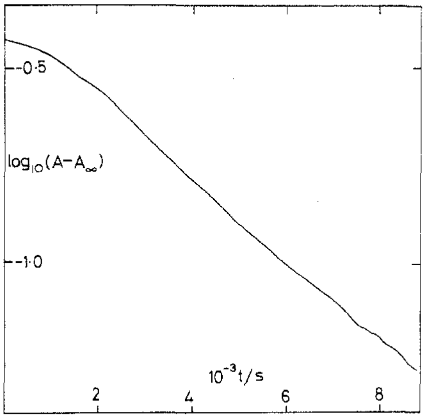

Figure 2. Semilogarithmic plot for the reaction $Cr(NH_3)_5Cl^{2+} + Cr^{II}$ in 0.050 M HOAc (Table V); path length 1 cm, wavelength 590 nm.

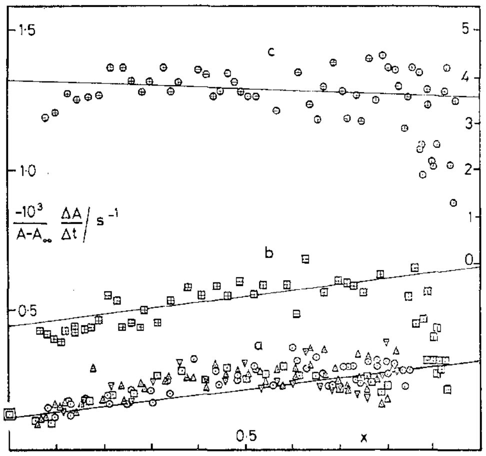

Figure 3. Specific rate k_{obsd} vs. extent of reaction x (eq 15) for the reaction $Cr(NH_3)_5Cl^{2+} + Cr^{II}$; temperature 25°, ionic strength 1.0 M ($NaClO_4$), $[Cr^{II}]_T = 3.96$ mM, $[Cr^{III}]_T = 4.0$ mM. Group (a) left-hand vertical scale: initial $[OAc^-] = 0$; initial $[HOAc] =$ 0.05 M (▽), 0.10 M (□), 0.15 M (○), 0.20 M (△). Group (b) left-hand vertical scale: initial $[OAc^-] = 0.020$ M, initial $[HOAc] =$ 0.050 M. Group (c) right-hand vertical scale: initial $[OAc^-] =$ 0.160 M, initial $[HOAc] = 0.050$ M. The straight lines are fitted by least squares to the data for $0 < x \leqslant 0.9$. The point at $x = 0$ is from experiments in perchloric acid media, extrapolated to $[H^+] =$ 0 (Table I).

$$k_{obsd} = -(A - A_\infty)^{-1}\Delta A/\Delta t \tag{14}$$

and the "extent of reaction" x has been defined as

$$x = (A_0 - A)/(A_0 - A_\infty) \tag{15}$$

As shown in curve a of Figure 3, there is a marked increase

Table V. Reactions $Cr(NH_3)_5Cl^{2+} + Cr^{2+}$ in Acetate–Acetic Acid Media[a]

[HOAc], M	[OAc^-], M	$10^2k_{obsd}[Cr^{II}]_T^{-1}$, M^{-1} sec^{-1}	[HOAc], M	[OAc^-], M	$10^2k_{obsd}[Cr^{II}]_T^{-1}$, M^{-1} sec^{-1}
0.000	0.000	3.25 ± 0.2[b]	0.050	0.100	16.8
Various[c]	0.000	2.75 ± 0.5[c]	0.050	0.120	17.1
0.040[d]	0.010[d]	6.7[d]	0.050	0.140	16.5
0.050	0.020	9.9	0.050	0.160	16.3
0.041[d]	0.029[d]	14.6[d]	0.050	0.180	15.9
0.050	0.040	17.0	0.050	0.200	16.0
0.050	0.060	17.8	0.050	0.300	17.0
0.050	0.080	16.7	0.050	0.400	17.4

[a] $[Cr^{III}]_T = 4 \times 10^{-3}$ M, $[Cr^{II}]_T = 3.96 \times 10^{-3}$ M, temperature 25°, ionic strength 1.0 M ($NaClO_4$). Except where otherwise shown, specific rates k_{obsd} were calculated for zero time as described in the text and concentrations [HOAc] and [OAc^-] are initial values. [b] From Table I. [c] Average of five experiments at [HOAc] = 0.050–0.200 M (see Figure 3 and caption). [d] Calculated for $x = 0.5$ (see text and ref 5).

in k_{obsd} with x, but no dependence on acetic acid concentration, and the value of k_{obsd} extrapolated to $x = 0$ is in satisfactory agreement with the value obtained in the absence of acetic acid.

The increase in k_{obsd} with x can be attributed to release of acetate ions (eq 1) giving complexes $CrOAc^+$, $Cr(OAc)_2$, etc., which are more effective reducing agents than Cr^{2+} (eq 16). This is confirmed by experiments with added acetate ion (Table V). At low concentrations ([OAc^-] ≤ 0.07 M) the kinetic behavior is similar to that just described while at higher concentrations pseudo-first-order kinetics are found (Figure 3, curves b and c). (It should be noted, however, that in all cases where the photometric data were sufficiently accurate, there was a drift to lower specific rates in the last 10% of reaction. This has been noted before and has been attributed to slow polymerization of the acetato-chromium(III) product.[1]) Specific rates k^0_{obsd} obtained by extrapolating to $x = 0$ are shown in Figure 4 for a series of experiments at fixed chromium(II) concentration and acetate concentrations from 0.20 to 0.4 M, together with values extrapolated from the preceding chromium(II)-dependence experiments. Two additional points have been obtained from the data of Figure 3, curves a and b, by estimating the acetate concentration at the half-reaction point, $x = 0.5$. The resulting curve shows a sharp and apparently linear increase in rate up to [OAc^-] = 0.05 M, followed by a leveling off with a flat maximum near [OAc^-] = 0.1 M.

Discussion

It has already been shown that under the conditions of this work the only effective reducing agents are mononuclear chromium(II) complexes.[1] A general reaction mechanism can therefore be written

$$Cr^{2+} + OAc^- \overset{K_1}{\rightleftharpoons} CrOAc^+ \qquad (16a)$$

$$CrOAc^+ + OAc^- \overset{K_2}{\rightleftharpoons} Cr(OAc)_2\text{, etc.} \qquad (16b)$$

$$Cr(NH_3)_5Cl^{2+} + Cr^{2+} \xrightarrow{k_0} \text{products} \qquad (17a)$$

$$Cr(NH_3)_5Cl^{2+} + CrOAc^+ \xrightarrow{k_1} \text{products} \qquad (17b)$$

$$Cr(NH_3)_5Cl^{2+} + Cr(OAc)_2 \xrightarrow{k_2} \text{products, etc.} \qquad (17c)$$

giving the rate constant k_M (eq 8) as

$$k_M = \sum_{i=0}^{N} k_i[Cr(OAc)_i{}^{(2-i)+}]/[Cr_I] \qquad (18a)$$

$$= \left\{\sum_{i=0}^{N} k_i\beta_i[OAc^-]^i\right\} \Big/ \sum_{i=0}^{N} \beta_i[OAc^-]^i \qquad (18b)$$

where $\beta_i = K_1K_2...K_i$, and N is the limit of coordination. For the purpose of fitting to experimental data this may be expanded as

$$k_M = q_0 + q_1[OAc^-] + q_2[OAc^-]^2 + ... \qquad (19)$$

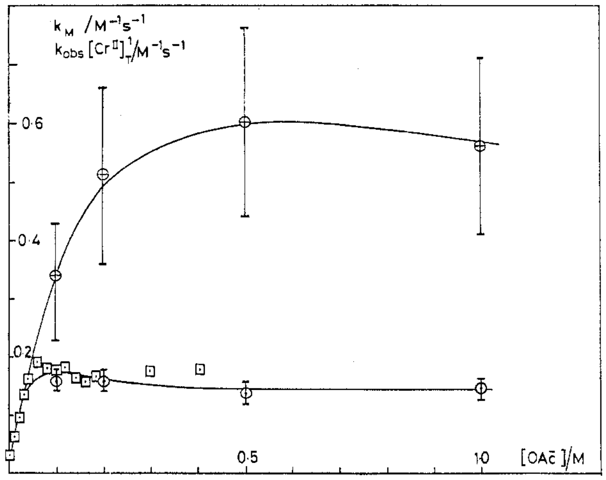

Figure 4. Acetate ion dependence of the reaction $Cr(NH_3)_5Cl^{2+}$ + Cr^{II}. Points ⊡ are from Table V; points ⊙ are interpolated from the chromium(II)-dependence data of Table II; points ⊕ show values of k_M defined by eq 9. The upper curve is calculated from eq 18b using the parameters $k_0 = 0.030$ M^{-1} sec^{-1}, $k_1 = 0.27$ M^{-1} sec^{-1}, $k_2 = 0.9$ M^{-1} sec^{-1}, $k_3 = 0.3$ M^{-1} sec^{-1}; $K_1 = 15$ M^{-1}, $K_2 = 5$ M^{-1}, $K_3 = 1$ M^{-1}.

where

$$q_0 = k_0 \qquad (20a)$$

$$q_1 = (k_1 - k_0)K_1 \qquad (20b)$$

$$q_2 = [(k_2 - k_0)K_2 - (k_1 - k_0)K_1]K_1\text{, etc.} \qquad (20c)$$

The experimental dependence of k_M upon [OAc^-] is plotted in Figure 4. The parameters q_0 and q_1 are well-defined, giving $k_0 = (3.0 \pm 0.2) \times 10^{-2}$ M^{-1} sec^{-1} and $(k_1 - k_0)K_1 = 3.8 \pm 0.3$ M^{-2} sec^{-1}; but more detailed fitting is not practicable except to say that q_2 is either negative or close to zero. Thus, as always with equations of the type (18b), it is not possible to deduce independent values of k_1, k_2, etc. and K_1, K_2, etc. From the argument which follows however, it is clear that the value of $k_M \approx 0.6$ M^{-1} sec^{-1} given by the flat portion of the curve of Figure 4 gives the order of magnitude of k_2. For it seems certain that at some point in the acetate concentration range used, the predominant *dimer* species is $Cr_2(OAc)_4$. This is the only acetatochromium(II) complex known in the solid state, and the absorption spectra of the dimers in aqueous acetate media[1] and in organic solvents such as dioxane[6] are closely similar. The fact that K_D varies little with acetate concentration between [OAc^-] = 0.2 M and [OAc^-] = 1.0 M then implies that over that range the average acetate:chromium ratio in the monomeric complexes is the same as in the dimer. Thus over the whole acetate concentration range, the predominant chromium(II) monomer species vary from Cr^{2+} to $Cr(OAc)_2$ and possibly to $Cr(OAc)_3^-$. This last can occur without disturbing the monomer–dimer equilibria provided that under the same conditions the dimer adds on acetate ions to form

$Cr_2(OAc)_5^-$ and $Cr_2(OAc)_6^{2-}$ (cf. the analogous vanadium(III) carboxylate structure[7]). Then if the stability constants K_i are widely separated, there is an acetate concentration at which $Cr(OAc)_2$ is the predominant complex, whence $k_2 \simeq 0.6\ M^{-1}\ sec^{-1}$; and, if not, there is a mixture of complexes which requires either $k_2 \approx k_3 \approx 0.6\ M^{-1}\ sec^{-1}$ or $k_1 < k_2 > 0.6\ M^{-1}\ sec^{-1} > k_3$. The curve shown in Figure 4 has been calculated using a set of parameters consistent with this discussion,[8] but as stated above, the only independently determined quantities are q_0 and q_1.

Chromium(II) acetate equilibria were previously studied spectrophotometrically by Yatsimirskiĭ and Federova.[9] With increasing acetate concentration, absorbance at 496 nm rose sharply, then leveled off, and remained constant within experimental error from 0.6 to 2.0 *M* acetate ion. Using a four-parameter equation and a double-extrapolation procedure, stability constants and extinction coefficients were derived for both 1:1 and 1:2 complexes; but the latter were incorrectly assumed to be mononuclear $Cr(OAc)_2$ and measurements were made at only a single chromium(II) concentration. Moreover, the method of calculation fails since it assumes that at the lowest acetate concentration used the formation of $Cr(OAc)^+$ is not extensive.[10] In fact the data can be fitted adequately to a two-parameter equation

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_\infty}\left(1 + \frac{1}{K[\mathrm{OAc}^-]}\right) \tag{21}$$

where ϵ is the average extinction coefficient per chromium atom and ϵ_∞ is the limiting value of ϵ at high acetate concentration. From Figure 5, at 20°, with $[Cr^{II}]_T = 9.2 \times 10^{-3}\ M$, we obtain $\epsilon_\infty = 77\ M^{-1}\ cm^{-1}$ and $K = 14.5\ M^{-1}$. This means that over the concentration range used the principal dissociation reactions of the dimer species are ones involving the loss of one acetate ion per chromium atom, for example

$$^1/_2\mathrm{Cr_2(OAc)_4} \xrightleftharpoons{K_{\mathrm{DO}}^{1/2}} \mathrm{Cr(OAc)_2} \xrightleftharpoons{K_1^{-1}} \mathrm{CrOAc^+} + \mathrm{OAc^-} \tag{22}$$

and the empirical constant *K* is identified as

$$K = \frac{[\mathrm{Cr(OAc)_2}] + {}^1/_2[\mathrm{Cr_2(OAc)_4}]}{[\mathrm{CrOAc^+}][\mathrm{OAc^-}]} \tag{23}$$

$$= K_2(1 + {}^1/_2([\mathrm{Cr_2(OAc)_4}]/K_{\mathrm{DO}})^{1/2}) \tag{24}$$

Our kinetically determined equilibrium constants K_D (Table III) can be expressed in terms of the same reactions to yield

$$K_{\mathrm{D}}^{1/2} = K_{\mathrm{DO}}^{1/2}\left(1 + \frac{1}{K_2[\mathrm{OAc}^-]}\right) \tag{25}$$

While our data are not sufficient to test the form of eq 25, the plot of $K_D^{1/2}$ against $[OAc^-]^{-1}$ (Figure 5) yields $K_2 = 5 \pm 2\ M^{-1}$, which appears reasonable[6] and $K_{DO} = (4 \pm 1) \times 10^{-4}\ M$ at 25° and ionic strength 1.0 *M* ($NaClO_4$). Applying this value of K_{DO} to the data of Yatsimirskiĭ and Federova and using eq 24, we then have $K_2 = 6\ M^{-1}$ at 20°. This agreement is fortuitous since in the latter work the ionic strength was not controlled, but it provides some support for our interpretations.

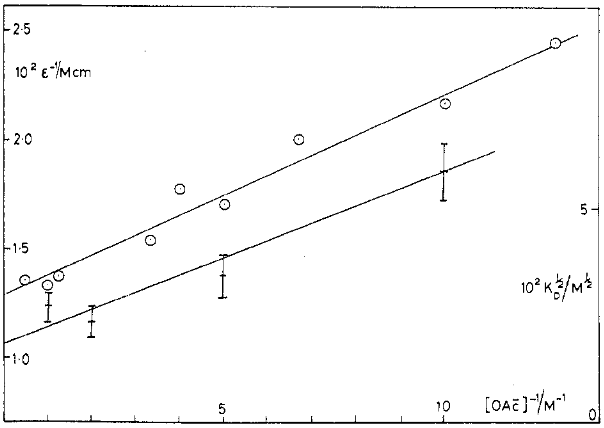

Figure 5. (1) Left-hand scale: dependence of average extinction coefficient ϵ, at 496 nm, on acetate concentration; $[Cr^{II}]_T = 9.2 \times 10^{-3}\ M$, temperature 20°, data from ref 7. (2) Right-hand scale: dependence of K_D (Table III) on acetate concentration; temperature 25°, ionic strength 1.0 *M* ($NaClO_4$).

Further study of this system will entail equilibrium measurements at lower acetate and chromium(II) concentrations, but this is rendered difficult by side oxidation of chromium(II) especially in the pH range of the acetate buffer. Work on this problem is continuing but we have not yet succeeded in improving on the data of Yatisimirskiĭ and Federova.

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Registry No. $Cr(NH_3)_5Cl^{2+}$, 14482-76-9; $Cr(NH_3)_5Br^{2+}$, 22289-65-2; Cr^{2+}, 22541-79-3; acetic acid, 64-19-7.

References and Notes

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$$\frac{-\mathrm{d}[\mathrm{OAc}^-]}{\mathrm{d}[\mathrm{Cr(NH_3)_5Cl^{2+}}]} = \frac{5k_0' + 4k_1'[\mathrm{OAc}^-]}{k_0' + k_1'[\mathrm{OAc}^-]} = 4 + k_0'/k_{\mathrm{obsd}}$$

The acetate concentration is not linear function of *x* but the error in assuming it to be so is small. Thus for $[Cr^{III}]_T = 4 \times 10^{-3}\ M$ and $[Cr^{II}]_T = 3.96 \times 10^{-3}\ M$ we obtain, when $[OAc^-] = 0$ initially, $k^0_{obsd} = k_0'$; hence at $x = 0.5$, $[OAc^-] = 10$ m*M*. When $[OAc^-] = 20$ m*M* initially, $k^0_{obsd} = 3.83 \times 10^{-4}\ sec^{-1}$ (Table II); hence at $x = 0.5$, $[OAc^-] = 28.6$ m*M*.
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