acetate protons is expected and this is observed at higher temperatures (80°).

The spectral changes which occur when the pH values of solutions of all of the 1:2 complexes are increased may indicate an increase in the palladium(II)–carboxylate bond labilities (particularly in the NTA case). When ammonia is used as base, mixed ammine–MIDA, –IDA, and –NTA species probably are formed.

The temperature studies of the 1:2 complexes indicate the presence of nonlabile metal–ligand bonding at low temperatures and labile palladium(II)–carboxylate bonding at elevated temperatures. The separate, sharp free ligand resonances observed when the ligands are added to solutions of the complexes implies also that intermolecular ligand exchange is slow; this presumably is a consequence of the relatively inert palladium(II)–nitrogen bonding. The present work is believed to represent the first good evidence for the presence of both labile and nonlabile bonding present simultaneously in this type of complex.

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Studies on the Acetatopentaaquochromium(III) Ion[1]

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The kinetics of the acid-assisted, chromium(II)-catalyzed and vanadium(II)-catalyzed aquations of the acetatopentaaquochromium(III) ion were investigated, as well as the rate of isotope exchange between this ion and chromium(II). The analysis of the kinetic data for the acid-catalyzed aquation suggests that substantial protonation of the coordinated acetate takes place. At 25°, $\mu = 4.00$, the protonation constant is $0.25 \pm 0.10\ F^{-1}$ ($\Delta H \approx 1$ kcal/mol). The specific rate constant (25°, $\mu = 4.00$) for the aquation of the protonated acetatochromium(III) ion is $(95 \pm 5) \times 10^{-6}\ \text{sec}^{-1}$ ($\Delta H^{\ddagger} = 18.6 \pm 1.0$ kcal/mol), and the specific rate constant for the unprotonated ion is $(0.74 \pm 0.02) \times 10^{-6}\ \text{sec}^{-1}$ ($\Delta H^{\ddagger}$ varies from 13 to 33 kcal/mol as the temperature varies from 25 to 55°). Chromium(II)-catalyzed aquation occurs predominantly by a path inverse in (H^+). With the acid dissociation constant of the acetatopentaaquochromium(III) ion at 25° and $\mu = 1.00$ measured as $(2.9 \pm 0.7) \times 10^{-5}\ F$ ($\Delta H = 5.5 \pm 1.5$ kcal/mol), the specific rate constant corresponding to the activated complex of composition $Cr^{2+} \cdot Cr(OH)OAc^{+}$ is $0.85 \pm 0.20\ M^{-1}\ \text{sec}^{-1}$ ($\Delta H^{\ddagger} = 16 \pm 3$ kcal/mol), and that for $Cr^{2+} \cdot CrOAc^{2+}$ is $(1.56 \pm 0.08) \times 10^{-5}\ M^{-1}\ \text{sec}^{-1}$ ($\Delta H^{\ddagger} = 26.7 \pm 1.5$ kcal/mol). The Cr^{2+}–$CrOAc^{2+}$ isotope-exchange reaction is inverse first order in acid, implying that the electron transfer proceeds *via* a double bridge; at 25°, $\mu = 1.00$, $k_{ex} = (5.8 \pm 0.2) \times 10^{-4}\ \text{sec}^{-1}$ ($\Delta H^{\ddagger} = 18.9 \pm 0.9$ kcal/mol). The vanadium(II)-catalyzed aquation is a complex reaction, being inhibited by acetic acid, chromium(II), and vanadium(III). At high concentrations of vanadium(II) ($\geqq 0.07\ F$) the rate law is $-d(CrOAc^{2+})/dt = (V^{2+})(CrOAc^{2+})(k_0 + A'/(H^+))$ with $k_0 = 0.163 \pm 0.009\ M^{-1}\ \text{sec}^{-1}$ and $A' = (6.7 \pm 1.4) \times 10^{-3}\ \text{sec}^{-1}$, at 25°, $\mu = 1.00$.

Introduction

Extensive studies of the inner-sphere electron-transfer reactions $(NH_3)_5Co^{III}X^{n+} + Cr^{2+} + 5H^+ \rightarrow Cr^{III}X^{n+} + Co^{2+} + 5NH_4^+$, where X is a carboxylate ion, have led to an interest in the chemistry of chromium(III) carboxylates as the primary products of these reactions. Butler and Taube[2] observed that the initial chromium(III) product of the chromium(II) reduction of the glycolatopentaamminecobalt(III) complex was metastable, decaying to a final product which was assumed to be the glycolatopentaaquochromium(III) ion. This behavior was taken as evidence for chromium being chelated by glycolate in the activated complex. Huchital and Taube[3] studied the rate of ring closure of the monodentate malonatochromium(III) complex in order to clarify the chemistry of the reduction by chromium(II) of the acid malonatopentaamminecobalt(III) ion[4] and the corresponding half-ester complex.[5] Since these two studies were carried only far enough to answer immediate questions, it was felt that a thorough and detailed study of one carboxylatochromium(III) ion would be a significant contribution to the understanding of inner-sphere reaction mechanisms as well as to the chemistry of chromium complexes in general.

Experimental Section

Materials.—All common laboratory chemicals were of reagent grade. Water was distilled three times (first distillation from alkaline permanganate) in Pyrex equipment. Lithium chloride, bromide, and perchlorate were crystallized at least two times before being used in kinetic runs. Hexaaquochromium(III) perchlorate was prepared by the reduction of chromium trioxide with formic acid in the presence of excess perchloric acid,[6] followed by crystallization from dilute perchloric acid and then from water. Vanadyl sulfate was converted to vanadyl perchlorate

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[1] Abstracted from the Ph.D. thesis of E. Deutsch, Stanford University, Stanford, Calif., 1967.

[2] R. D. Butler and H. Taube, *J. Am. Chem. Soc.*, **87**, 5597 (1965).

[3] D. H. Huchital and H. Taube, *Inorg. Chem.*, **4**, 1660 (1965).

[4] G. Svatos and H. Taube, *J. Am. Chem. Soc.*, **83**, 4172 (1961).

[5] D. H. Huchital and H. Taube, *ibid.*, **87**, 5371 (1965).

[6] J. B. Kirwin, P. J. Proll, and L. H. Sutcliffe, *Trans. Faraday Soc.*, **60**, 120 (1964).

by the method of Rossotti and Rossotti.[7] Chromium(II) and vanadium(II) solutions were prepared by reducing chromium(III) perchlorate and vanadium(IV) perchlorate solutions with zinc amalgam under an atmosphere of nitrogen. Chromium(II) solutions, enriched in chromium-51, were made up by diluting a solution of chromium-51 of high specific activity (1 mCi obtained from Nuclear Science and Engineering Corp. as 0.01 ml of chromium(III) solution in 0.5 *F* hydrochloric acid) to about 50 ml with a standardized stock solution of 2 *F* chromium(III) perchlorate, followed by zinc amalgam reduction under a nitrogen atmosphere. Carboxylatopentaamminecobalt(III) perchlorates were synthesized by the method of Sebera and Taube.[8] Analytical grade Dowex 50W-X2 resin, 200–400 mesh, was purchased from Bio-Rad and cleaned by successive washings with water, acid, base, basic peroxide, water, acid, acetone, and water (twice). It was then converted to the lithium form with lithium hydroxide and washed with water until the eluent was neutral.

Preparation of Acetatochromium(III) Solutions.—Solutions of the acetatopentaaquochromium(III) ion were prepared by reduction of the acetatopentaamminecobalt(III) ion with chromium(II) and subsequent ion exchange of the reaction mixture. Forty mmoles of acetatopentaamminecobalt(III) perchlorate was completely dissolved in 2–3 l. of water and the resulting solution was deoxygenated by bubbling nitrogen through it. Forty-one mmoles of hexaaquochromium(III) perchlorate and 225 mmol of perchloric acid were mixed, diluted to about 500 ml, and reduced over zinc amalgam. The chromium(II)–acid mixture was slowly added to the cobalt(III) solution, nitrogen being continually bubbled through while a magnetic stirring bar mixed the solution; slow addition is necessary or else the high perchlorate concentration of the chromium(II) solution precipitates acetatopentaamminecobalt(III) perchlorate, and the reaction of chromium(II) with this solid produces hexaaquochromium(III) to a large extent. The reaction mixture was allowed to stand for 2 hr while being stirred and purged with the nitrogen stream. It was then absorbed on an ion-exchange column containing about 1.5 lb of the resin prepared as described above. The acetatochromium(III) ion was slowly eluted with a solution 0.360 *F* in $LiClO_4$ and 0.040 *F* in $HClO_4$; the column and all of the solutions were held at 5° by carrying out the separation in a cold room, the entire separation taking 2 days. The conditions of low temperature, low acid, and low cross-linking in the resin were chosen to minimize column hydrolysis. It was shown that under these conditions a solution of pure acetatochromium(III) ion could be put on the column and eluted with no detectable formation of hexaaquochromium(III). However, the resolution of the X2 resin is poor, and a complete separation of $CrOAc^{2+}$ and Co^{2+} could not be made on a column of reasonable length; since the cobaltous band followed the acetatochromium(III) band, only the first 50% of the chromium band was collected. A qualitative test[9] on the final chromium solution showed that the concentration of the cobaltous ion was less than 10^{-5} *F*. The acetatochromium(III) solution was stored at 0°; the concentration of the acetatopentaaquochromium(III) ion was assumed to be equal to the total chromium concentration of the solution and was usually around 0.06 *F*. The chloropentaaquochromium(III) ion was prepared exactly as was the acetato ion, except that chloropentaamminecobalt(III) perchlorate was used as the starting material, and the total reaction was just the time of mixing.

Analyses.—The total chromium concentration of a solution was measured by oxidizing an aliquot with basic peroxide, destroying the excess peroxide, and spectrophotometrically determining the concentration of chromate at 373 mμ (ϵ_{373} 4815 ± 15).

The total perchlorate concentration of a solution, or the total ClO_4 percentage of a solid, was determined by a method modified from that of Gould and Taube[10] and that of Glover and Rosen.[11] A sample containing enough perchlorate to give 0.1–0.2 g of tetraphenylarsonium perchlorate was diluted to about 30 ml with a solution 2.5 *F* in NH_4Cl and 0.1 *F* in HCl. If the sample did not contain either aquopentaamminecobalt(III) or a carboxylatopentaammine, the solution was heated to 70° and a twofold excess of a 0.06 *F* tetraphenylarsonium chloride solution was added slowly from a pipet while the mixture was vigorously stirred; the sample was allowed to cool and stand for at least 3 hr, preferably overnight. If the original sample did contain aquopentaammine or a carboxylatopentaammine, heating it in 2.6 *F* chloride solution produced the relatively insoluble chloropentaamminecobalt(III) chloride, leading to high results; in these cases the precipitation was done at room temperature, and the sample was allowed to coagulate for a minimum of 8 hr. The precipitate was collected on a tared sintered-glass crucible and washed with a saturated solution of tetraphenylarsonium perchlorate. Samples were dried at 110° for 3 hr and weighed as $C_{24}H_{20}AsClO_4$.

The total vanadium concentration of vanadyl perchlorate stock solutions was determined by oxidizing an aliquot with permanganate, destroying the excess permanganate with nitrite followed by urea, and titrating the sample with a standardized ferrous solution using a platinum indicator electrode.[12]

The concentration of chromium(II) in a solution was assumed to be equal to the total chromium concentration of the solution from which it was made. This assumption was checked in several cases by adding aliquots of a chromium(II) solution to an excess of acidic standard dichromate. The excess dichromate was determined spectrophotometrically at 350 mμ after correction for the absorbance of chromium(III) at this wavelength. In a typical case $(Cr)_{total} = 0.695 \pm 0.005$ *F* and $(Cr^{2+}) = 0.69 \pm 0.01$ *F*. Likewise the concentration of vanadium(II) was assumed to be equal to the total vanadium concentration of the solution that was reduced.

The concentration of free acid in hexaaquochromium(III) perchlorate solutions was determined by the method of King and Neptune.[13] The acid concentration of acetatochromium(III) solutions was calculated from the known Li/H ratio of the ion-exchange eluent and the total perchlorate and $CrOAc^{2+}$ concentrations of the final solution. A rough measure of the free acid concentration in vanadyl perchlorate stock solutions was obtained by titrating them potentiometrically with a standardized ethylenediamine solution. However, the end point of this titration is not sharp and it was deemed more accurate to calculate the free acid concentration from the known total perchlorate and total vanadium concentrations.

Equipment.—A Cary Model 14, or Model 15, recording spectrophotometer was used to take all visible and ultraviolet spectra. These machines, and a Beckman DU spectrophotometer, were equipped with thermostated cell compartments and were used to follow kinetic runs. The temperature of reacting solutions was maintained to better than ±0.2° by apparatus that is described in detail elsewhere.[1] Counting of radioactive samples was done on a Nuclear-Chicago Model No. 8785 analyzer–scaler, coupled with a Nuclear-Chicago DS303(V) well-scintillation detector. Computer calculations were done on a Burroughs B5500 located at the Stanford University Computation Center. Programs were written in ALGOL 60.

Handling and Preparation of Reaction Mixtures.—Solutions containing air-sensitive reagents were prepared, stored, transferred, mixed, and allowed to react under an atmosphere of deoxygenated nitrogen by one of the three techniques described below. Vanadium(II) solutions were always used within 8 hr of their initial reduction; chromium(II) solutions were used within 24 hr. The ionic strength of all reaction mixtures was adjusted to either 1.00 or 4.00 *F* using lithium perchlorate; volumetric measurements were made at room temperature and the

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[7] F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1177 (1955).

[8] D. K. Sebera and H. Taube, *J. Am. Chem. Soc.*, **83**, 1785 (1961).

[9] H. A. Potratz and J. M. Rosen, *Anal. Chem.*, **21**, 1276 (1949).

[10] E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

[11] D. J. Glover and J. M. Rosen, *Anal. Chem.*, **37**, 306 (1965).

[12] L. Meites, "Handbook of Analytical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1963, pp 3–73.

[13] E. L. King and J. A. Neptune, *J. Am. Chem. Soc.*, **77**, 3186 (1955).

final volume of the reaction mixture was assumed to be the sum of the volumes of all of the reagents that were mixed.

Syringe techniques were used in some of the runs, and by these means the first significant point could be taken about 10 sec after mixing. In others, an all-glass apparatus similar to that described by Zwickel[14] was used; with this technique the first significant point on a run could be obtained about 1.5 min after mixing. In the experiments using Cr^{51}, the radioactive chromous ion solution was added to a deaerated chromium(III) solution using the all-glass apparatus, and then, at various time intervals, aliquots of this solut on were removed through a serum-capped neck on the flask by means of a syringe. Great care had to be taken to ensure that the nitrogen stream was completely deoxygenated. Thus, instead of the usual rubber tubing, through which atmospheric oxygen can diffuse, the nitrogen line was constructed completely of Pyrex glass tubing, connected by ball joints to give it flexibility. As an added precaution, a venting stopcock was placed just before the stopcock on the reaction vessel, and the entire line was vented through it before letting nitrogen enter the reaction mixture so that a sample could be taken. Using this apparatus, it was shown that samples could be taken for a period of over 12 hr with no significant loss of reducing power.

Tracer Experiments.—Aliquots of the chromium(II)–chromium(III) isotope-exchange reaction mixture were quenched by injecting them into a deoxygenated solution of 0.06 *F* $HClO_4$ and 0.01 *F* $(NH_3)_5CoC_2O_4H^{2+}$, the number of mmoles of Co(III) being about 10% greater than the number of mmoles of Cr^{2+} being injected. Chromium(II) reacts quickly and quantitatively with the binoxoalato complex to give $CrC_2O_4^+$,[15] while $CrOAc^{2+}$ is unaffected by this procedure. The quenched solution was added to a Dowex 50-X2 ion-exchange column and the components were separated. The 1+ fraction had the specific activity of the chromium(II) in the reaction mixture, and the 2+ fraction had the specific activity of the $CrOAc^{2+}$.

Results

Spectra and Stoichiometry.—In Figures 1 and 2 are compared the spectra of $CrOAc^{2+}$ to Cr^{3+} and V^{2+} to V^{3+}. Vanadium(III) was prepared by the reaction of equivalent amounts of vanadium(II) and vanadium(IV) under an atmosphere of nitrogen and then by waiting at least 4 hr for the system to come to equilibrium.[16] The V^{3+} spectrum is acid dependent.[17] It is tabulated at three different acid concentrations in ref 1, where also appear detailed tabulations of the spectra of the $CrOAc^{2+}$, Cr^{2+}, V^{2+},[17a] Co^{2+}, and Cr^{3+} ions.

The product of the acid-catalyzed, chromous-catalyzed, and vanadous-catalyzed aquations of $CrOAc^{2+}$ was confirmed to be Cr^{3+} by comparing the total absorbance change of the reaction mixture to that expected from calculations using the known extinction coefficients of $CrOAc^{2+}$ and Cr^{3+}. This was done at the two $CrOAc^{2+}$ peak wavelengths (410 and 570 mμ) and in the vanadous-catalyzed aquation also at the V^{2+}–V^{3+} isosbestic wavelength (534 mμ). Ion-exchange experiments also showed that the only detectable chromium(III) product of the acid-catalyzed aquation of $CrOAc^{2+}$ was the hexaaquochromium(III) ion.

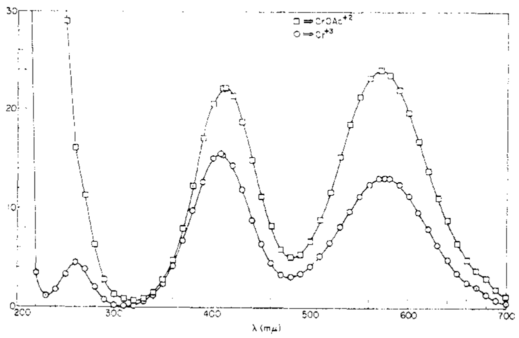

Figure 1.—Absorption spectra of the hexaaquochromium(III) and acetatopentaaquochromium(III) ions in $HClO_4$ at 25°. For Cr^{3+}, $\mu = 0.45$, $(H^+) = 0.034$ *F;* for $CrOAc^{2+}$, $\mu = 0.61$, $(H^+) = 0.021$ *F*.

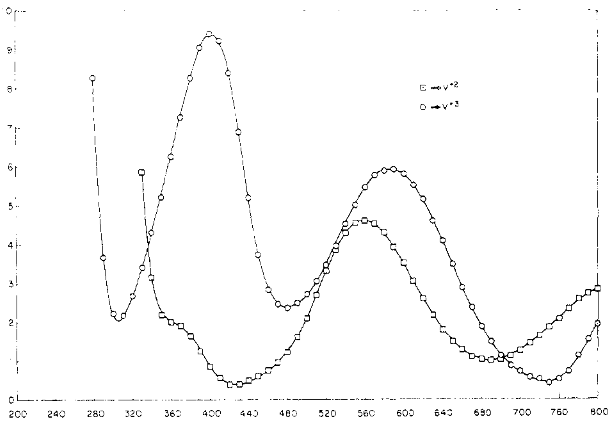

Figure 2.—Absorption spectra of the hydrated vanadium(II) and vanadium(III) ions in $HClO_4$ at 25°, $\mu = 1.00$, and $(H^+) = 0.100$ *F*.

Aquation of $CrOAc^{2+}$ at $\mu = 1.00$.—The rate of aquation of the $CrOAc^{2+}$ ion in acidic solutions, at 25° and $\mu = 1.00$, was determined spectrophotometrically at both 410 and 570 mμ and found to increase linearly with acid concentration in the range $(H^+) = 0.040$–0.970 *F* (see Figure 3). Acid-catalyzed aquation pathways have been observed for other monosubstituted chromium(III) complexes, $Cr(H_2O)_5X^{n+}$, where X is a basic ligand,[18–21] and thus the two-term rate law

$$\frac{-\mathrm{d}\ln(\mathrm{CrOAc}^{2+})}{\mathrm{d}t} = k_{\mathrm{obsd}} = k_1 + k_2'(\mathrm{H}^+) \qquad (1)$$

is not unexpected. The steps

$$\mathrm{CrOAc}^{2+} \xrightarrow{k_1} \mathrm{Cr}^{3+} \qquad (2)$$

$$\mathrm{H}^+ + \mathrm{CrOAc}^{2+} \xrightarrow{k_2'} \mathrm{Cr}^{3+} \qquad (3)$$

are sufficient to describe these observations. A least-squares analysis of the data shown in Figure 3 gives $k_1 = (0.41 \pm 0.15) \times 10^{-6}$ sec^{-1} and $k_2' = (7.70 \pm 0.30) \times 10^{-6}$ M^{-1} sec^{-1}, at 25° and $\mu = 1.00$.

Aquation of $CrOAc^{2+}$ at $\mu = 4.00$.—Figure 4 shows the acid dependence of the rate of aquation of the

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(14) A. M. Zwickel, Ph.D. Thesis, University of Chicago, 1959.

(15) H. J. Price and H. Taube, *Inorg. Chem.*, **7**, 1 (1968).

(16) A. Adin and A. G. Sykes, *J. Chem. Soc., A*, 1230 (1966).

(17) S. C. Furman and C. S. Garner, *J. Am. Chem. Soc.*, **72**, 1785 (1950).

(17a) NOTE ADDED IN PROOF.—These data are in good agreement with the V^{2+} spectrum determined by J. W. Malin and J. H. Swinehart, *Inorg. Chem.*, **7**, 250 (1968).

(18) T. W. Swaddle and E. L. King, *ibid.*, **4**, 532 (1965) ($X = F^-$).

(19) D. K. Wakefield and W. B. Schaap, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 12, 1967, Abstract L96 ($X = CN^-$); J. P. Birk and J. H. Espenson, *Inorg. Chem.*, **7**, 991 (1968) ($X = CN^-$).

(20) T. B. Swaddle and E. L. King, *ibid.*, **3**, 234 (1964) ($X = N_3^-$).

(21) J. E. Finholt and S. N. Deming, *ibid.*, **6**, 1533 (1967) ($X = SO_4^{2-}$).

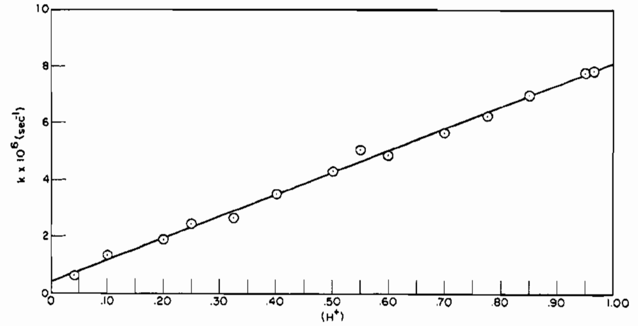

Figure 3.—Plot of k_{obsd} *vs.* (H^+) for aquation of the acetatopentaaquochromium(III) ion at 25° and μ = 1.00. Each point is the average of two runs, one at 570 and one at 410 mμ.

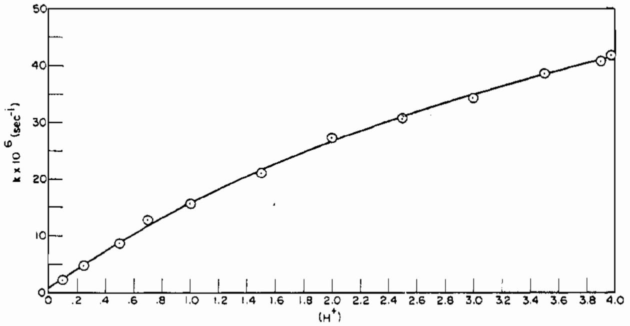

Figure 4.—Plot of k_{obsd} *vs.* (H^+) for aquation of the acetatopentaaquochromium(III) ion at 25° and μ = 4.00. Each point is the average of two runs, one at 570 and one at 410 mμ. The line is the least-squares fit calculated by computer.

$CrOAc^{2+}$ ion at 25°, μ = 4.00, in the range (H^+) = 0.10–3.97 *F*. When the measurements are carried out to high concentrations of acid, k_{obsd} is no longer strictly linear in (H^+) but instead the slope of the curve now continuously decreases as higher acid concentrations are used. It is suggested that this behavior is due to a protonation equilibrium involving the $CrOAc^{2+}$ ion, *i.e.*

$$CrOAcH^{3+} \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + CrOAc^{2+} \tag{4}$$

Incorporating this equilibrium into the mechanism and rewriting the k_2' step in the kinetically equivalent form

$$CrOAcH^{3+} \xrightarrow{k_2} Cr^{3+} \tag{5}$$

leads to the rate law

$$\frac{-d \ln (Cr_T)}{dt} = k_{obsd} = \frac{k_1 + k_2(H^+)/K_a}{1 + (H^+)/K_a} \tag{6}$$

where (Cr_T) represents the total concentration of the acetatopentaaquochromium(III) complex in both the protonated and unprotonated forms. At ionic strength 1.00, linearity is observed in the plot of k_{obsd} *vs.* (H^+) because $(H^+)/K_a \ll 1$ and the rate law then reduces to

$$k_{obsd} = k_1 + \frac{k_2(H^+)}{K_a} \tag{7}$$

where k_2' is equal to k_2/K_a.

The concentration quotient K_a is related to the thermodynamic equilibrium constant K_a' by the ratio of the activity coefficients of the species involved

$$K_a' = K_a \frac{\gamma_{H^+}\gamma_{CrOAc^{2+}}}{\gamma_{CrOAcH^{3+}}} \tag{8}$$

Arguments presented later suggest that this ratio of activity coefficients remains constant as the medium is changed from 4 *F* $LiClO_4$ to 4 *F* $HClO_4$; thus K_a will be an apparent constant for the medium under discussion (μ = 4.00).

At sufficiently high acid concentrations the $CrOAc^{2+}$ ion will be completely protonated and the rate law for aquation reduces to $k_{obsd} = k_2$. Unfortunately, the solubility of $LiClO_4$ (around 4.2 *F* at 20°) imposes an upper limit of 4.0 on the ionic strength that can be used, and so the highest acid concentration studied was 3.97 *F* which is insufficient to protonate the acetato complex completely and make the aquation rate independent of acid. Since k_2 could not be experimentally determined, a computer optimization program was used to calculate the values of the parameters k_1, k_2, and K_a which best describe the data (collected at four different temperatures). Rate constants calculated from the optimized values of k_1, k_2, and K_a differed an average of 2.2% from the observed rate constants, no systematic trend being noted in the deviations. In Figure 4 the smooth curve results when the optimized rate parameters are used to calculate values of k_{obsd}. The uncertainties in the calculated values of the parameters are estimated as ±2% for k_1, ±4% for k_2, and ±10% for K_a.

Figures 5 and 6 show the Eyring plots for k_1 and k_2. The data for k_2 lie on a straight line which gives a $\Delta H_2^{\ddagger}$ of 18.6 ± 1.0 kcal/mol, and a $\Delta S_2^{\ddagger}$ of −14.6 ± 3.3 eu, but the plot for k_1 shows a marked curvature that is far outside the limits of experimental error. Between 55 and 45° the chord corresponds to $\Delta H_1^{\ddagger}$ = 33 kcal/mol, and between 35 and 25°, to $\Delta H_1^{\ddagger}$ = 13 kcal/mol. The points in the plot of log K_a *vs.* $1/T$ are so scattered that no significant line can be drawn through them. All that can be said is that the enthalpy change of reaction 4 (ΔH_a) probably lies in the range 0 to −2 kcal/mol.

The interpretation of the kinetic data at ionic strength 4.00 which has been advanced might be questioned on the basis that nothing is known about the activity coefficients of the species involved in the reaction. Thus the nonlinearity of the rate plot in Figure 4 might be due to an activity effect, produced by changing the solvent from 4 *F* $LiClO_4$ to 4 *F* $HClO_4$, and not caused by a protonation equilibrium at all. This argument must be taken seriously since it was not possible to raise the acid concentration high enough to make the observed rate constant independent of acid. (Assuming that the protonation hypothesis is correct, less than 50% of the $CrOAc^{2+}$ is in the protonated form at the highest acid concentration studied.) The following arguments are presented in defense of our interpretation.

(1) Lithium ion closely resembles hydrogen ion in

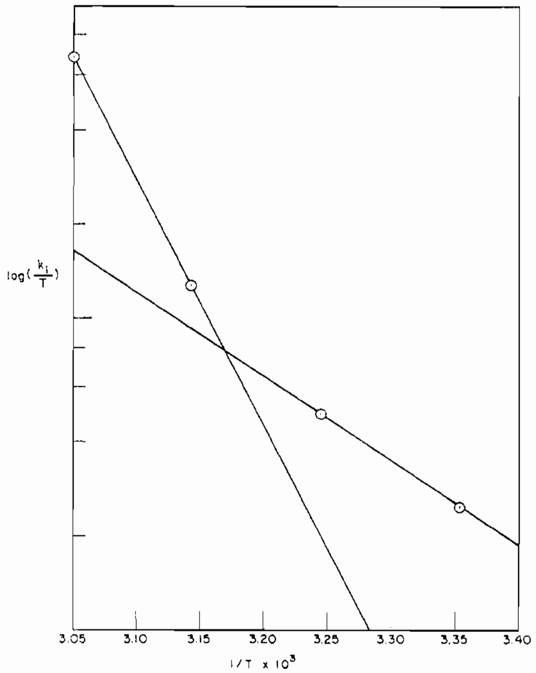

Figure 5.—Eyring plot of rate data for the acid-independent aquation of the acetatopentaaquochromium(III) ion at μ = 4.00.

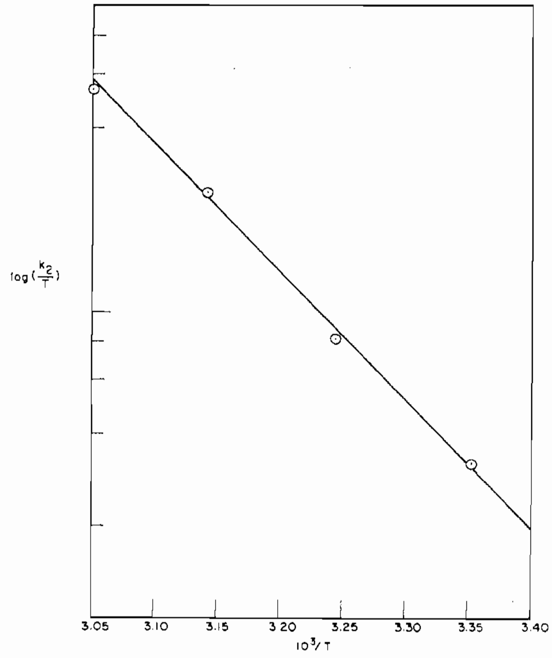

Figure 6.—Eyring plot of the rate data for the aquation of the protonated acetatopentaaquochromium(III) ion at μ = 4.00.

thermodynamic properties as evidenced by tables of osmotic coefficients.[22]

(2) The mean activity coefficient of HCl remains constant in LiCl–HCl mixtures of constant ionic strength.[23] This fact, coupled with the equation developed by Glueckauf,[24] suggests that the activity coefficients of ionic species in $LiClO_4$–$HClO_4$ mixtures of constant ionic strength are reasonably constant.

(3) Acidity function measurements, made recently by Day and Wyatt,[25] show that in $LiClO_4$–$HClO_4$ mixtures of constant ionic strength (both 3 and 6 F) the activity of water remains a constant, and h_0 is a linear function of acid concentration (Hammett acidity function = H_0 = $-\log h_0$).

(4) Wakefield and Schaap[19] have observed the same kind of protonation equilibrium in the aquation of the cyanopentaaquochromium(III) ion.

(5) Stritar[26] has observed the same kind of protonation equilibrium in the aquation of the acetato- and formatopentaammineruthenium(II) ions. In these cases, the rate of aquation becomes independent of acid at an acid concentration so low (0.08 F for the acetato complex at μ = 0.10) that the activity effect arguments which might be advanced against the interpretation of our data lose their force.

(6) Spectral measurements show that there is an interaction between protons and $CrOAc^{2+}$ that does not exist between protons and $CrCl^{2+}$.

Spectral Study of $CrOAc^{2+}$ at μ = 4.00.—Any determination of the apparent equilibrium constant K_a involves the assumption that the ratio of activity coefficients $\gamma_{H^+}\gamma_{CrOAc^{2+}}/\gamma_{CrOAcH^{3-}}$ remains constant in the media under consideration. When K_a is derived from kinetic data (as above), it is also necessary to assume that $\gamma_{H}\text{-}\gamma_{CrOAc^{2+}}/\gamma_{\ddagger}$ remains constant, where $\gamma_{\ddagger}$ is the activity coefficient for the activated complex of the acid-catalyzed aquation pathway. The need to make this assumption has been avoided by deriving K_a from spectral data.

As Table I shows, the visible absorption spectra of chromium(III) ions vary markedly when the medium is changed from water to 10.4 F $HClO_4$. However, when the medium changes from 4 F $LiClO_4$ to 4 F $HClO_4$, neither the spectrum of Cr^{3+} nor that of $CrCl^{2+}$ changes, but that of $CrOAc^{2+}$ is significantly affected (see Figure 7). If it is assumed that, as the concentration of acid is increased, $CrOAc^{2+}$ is converted to the protonated form, the relationship

$$\epsilon_\lambda^{\mathrm{obsd}} = \frac{\epsilon_\lambda^{\mathrm{CrOAc}^{2+}} + [(\mathrm{H}^+)/K_a]\,\epsilon_\lambda^{\mathrm{CrOAcH}^{3+}}}{1 + [(\mathrm{H}^+)/K_a]}$$

applies. The extinction coefficients of the protonated form cannot be directly determined at ionic strength 4.00, because even at the highest acidity possible, $CrOAc^{2+}$ is only partly protonated and those determined in 10.4 F $HClO_4$ cannot be applied to this medium because of the sensitivity of chromium(III) spectra to medium changes (see Table I). Therefore, the previously described computer program was used to calculate the values of K_a, $\epsilon_\lambda^{\mathrm{CrOAc}^{2+}}$, and $\epsilon_\lambda^{\mathrm{CrOAcH}^{3+}}$ which best fit the observed data. Extinction coefficients calculated using the otpimized values of $\epsilon_\lambda^{\mathrm{CrOAc}^{2+}}$, $\epsilon_\lambda^{\mathrm{CrOAcH}^{3+}}$, and K_a differed an average of 0.08% from the observed extinction coefficients. The lack of a systematic trend in this difference is internal support for the form of the equation which was used to calculate extinc-

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[22] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworth and Co. Ltd., London, 1955, p 468.

[23] H. S. Harned, *J. Am. Chem. Soc.*, **48**, 326 (1926).

[24] E. Glueckauf, *Nature*, **163**, 414 (1949).

[25] J. S. Day and P. A. H. Wyatt, *J. Chem. Soc., B*, 343 (1966).

[26] J. A. Stritar, Ph.D Thesis, Department of Chemistry, Stanford University, 1967.

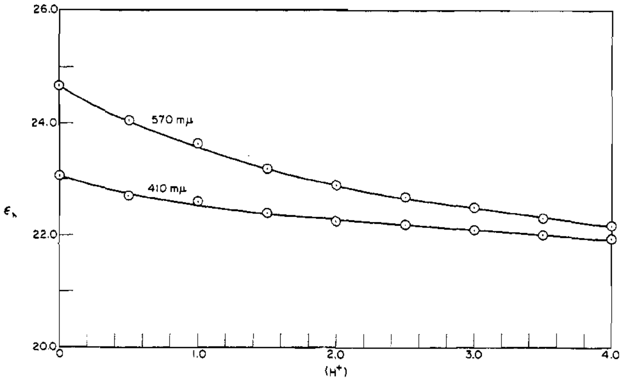

Figure 7.—Plot of the extinction coefficients of the acetatopentaaquochromium(III) ion *vs.* (H^+) at 25° and $\mu = 4.00$. Points are experimental; the smooth curves are the least-squares fits calculated by computer.

TABLE I

EXTINCTION COEFFICIENTS OF CHROMIUM(III) IONS IN WATER AND 10.4 F $HClO_4$[a]

		ϵ, M^{-1} cm^{-1}	
Ion	λ, mμ	H_2O	10.4 F $HClO_4$
Cr^{3+}	410	15.8	16.4
Cr^{3+}	570	13.3	13.5
$CrCl^{2+}$[b]	428	20.9	23.2
$CrCl^{2+}$[b]	608	16.5	15.4
$CrOAc^{2+}$	410	22.2	21.0
$CrOAc^{2+}$	570	24.4	19.8

[a] The extinction coefficients in 10.4 F $HClO_4$ were determined within *ca.* 2 min after mixing. [b] These results are in good agreement with those reported by J. E. Finholt, K. G. Caulton, and W. J. Libbey, *Inorg. Chem.*, **3**, 1801 (1964).

tion coefficients and, therefore, for the original assumption of a protonation equilibrium. The uncertainties in the optimized values of the parameters are estimated as ±1% for $\epsilon_\lambda^{CrOAc^{2+}}$, ±2% for $\epsilon_\lambda^{CrOAcH^{3+}}$, and ±6% for K_a. The values of K_a determined at 410 and 570 mμ agree within this error estimate and it is concluded that, as measured spectrophotometrically, $K_a = 3.25 \pm 0.20$ F at 25° and $\mu = 4.00$ ($\epsilon_{410}^{CrOAcH^{3+}}$ 21.1; $\epsilon_{410}^{CrOAc^{2+}}$ 23.0; $\epsilon_{570}^{CrOAcH^{3+}}$ 20.2; $\epsilon_{570}^{CrOAc^{2+}}$ 24.7).

The value of K_a at 25° and $\mu = 4.00$, determined by the kinetic method, is 5.3 ± 0.5 F. The disagreement between this and the spectrophotometric value may come about because of the failure of the condition on $\gamma_\pm$ required by the kinetic method, and, on this basis, the spectrophotometrically determined value of K_a would seem to be the more reliable one. However, because of our limited knowledge of the activity coefficients in these media, it cannot be claimed that we know the value of K_a to any better than an order of magnitude by either method. The error limits on the values of K_a determined by the two methods are limits of precision and not estimates of accuracy. Therefore, we can only say that it is very probable that protonation of the $CrOAc^{2+}$ ion does take place, and the value of K_a(25°, $\mu = 4.00$) is around 4 F.

Using the values of $\epsilon^{CrOAc^{2+}}$ and $\epsilon^{CrOAcH^{3+}}$ calculated at $\mu = 4.00$ as estimates of the extinction coefficients at other ionic strengths, the following estimates of K_a(25°) were made: at $\mu = 4.00$, $K_a = 3.2$; at $\mu = 5.2$, $K_a = 1.3$; at $\mu = 6.0$, $K_a = 0.4$. With this trend it is reasonable that no deviation from linearity was observed in the rate plot at $\mu = 1.00$ (Figure 3), because at this ionic strength $CrOAcH^{3+}$ should be a very strong acid and even in 1 F $HClO_4$ probably less than 5% of the total acetatochromium(III) exists in the protonated form.

Aquation of $CrOAc^{2+}$ in $HClO_4$–H_2O Mixtures.—Figure 8 shows the variation in the rate of aquation of acetatopentaaquochromium(III) as a function of acid concentration, the ionic strength changing with the concentration of the acid. The initial increase in rate with increasing $(HClO_4)$ is, of course, expected from the previous aquation studies. However, the decrease in rate as $(HClO_4)$ is increased from 5 to 10.7 F must be due to another effect. It is hypothesized that, in this range of solvent compositions, water is a limiting reagent rather than a reagent that is present in great excess, as is usual in reactions carried out at lower ionic strengths. This is supported by the observation that in the range 6–8 F $HClO_4$ the rate of aquation is proportional to the activity of water in the solvent[27] (see Figure 9) and at least in this narrow range of solvent composition the rate law can be written as

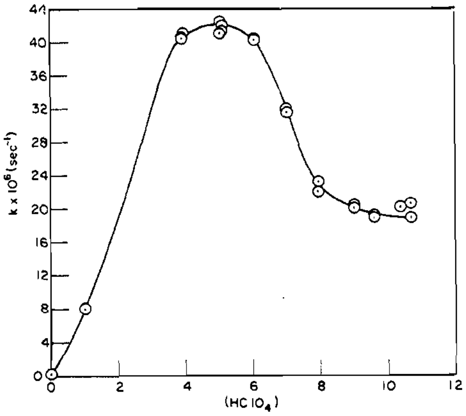

Figure 8.—The rate of aquation of the acetatopentaaquochromium(III) ion as a function of $HClO_4$ concentration at 25°, μ varying with $(HClO_4)$.

$$\frac{-d(Cr_T)}{dt} = k_{obsd}(CrOAc^{3+})a_{H_2O} \qquad (9)$$

This type of rate law has been described before by Jones and Bjerrum,[28] who report

$$\frac{d(CrClO_4^{2+})}{dt} = k_b'(Cr^{3+} \cdot ClO_4^-) - k_{-b}(CrClO_4^{2+})a_{H_2O}$$

as the rate law for the formation of the monoperchloratochromium(III) ion in concentrated perchloric acid solutions (5–10 F).

Aquation of $CrOAc^{2+}$ Catalyzed by Cr^{2+}.—Figures 10 and 11 show how the specific rate for the aquation of $CrOAc^{2+}$ (defined as $-d \ln (CrOAc^{2+})/dt$) in the presence of Cr^{2+} depends on the concentration of Cr^{2+} and of H^+. It is clear from the evidence that the Cr^{2+}-

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(27) R. A. Robinson and O. J. Baker, *Trans. Roy. Soc. New Zealand*, **76**, 250 (1946).

(28) K. M. Jones and J. Bjerrum, *Acta Chem. Scand.*, **19**, 974 (1965).

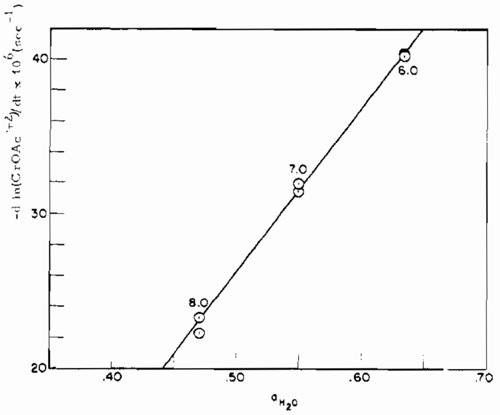

Figure 9.—The rate of aquation of the acetatopentaaquochromium(III) ion as a function of water activity in the media 6-8 F $HClO_4$ at 25°.

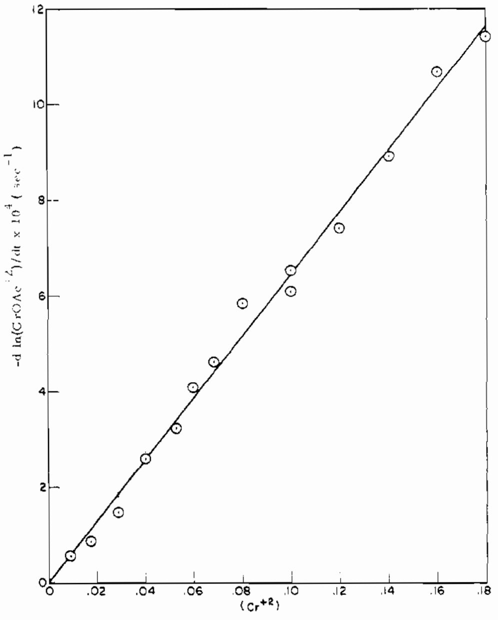

Figure 10.—The variation of the rate of the Cr^{2+}-catalyzed reaction with (Cr^{2+}) at 25°, μ = 1.00, and (H^+) = 0.040 F. The specific rates have been corrected for spontaneous reaction.

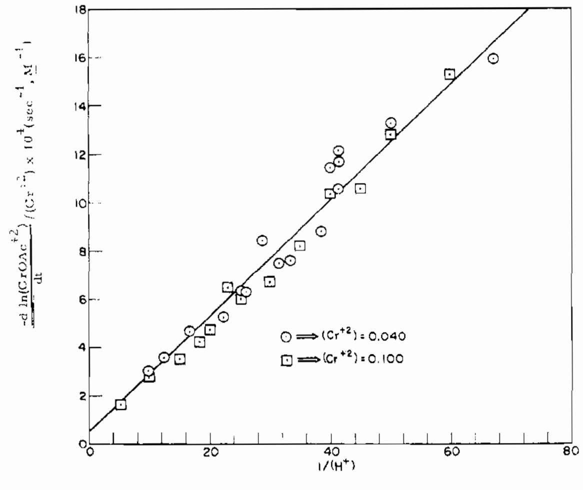

Figure 11.—The rate of the Cr^{2+}-catalyzed reaction as a function of $1/(H^+)$. The specific rates have been corrected for spontaneous reaction. Conditions: 25°, μ = 1.00.

catalyzed reaction is governed by a rate law of the form

$$-\mathrm{d}\ln(\mathrm{CrOAc}^{2+})/\mathrm{d}t = \left[k_0 + \frac{A}{(\mathrm{H}^+)}\right](\mathrm{Cr}^{2+}) \qquad (10)$$

The data in Figures 10 and 11 have been corrected by subtracting from the observed rate the part contributed by the intrinsic aquation reaction. The present data were obtained at μ = 1.00 but $\Delta H^{\ddagger}$ for the intrinsic aquation was obtained only at μ = 4.00. In making the corrections at μ = 1.00, $\Delta H^{\ddagger}$ was assumed to be independent of ionic strength. This assumption is, of course, only approximately valid, but it is adequate because the intrinsic aquation under the conditions studied contributes only a small fraction (almost always much less than 5%) of the total reaction, and even a 50% error in calculating its contribution would not significantly affect the results.

The parameters $k_0 \times 10^5$ (M^{-1} sec^{-1}) and $A \times 10^5$ (sec^{-1}) in eq 10 for data at 25.0, 45.0, and 55.0° were determined as 1.56 ± 0.08 and 2.46 ± 0.10, 27.3 ± 1.4 and 24.0 ± 1.0, 104 ± 6 and 81.6 ± 4.0. The Eyring plots are satisfactory and yield the following values of the activation parameters: $\Delta H_0^{\ddagger}$ = 26.7 ± 1.5 kcal/mol; $\Delta S_0^{\ddagger}$ = +9.0 ± 4.0 eu; $\Delta H_A^{\ddagger}$ = 22.1 ± 2.0 kcal/mol; $\Delta S_A^{\ddagger}$ = −5.5 ± 5.0 eu.

The Exchange of Chromium between Cr^{2+} and $CrOAc^{2+}$.—The study of the Cr^{2+}–$CrOAc^{2+}$ exchange reaction is complicated by the aquation of $CrOAc^{2+}$. Though the intrinsic aquation rate is too slow to affect the data, the contribution by the V^{2+}-catalyzed reaction is significant even though vanadium, which enters as the decay product of Cr^{51}, is very low in concentration, *i.e.*, of the order of 10^{-10} to 10^{-6} M. In addition, the exchange of Cr^{2+} with Cr^{3+} is slow enough so that the assumption that Cr^{2+} is always in isotopic equilibrium with Cr(III) does not apply. The difficulties arising from these complications were circumvented, following Norris,[29] by expressing $1 - F$ [defined by the McKay equation, $R = (-2.303/t)(ab/(a + b)) \log (1 - F)$, where R is the rate of the reaction carrying the exchange, $a \equiv (^*\mathrm{CrOAc}^{2+}) + (\mathrm{CrOAc}^{2+})$, $b \equiv (^*\mathrm{Cr}^{2+}) + (\mathrm{Cr}^{2+})$] as $(y - x)/(y_0 - x_0) = (y - x)/y_0$ when, as in our case, $x_0 = 0$. Here $x = (^*\mathrm{CrOAc}^{2+})$, $y = (^*\mathrm{Cr}^{2+})$ at a time t, and the subscript 0 specifies $t = 0$. In a given experiment the plot of $-\log [(y - x)/y_0]$ *vs.* time is a straight line, and the slope moreover is identical with the initial slopes obtained when the data for the disappearance of radioactivity from Cr^{2+} $[1 - F = (y_\infty - y)/(y_\infty - y_0)]$ or for the appearance in $CrOAc^{2+}$ $[1 - F = (x - x_\infty)/(x_0 - x_\infty) = 1 - (x/x_\infty)$, since $x_0 = 0]$ are plotted *vs.* time. In the latter cases, owing to the complications referred to, deviations from linearity do occur as the reaction progresses.

The rate data for chromium exchange between Cr^{2+} and $CrOAc^{2+}$ are summarized in Table II. The specific rate k is calculated from the assumed rate law: $R = k(\mathrm{Cr}^{2+})(\mathrm{CrOAc}^{2+})$. Experiments 3–6 show that this rate law correctly describes the variation of rate with

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[29] T. N. Norris, *J. Phys. Colloid Chem.*, **54**, 777 (1950).

TABLE II

RATE DATA FOR THE Cr^{2+}–$CrOAc^{2+}$ ISOTOPE-EXCHANGE REACTION (μ = 1.00)

Run no.	$(a + b)^a$	(Cr^{2+}), M	Temp, °C	(H^+), M	10^3k, M^{-1} sec^{-1}	10^3k^{ex}, sec^{-1}
3	0.0838	0.0500	25.0	0.200	2.95	0.590
4	0.0630	0.0260	25.0	0.200	2.70	0.540
5	0.1093	0.0521	25.0	0.200	2.90	0.580
6	0.1064	0.0521	25.0	0.200	2.79	0.558
7	0.0640	0.0326	25.0	0.500	1.02	0.510
8	0.0650	0.0326	25.0	0.100	5.67	0.567
9	0.0517	0.0260	25.0	0.050	11.7	0.585
10	0.0696	0.0339	35.0	0.580	2.90	1.68
11	0.0700	0.0339	35.0	0.200	8.65	1.73
12	0.0370	0.0177	35.0	0.100	16.1	1.61
13	0.0370	0.0177	35.0	0.067	24.4	1.64
14	0.0847	0.0434	15.0	0.100	1.83	0.183
15	0.0855	0.0434	15.0	0.067	2.36	0.158
16	0.0877	0.0434	15.0	0.050	3.50	0.175
17	0.0877	0.0434	15.0	0.200	0.78	0.156

[a] See text for definition.

(Cr^{2+}) and $(CrOAc^{2+})$ at constant (H^+) and they provide a measure of the precision in the values of k as ±3%. In the final column are entered the values of k^{ex} calculated as the product $k(H^+)$. The rate law for the exchange reaction is evidently of the form

$$R = k^{ex}\frac{(Cr^{2+})(CrOAc^{2+})}{(H^+)} \tag{11}$$

with the upper limit on the coefficient for an acid-independent term at 25° as $6 \times 10^{-5}\ M^{-1}\ sec^{-1}$.

In Figure 12 the isotopic-exchange data are shown in an Eyring plot. This plot yields the activation parameters $\Delta H^{\ddagger}_{ex}$ = 18.9 ± 0.9 kcal/mol and $\Delta S^{\ddagger}_{ex}$ = −10.0 ± 3.0 eu.

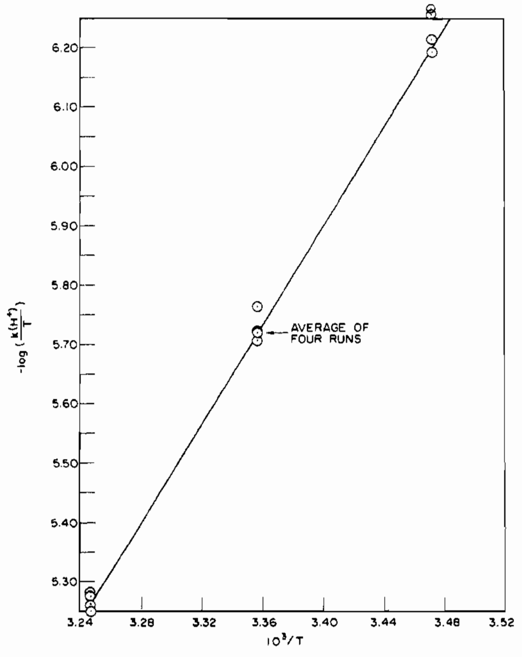

Figure 12.—Eyring plot for the Cr^{2+}–$CrOAc^{2+}$ isotope-exchange reaction at μ = 1.00.

The Cr^{2+}–Cr^{3+} Isotopic-Exchange Reaction.—The Cr^{2+}–Cr^{3+} exchange reaction was studied by Anderson and Bonner.[30] The mechanism for the exchange has not been established, but because it can, in principle, be determined by a comparison of the rate of chromium exchange with that of the exchange of H_2O between $Cr(H_2O)_6^{3+}$ and solvent as catalyzed by Cr^{2+} and because the relevant data need to be determined accurately, it seemed worthwhile to repeat the measurements. We hoped, moreover, that our quenching procedure, which we think is an improvement over theirs, would put us in position better to fix the value of the rate for the (H^+)-independent term.

Our data are summarized in Figure 13. They may be interpreted as was done in drawing in the lower line, thus leaving scope for a term inverse in $(H^+)^2$ at low (H^+). On this basis k^{ex} is calculated as (1.07 ± 0.05) × 10^{-4} sec^{-1} for the range $1/(H^+)$ = 2.0–12.5 F^{-1}. On the other hand, all of the data points can be represented by the upper line of the graph corresponding to k^{ex} = (1.14 ± 0.03) × 10^{-4} sec^{-1} over the range $1/(H^+)$ = 2.0–20.5 F^{-1}. These values are to be compared to Anderson and Bonner's specific rate of 1.04 × 10^{-4} sec^{-1} in the range $1/(H^+)$ = 1–5 F^{-1}, showing gratifying agreement in the two sets of measurements. We must, moreover, admit that we have not in this series of experiments improved on the upper limit of 2 × 10^{-5} F^{-1} sec^{-1} which Bonner and Anderson place on the specific rate for the (H^+)-independent term.

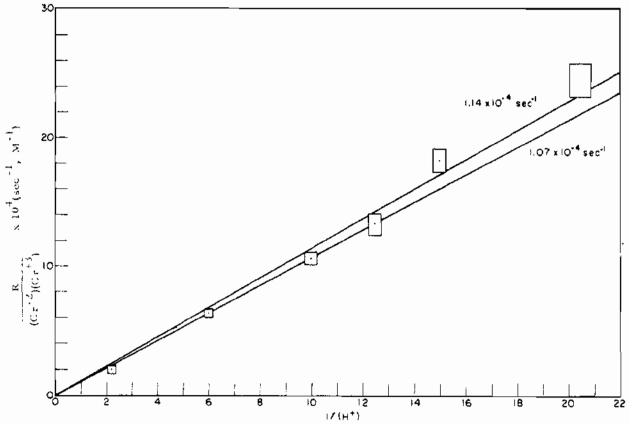

Figure 13.—The rate of the Cr^{2+}–Cr^{3+} isotope-exchange reaction *vs.* $1/(H^+)$. Conditions: 25°, μ = 1.00, (Cr^{2+}) = 0.052 F, (Cr^{3+}) = 0.054 F. Error limits: ±2% in the abscissa; ±5% in the ordinate.

The Determination of the Acid Dissociation Constants of Cr^{3+} and $CrOAc.^{2+}$—If a rate law of the kind shown in eq 10 or 11 is to be interpreted in terms of the concentration of $Cr(OH)OAc^+$, the equilibrium constant K_{CrOAc} for the reaction

$$(H_2O)_5CrOAc^{2+} = (H_2O)_4Cr(OH)Ac^+ + H^+ \tag{12}$$

must be determined. To develop and test the method of determining K_{CrOAc} it seemed in order also to determine the equilibrium constant K_{Cr} for the reaction

$$(H_2O)_5CrOH_2^{3+} = (H_2O)_5CrOH^{2+} + H^+$$

Values of K_{Cr} have been measured by many workers[31]

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(30) A. Anderson and N. A. Bonner, *J. Am. Chem. Soc.*, **76**, 3826 (1954).

(31) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," Special Publication No. 17, The Chemical Society, London, 1964, p 48.

but no extensive data have been collected at μ = 1.00.

K_{Cr} and K_{CrOAc} were determined by a titrimetric technique, using the readings on a pH meter (glass electrode) as an index of the concentration of (H^+). Elsewhere[1] we described how the pH meter readings were calibrated in terms of hydrogen ion concentration at μ = 1.00 (it should be noted here that in the calibration the conditions of the actual titration were simulated as much as possible, using electrolytes of similar charge type).

In one set of experiments a thermostated solution at μ = 1.00 containing Cr^{3+}, H^+, Li^+, and ClO_4^-, all at known concentrations, was titrated with a standardized solution of LiOH and $LiClO_4$ (μ = 1.00). The values of K_{Cr} calculated from the data over the range of 3–60% neutralization were satisfactorily constant and the average was taken to define the value of K_{Cr}. At a small percentage of neutralization, the results are expected to be inherently inaccurate; when the extent of neutralization is large, K_{Cr} tends to increase and this effect can be ascribed to the condensation of Cr(III) which produces excess acid. Data were gathered at various temperatures and these are summarized in Table III.

TABLE III

COMPARISONS OF K_{Cr} AND K_{CrOAc}

Temp, °C	$-$Log K_{Cr}[a]	$-$Log K_{Cr}[b]	$-$Log K_{CrOAc}[c]
25.0	4.35 ± 0.03	4.40 ± 0.05	4.54 ± 0.10
35.0	4.12 ± 0.05	4.18 ± 0.06	4.41 ± 0.10
45.0	3.95 ± 0.03	4.01 ± 0.06	4.28 ± 0.10
55.0	3.79 ± 0.04	3.83 ± 0.05	4.17 ± 0.10

[a] Determined at (ClO_4^-) = 0.88 *F*; μ ranges from 1.00 ot 0.92 during titration. [b] Determined at μ = 1.00; (ClO_4^-) ranges from 0.88 to 0.96 *F* during titration. [c] μ = 1.00; (ClO_4^-) = 0.90 *F* throughout titration.

The experiments done as described correspond to (ClO_4^-), rather than to μ, being constant during the course of a titration. Another set of experiments was done keeping μ constant by using just enough $LiClO_4$ in the LiOH solution to account for the loss in ionic strength resulting from the conversion by OH^- of a +3 to a +2 ion. In these runs (ClO_4^-) varied from 0.88 *F* at the beginning to 0.96 *F* at the end of the titrations. Done in this way, the titrations had much smaller regions of constant K_{Cr} than did the previous set, and K_{Cr} decreased rather than increased toward the end of the titration.

The values of ΔH and ΔS calculated from the data at constant (ClO_4^-) = 0.88 *F* are 7.7 ± 0.9 kcal/mol and 5.9 ± 3.0 eu; from the data at constant μ = 1.00 they are 8.3 ± 1.6 kcal/mol and 7.5 ± 5.4 eu. Our determinations agree well with literature values reported for comparable media. Schaffer[32] gives $-\log K_{Cr}$ = 4.38 in 1 *F* $NaNO_3$. Postmus and King[33] determined ΔH to be 9.4 ± 0.4 kcal/mol, assuming that ΔH is independent of μ, and showed that ΔS = 13.5 eu at μ = 0.48 and that it decreases as μ increases.

The dissociation constant, K_{CrOAc}, of $CrOAc^{2+}$ was also determined by the titrimetric procedure. During a titration the concentration of ClO_4^- was kept at 0.90 *F* and ionic strength at 1.00. This was accomplished by titrating with a solution in which the concentration of Ba^{2+} exactly equaled the concentration of OH^-. A typical titrating solution had the composition: (Ba^{2+}) = 0.040 *F;* (OH^-) = 0.040 *F;* (Li^+) = 0.860 *F;* (ClO_4^-) = 0.900 *F*. To simulate the conditions of a kinetic run with Cr^{2+} present, Ba^{2+} was added also to the $CrOAc^{2+}$ solution. A typical composition for the latter was: ($CrOAc^{2+}$) = 0.020 *F;* (Ba^{2+}) = 0.080 *F;* (Li^+) = 0.694 *F;* (H^+) = 0.006 *F;* (ClO_4^-) = 0.900 *F*.

Polymerization is a much more serious problem during the titration of $CrOAc^{2+}$ than it was during the Cr^{3+}. Even at 1°, the titration could be carried usefully to only 50% neutralization and at 55°, to only about 8%, and thus the results are less precise than for Cr^{3+}. The data obtained in 25 experiments using three different preparations of $CrOAc^{2+}$ are shown in Figure 14, where $-\log K_{CrOAc}$ is plotted *vs.* $1/T$. Though the points are widely scattered, the temperature range is large enough (0.1–55°) to permit the approximation of ΔH and ΔS as 5.5 ± 1.5 kcal/mol and −2 ± 5 eu.

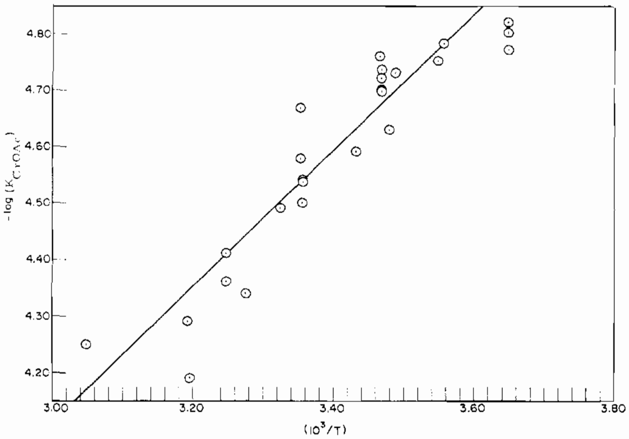

Figure 14.—Plot of $-\log$ (K_{CrOAc}) *vs.* $1/T$, at μ = 1.00. K_{CrOAc} = (H^+)($Cr(OH)OAc^+$)/($CrOAc^{2+}$).

The comparison in Table III shows $CrOAc^{2+}$ to be only slightly less acidic than Cr^{3+}, and if the trend in *K* with temperature were to continue, it would in fact become more acidic at low temperatures.

Vanadium(II)-Catalyzed Aquation of $CrOAc^{2+}$.—This system has proved to be unexpectedly complicated. Many of the complications are interesting in themselves, but unless they are directly germane to the original purpose of this part of the work, which was to determine the rates and rate law for the process $CrOAc^{2+} + H^+ \rightarrow Cr^{3+} + HOAc$, as catalyzed by V^{2+}, they will not be reported in detail here.

A complication which was expected and is easily dealt with is the reduction of ClO_4^- by V^{2+}. We determined the coefficient for the rate function (V^{2+}) (ClO_4^-) to be (7.6 ± 0.5) × 10^{-7} M^{-1} sec^{-1} at 25°, μ = 1.00, and (H^+) = 0.100 *F;* this is in reasonable agreement with

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(32) G. E. Schaffer, private communication to A. E. Martell in ref 31.
(33) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

the value of $5.26 \times 10^{-7}\ M^{-1}\ \text{sec}^{-1}$ at 25° obtained by Adin and Sykes[16] at $\mu = 2.00$ and $(H^+) = 0.50\ M$. Quite unexpected, however, was the fact that the rate of reduction of ClO_4^- by V^{2+} was greatly increased by either $CrOAc^{2+}$ or the mixture Cr^{3+} and HOAc. The effect amounts to as much as a factor of 1000 in the early stages of the reaction, but the rate eventually slows down to the normal value. The catalysis is strongly suppressed by Cr^{2+}, even though the net change now involves Cr^{2+} as reactant (note that Cr^{2+} reduces V^{3+} quite rapidly).

As appropriate, one or a combination of the following lines of strategy was adopted to minimize the effect of the catalysis of the reduction of ClO_4^-. (1) A high concentration of V^{2+} was used (this decreases the concentration of ClO_4^- needed to keep μ constant). (2) Reactions were followed at the V^{2+}–V^{3+} isosbestic point (534 mμ). (3) When the reaction was followed at 570 or 410 mμ, the Guggenheim[34] method was used to calculate the rate of reaction. These measures were effective enough so that there is no reason to believe that our results on the aquation rate of $CrOAc^{2+}$, catalyzed by V^{2+}, are seriously affected by the catalysis of the V^{2+}–ClO_4^- reaction referred to.

Quite apart from the interference which has been described, the kinetics of the aquation of $CrOAc^{2+}$ as catalyzed by V^{2+} are remarkably complex. As the concentration of the catalyst V^{2+} increases in a series of experiments with $(CrOAc^{2+}) \sim 0.005\ F$ and $(H^+) \sim 0.10\ F$, the following kind of behavior is observed. When $(V^{2+}) < 0.02\ F$ the kinetic plot describing the course of reaction 12 is a straight line except for a "hook" at the beginning indicating an initial, more rapid reaction. When (V^{2+}) is in the range 0.02–0.07 F, the initial portion describing a more rapid reaction is sufficiently extended to give a straight-line plot but is superseded by a slower portion (but slower by a factor of less than 2) which corresponds to the major part of the plot at the lowest (V^{2+}) concentrations. When $(V^{2+}) > 0.07\ F$, simple behavior is observed over the whole course of the reaction, and the slope corresponds to the early part of the plot at lower (V^{2+}). A qualitative, consistent interpretation of all of the observations can be given if we take the "rapid" reaction as measuring the intrinsic rate of the process

$$V^{2+} + CrOAc^{2+} \longrightarrow VOAc^{2+} + Cr^{2+} \qquad (13)$$

while the slower phase shows the response of the system to interference by the products of the reaction.

The validity of the law

$$\frac{-d(CrOAc^{2+})}{dt} = k_v(V^{2+})(CrOAc^{2+})$$

governing the rate of reaction 13 was tested over at least a 16-fold range in $CrOAc^{2+}$ concentration, as this decreases within a run, and V^{2+} concentrations covering the range 0.02–0.14 F. A summary of the results obtained on the kinetics of process 13 appears in Table IV.

TABLE IV

KINETIC PARAMETERS GOVERNING REACTION 13

($\mu = 1.00$; $(H^+) = 0.100$)

Temp, °C	k_v, M^{-1} sec^{-1}
15	0.104 ± 0.005
25	0.228 ± 0.011
35	0.477 ± 0.025

$\Delta H_v^{\ddagger} = 12.9 \pm 0.6$ kcal/mole

$\Delta S_v^{\ddagger} = -18.4 \pm 2.2$ eu

The specific rate k_v appears to be mildly sensitive to (H^+). The variation with (H^+) as determined by experiments covering the range 0.044–0.29 F is expressed by the rate law $k_v = k_0' + A'/(H^+)$, where at 25° and $\mu = 1.00$, $k_0' = 0.163 \pm 0.009\ M^{-1}\ \text{sec}^{-1}$, and $A' = (6.7 \pm 1.4) \times 10^{-3}\ \text{sec}^{-1}$. The contribution of the A' term is large enough so that the activation parameters shown in Table IV do not correspond exactly to those of the k_0' path.

When HOAc at 0.17 F, or V^{3+} at 0.02 F, is present in a solution with $(V^{2+}) = 0.105\ F$, $(H^+) = 0.100\ F$, and $\mu = 1.00$ at 25°, the initial specific reaction rate is unaffected but the specific rate declines after some reaction has taken place. The species HOAc and V^{3+} in combination exert a profound effect even in the early stages of the reaction and there is now continuous curvature in the rate plots in the direction of a declining specific rate. Chromous ion exerts a strong inhibiting effect which is felt at the very onset of the reaction.

Discussion

The Aquation of $CrOAc^{2+}$.—In common with the aquation reactions in acidic solution of carboxylate complexes of other metal ions,[35] that of $CrOAc^{2+}$ proceeds by parallel paths, one zero order and the other first order in (H^+). A point of interest is the position of bond breaking by each of the two paths. This question can probably be settled by a tracer experiment for the acid-assisted path, but even in the absence of the results of the direct experiment, there are strong arguments which point to the conclusion that, for this path, C–O bond cleavage occurs. The kinetic parameters for the acid-assisted aquations of the acetate complexes of $(NH_3)_5Co^{III}$, $(NH_3)_5Rh^{III}$, and $(NH_3)_5Ir^{III}$ are very much alike, and this argues for a common aquation mechanism for the three complexes.[35] The unit $(H_2O)_5Cr^{III}$ is remarkably similar to $(NH_3)_5Co^{III}$ in many substitution reactions, and it would be surprising to find a difference with acetate as a ligand. Moreover, the activation enthalpy for the process

$$H^+ + CrOAc^{2+} \longrightarrow Cr^{3+} + HOAc$$

is around 19 kcal/mol (the difference between $\Delta H_2^{\ddagger}$ and ΔH_a) and thus is reasonably close to the 16.4 kcal/mol observed[36] as the activation enthalpy for the similar process

$$H^+ + CH_3OAc \longrightarrow CH_3OH + HOAc$$

which of course proceeds by C–O bond fission. $\Delta H_2^{\ddagger}$ directly corresponds to the pseudo-first-order process

$$CrOAcH^{3+} + H_2O \xrightarrow{k_2} Cr^{3+} + HOAc$$

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(34) E. A. Guggenheim, *Phil. Mag.*, (7) **2**, 538 (1926).

(35) F. Monacelli, F. Basolo, and R. G. Pearson, *J. Inorg. Nucl. Chem.*, **24**, 1241 (1962).

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and its value of 18.6 ± 1.0 kcal/mol is considerably less than the 24–28 kcal/mol observed for the processes[37,38]

$$Cr(H_2O)_6^{3+} + H_2O^* \longrightarrow Cr(H_2O)_5(H_2O^*)^{3+} + H_2O$$

$$(H_2O)_5CrOHCH_3^{3+} + H_2O \longrightarrow Cr(H_2O)_6^{3+} + CH_3OH$$

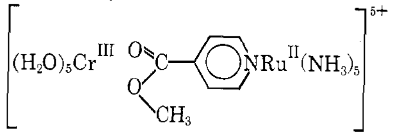
$$(H_2O)_5CrOHC_2H_5^{3+} + H_2O \longrightarrow Cr(H_2O)_6^{3+} + C_2H_5OH$$

which involve Cr–O bond cleavage. Thus, the acid-assisted aquation path probably proceeds *via* C–O bond fission.

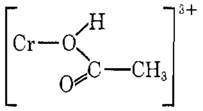
A point of some concern is that the value of $\Delta H^{\ddagger}$ we have determined is considerably less than that reported[35] for the acid-assisted aquation of $(NH_3)_5CoOAc^{2+}$, namely, 25 kcal/mol. In view of the general similarity of the rates already noted, this difference is surprising. It may be a consequence of the fact that the temperature range covered in our work was lower than that covered by Monacelli and coworkers, and there is the possibility that $\Delta H^{\ddagger}$ does change significantly with temperature, even though no trend with temperature is discernible in our data.

For the acid-independent path, $\Delta H_1^{\ddagger}$ is clearly a function of temperature, the activation energy increasing as the temperature rises. This suggests a change in mechanism as the temperature changes, C–O bond cleavage being dominant at low temperature and Cr–O bond cleavage taking over at the higher temperature.

In considering the association of $CrOAc^{2+}$ with H^+, it is of interest to learn whether the proton attaches to the carbonyl oxygen or the oxygen bound to chromium. By analogy to the case of a carboxyl group bound to $(NH_3)_5Co^{3+}$ [39] the two carboxyl oxygens in $CrOAc^{2+}$ are probably distinct. Though at first sight it seems more reasonable that the proton will be attached to the carbonyl oxygen, it is by no means certain that this is the case. Some interesting conclusions are suggested when the rate of aquation of $CrOAcH^{3+}$ is compared with that of ester complexes. The complex



is formed[40] when Cr^{2+} reduces the appropriate Ru(III) complex and the specific rate for aquation to Cr^{3+} by the (H^+)-independent path is 0.035 sec^{-1} at 25°. For the methyl acetate complex[41] of $(NH_3)_5Co^{3+}$, the specific rate for aquation appears to be greater than 0.02 sec^{-1}. These rates are much higher than the specific rate of aquation measured in this work for $CrOAcH^{3+}$, namely, 9.5×10^{-5} sec^{-1}, also at 25°. In view of the similar inductive effects of CH_3^+ and H^+, if CH_3^+ occupies a position in the ester complex equivalent to that occupied by H^+ in $CrOAcH^{3+}$, very similar reaction rates would be expected—particularly when Cr(III) complexes are compared. Since the complex formed by electron transfer probably has Cr(III) on the carbonyl oxygen, we incline to the view that the dominant form of $CrOAcH^{3+}$ has the structure



Reactions between Cr^{2+} and the $CrOAc^{2+}$ Ion.—Both the Cr^{2+}-catalyzed aquation of the acetatopentaaquochromium(III) ion and the isotopic-exchange reaction between Cr^{2+} and $CrOAc^{2+}$ proceed *via* an electron-transfer mechanism, the Cr^{2+} reducing the chromium(III) complex and thereby labilizing it. Since chromium–acetate bonds are conserved in the isotope-exchange reaction, this electron transfer must proceed by an inner-sphere mechanism with acetate as the bridging group

$$CrOAc^{2+} + {}^*Cr^{2+} \longrightarrow Cr\text{---}OAc\text{---}{}^*Cr^{4+} \longrightarrow Cr^{2+} + {}^*CrOAc^{2+}$$

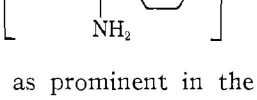
It is a reasonable assumption that the Cr^{2+}-catalyzed aquation of $Cr(H_2O)_5OAc^{2+}$ also proceeds by an inner-sphere mechanism, but now without participation by acetate as the bridging group. This assumption is supported by the strong preference which Cr^{2+} shows for reaction by an inner-sphere mechanism and the fact that both the acid-independent and inverse acid paths for the Cr^{2+} reduction of $(NH_3)_5CoO^{18}H_2^{3+}$ lead to incorporation of H_2O^{18} in the coordination sphere of the chromium(III) product.[42] An entirely analogous mechanism has been proposed for the Cr^{2+}-induced aquation of $CrCl^{2+}$ [43] and CrI^{2+}.[44] Other mechanisms for electron transfer, such as outer-sphere reactions or hydrogen atom transfer, cannot be ruled out, but seem less likely.

In terms of a mechanism showing aquation by the parallel paths

$$Cr^{2+} + CrOAc^{2+} \longrightarrow Cr^{2+} + Cr^{3+} + OAc^- \qquad (14)$$

$$Cr^{2+} + Cr(OH)OAc^+ \longrightarrow Cr^{2+} + Cr(OH)^{2+} + OAc^- \qquad (15)$$

the specific rate for reaction 14 is k_0 and that for reaction 15 is A/K_{CrOAc}. It should be noted that a k_0 path was not observed in the Cr^{2+}-catalyzed dissociations of $CrCl^{2+}$, [43] of CrI^{2+}, [44] or of[45]



nor is it by far as prominent in the Cr^{2+}-catalyzed aquation[46] of $CrNH_3^{3+}$ as it is in our system. To explain the conspicuous contribution by the k_0 path in our system, we suggest that this path does not arise from electron transfer through a water bridge, but rather as in reaction 15, from transfer through an OH^- bridge, but in this case the coordinated acetate bears the

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(37) R. A. Plane and J. P. Hunt, *J. Am. Chem. Soc.*, **79**, 3343 (1957).

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proton which is released in converting coordinated H_2O to OH^-. In accord with this suggestion, the

$$\ddagger = \left[\mathrm{Cr^{II}}\text{--}\underset{\mathrm{H}}{\mathrm{O}}\text{--}\mathrm{Cr^{III}(H_2O)_4(HOAc)}\right]^{4+}$$

activation parameters $\Delta H_0^\ddagger$ and $\Delta S_0^\ddagger$ for the k_0 path in our system (26.7 kcal/mol and +9.0 eu) are quite different from those reported for the same path in the $CrNH_3^{3+}$ system[46] (13.9 kcal/mol and −33 eu), and the difference, at least with respect to the value of $\Delta H_0^\ddagger$, is in the direction expected if, as suggested, a proton is transferred in forming the activated complex.

The dissociation constants K_{Cr} and K_{CrOAc} having been determined, it is possible to calculate the kinetic parameters for process 15 and for process 16 (isotopic

$$(H_2O)_5CrOH^{2+} + {}^*Cr^{2+} \longrightarrow \qquad (16)$$

exchange). The second-order specific rates for reactions 15 and 16 at 25° and $\mu = 1.00$ are found to be 0.85 ± 0.20 and 2.3 ± 0.2 M^{-1} sec^{-1} and the corresponding values of $\Delta H^\ddagger$ are 16 ± 3 and 14 ± 3 kcal/mol. The agreement of the parameters suggests a common mechanism for the two reactions though it does, of course, not prove that either proceeds by way of a bridged activated complex. A further argument in favor of an inner-sphere mechanism is that the bimolecular rate constants for reactions 15 and 16 are much higher than the corresponding k_0 terms; in several systems[47,48] it has been found that when a reaction is restricted to an outer-sphere activated complex, the aquo complex reacts more rapidly than the hydroxy.

It should be pointed out that the above calculation which we have made for process 15 is incomplete. The ion $(H_2O)_5CrOAc^{2+}$ contains one water molecule *trans* to OAc^- and four located in *cis* positions. It is not known whether the water molecule which determines the value of K_{CrOAc} also provides the hydroxide ion for the bridging function, but it seems likely that it is the *trans* water (the *trans* ammonia molecules in $(NH_3)_5Co^{2+}$ are more acidic than the *cis*[49]) in both cases. This problem is not encountered in reaction 16 since all six coordinated waters of $Cr(H_2O)_6^{3+}$ are equivalent.

The very occurrence of chromium exchange between Cr^{2+} and $CrOAc^{2+}$ proves that OAc^- functions as the bridging group in the reaction. The rate law for the exchange showing an inverse dependence of rate on (H^+) implies that OH^- is present in the activated complex but the role of OH^- cannot be assigned with the certainty which is justified for OAc^-. A doubly bridged[50] activated complex has been demonstrated for the Cr^{2+}–$Cr(N_3)_2^+$ exchange; also, Kopple and Miller[51] report that the rate of reduction of *cis*-$(NH_3)_4Co(H_2O)OAc^{2+}$ is inverse in (H^+), and, since the dominant Cr(III) product is $CrOAc^{2+}$, it can reasonably be inferred that both OH^- and OAc^- act in a bridging capacity in the activated complex. Similar kinds of evidence have been used to infer the operation of doubly bridged activated complexes for the Cr^{2+}–$Cr(SCN)^{2+}$ [52] and Cr^{2+}–$Cr(H_2PO_2)^{2+}$ [53] exchanges, and it seems reasonable to suppose that a doubly bridged activated complex operates also in our system. At the same time we must reckon with the facts that such an activated complex does not provide the path for the reaction of Cr^{2+} with *cis*-$(NH_3)_4Co(OH)_2^{3+}$ [42] or with *cis*-CrF_2^+.[54] The point of difference may be that neither H_2O nor F^- has low-lying π orbitals so that electron transfer here takes place through a σ system (for a pσ orbital a linear arrangement in the $M^{III}OM^{II}$ framework would be optimum) while, when N_3^-, OAc^-, or H_2PO_2 is the ligand, the π systems may be involved. It is a matter of interest that the coefficients for the rate terms $(Cr^{2+})(Cr^{3+})/(H^+)$ (chromium exchange), $(Cr^{2+})(CrOAc^{2+})/(H^+)$ (aquation), and $(Cr^{2+})(CrOAc^{2+})/(H^+)$ (chromium exchange) are so little different. They are 1.04×10^{-4}, 0.25×10^{-4} and 5.8×10^{-4} sec^{-1}, respectively (at 25°); the corresponding values of $\Delta H^\ddagger$ are 22 ± 2, 22 ± 2, and 19 ± 1 kcal/mol, and of $\Delta S^\ddagger$ are −3, -5 ± 5, and -10 ± 3 eu. It is especially interesting that they are so nearly alike for two activated complexes of the same compositions, one of which is singly bridged and the other doubly bridged. This seems to imply that the dominant interaction governing the energetics involves the common bridging group OH^-.

The V^{2+}-Catalyzed Aquation of $CrOAc^{2+}$.—The data obtained for this complex system have not been presented in complete detail, nor will a detailed interpretation of the observations be attempted. The starting point for this discussion is that the data recorded in Table IV do represent a measure of the rate of process 13 (for the present applications of the data it suffices that the entries in Table IV represent at least a lower limit and this seems to be a very safe assumption), and in the following only a general interpretation of the inhibitory effects will be attempted.

Consideration of process 13 makes it obvious that Cr^{2+} should exert an inhibitory effect. Chromous ion is a stronger reducing agent than is V^{2+} and can be expected to react rapidly with $VOAc^{2+}$ to regenerate V^{2+} and $CrOAc.^{2+}$ The success of the catalytic reactions depends on $VOAc^{2+}$, when formed from V^{2+} and $CrOAc^{2+}$, being able to dissociate to V^{3+} and HOAc before reaction with Cr^{2+} can take place. Once $VOAc^{2+}$ has dissociated, Cr^{2+} can react with V^{3+} without regenerating $CrOAc^{2+}$. It is clear that when enough HOAc has been formed so that V(III) is significantly converted at equilibrium to $VOAc^{2+}$, adding Cr^{2+} will cause inhibition. Unless HOAc is added initially, such inhibition can only set in after HOAc has built up by the progress of the aquation reaction. Since it is observed that Cr^{2+} inhibits from the very onset of reaction, we conclude that $VOAc^{2+}$ is indeed a primary

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(47) A. M. Zwickel and H. Taube, *Discussions Faraday Soc.*, **29**, 73 (1960).

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product of reaction 13 and that Cr^{2+}, when present at appreciable concentrations, reacts with $VOAc^{2+}$ to regenerate V^{2+} and $CrOAc^{2+}$ before $VOAc^{2+}$ aquates. If this analysis is accepted, we must conclude that reaction 13 takes place to a significant extent *via* an inner-sphere activated complex with acetate transfer.

The inhibition observed in the later stages of reaction, or when both V^{3+} and HOAc are added initially, can arise from the fact that $VOAc^{2+}$ is generated from them and, in reacting with Cr^{2+}, the starting substances are regenerated.

One of the most interesting observations made is that the inhibitory effects described are much suppressed when V^{2+} is at a high concentration. This is accounted for by assuming that V^{2+} catalyzes the aquation of $VOAc^{2+}$ by electron transfer *via* an outer-sphere activated complex or *via* a water bridge

$$V^{2+} + VOAc^{2+} \longrightarrow V^{3+} + V^{2+} + OAc^- \qquad (17)$$

Reaction 17 will lead to catalysis of $VOAc^{2+}$ aquation only if $VOAc^+$ aquates more rapidly than does $VOAc^{2+}$. Though, for reactions with zero driving force, V^{2+} seems to be slightly less labile than V^{3+}, it is not unreasonable to expect a greater rate for the V(II) complex when it is less stable than the corresponding V(III) complex. Furthermore, the aquation of the acetate complex is probably assisted by H^+, and the influence of H^+ on the rate for the V(II) complex is probably greater than for the V(III). Reaction 17 is entirely analogous to a reaction which Espenson[55] has postulated to explain the kinetics of the aquation of VN_3^{2+} in the presence of V^{2+}.

The evidence, based on the work just discussed, that reaction 13 takes place mainly by an inner-sphere activated complex involving acetate transfer seems convincing, and it is therefore of interest to compare the specific rate of this reaction with the corresponding one with Cr^{2+} as the reductant (the latter reaction then involves chromium exchange between Cr^{2+} and $CrOAc^{2+}$ by the acid-independent path). At 25° the specific rates in question are $0.163\ M^{-1}\ sec^{-1}$ for the former reaction and $\leq 6 \times 10^{-5}\ M^{-1}\ sec^{-1}$ for the latter. Electron transfer through acetate from V^{2+} is therefore at least 10^3 times more rapid than from Cr^{2+}, despite a more favorable driving force for the latter reaction. This remarkable difference in rate may reflect the fact that V^{2+} donates a π, while Cr^{2+} donates a σ electron, and the π electrons, in making use of the π system of the carboxyl group, require less in the way of activation for the system.

When the coefficient for the term in the rate expression for the V^{2+}-catalyzed aquation of $CrOAc^{2+}$ which is inverse in H^+ is converted into the second-order specific rate that would correspond to the reaction

$$Cr(OH)OAc^+ + V^{2+} \longrightarrow$$

the value $2.2 \times 10^2\ M^{-1}\ sec^{-1}$ at 25° is calculated. There is some difficulty in understanding this coefficient in terms of a mechanism. It is unlikely that the reaction takes place by an outer-sphere activated complex because OH^- as a ligand on a 3+ ion would tend to stabilize it relative to the 2+ state and the rate would therefore be expected to be less than for the aquo complex.[47,48] On the other hand, the specific rate is so large that it exceeds the maximum rate of *ca.* $10\ M^{-1}\ sec^{-1}$ which can be expected if substitution in a normal coordination position for V^{2+} must precede electron transfer. One may argue that the term is not real but is an apparent one introduced by the change in ionic medium as $HClO_4$ is replaced by $LiClO_4$. This seems unlikely because the effect expressed by the term is rather large, and, moreover, it becomes pronounced toward the end of the composition range where the electrolyte is already mainly $LiClO_4$. The possibility exists that it represents a mode of attack by an inner-sphere activated complex which does not make use of a normal coordination position on V^{2+}. If the oxidant presents a group to an octahedral face of V^{2+}, an electron can be removed from the reducing agent and its place can be taken by the group presented by the oxidant. In such a mechanism, it is likely that OH^- rather than OAc^- is presented to V^{2+} by the Cr(III) complex because, for the geometry specified, σ rather than π interactions are in question. This kind of mechanism may operate in the reaction[56] of H_2O_2 and O_2 with V^{2+} and a search for it in other systems is in progress.

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