Inorg. Chem. 1984, 23, 84–87

formation of PdTPP occurs in dimethylformamide without the addition of di-*n*-butylamine at a rate comparable to that found in the presence of amine. In some cases, however, the spectral changes for these reactions could not be fit to any reasonable reaction order and they were less reproducible than those in the presence of amine. Overall, the observed first-order rate constants do not correlate well with Pd(II) concentration (a genereally positive but not well-defined effect) nor with the concentration of amine (a generally negative but again poorly defined effect). The values for the rate constants are inconsistent with respect to temperature changes and even vary considerably from one stock solution of Pd(II) to another. All of the rate constants at 25 °C with amine present do fall within a reasonably narrow range (0.19×10^{-3} to 3.5×10^{-3} s^{-1}). With such data at hand, any mechanistic interpretation is highly speculative. Our interpretation is that the most important factor determining overall conversion of *N*-CH$_3$HTPP to the complex PdTPP is the formation of the Pd(*N*-CH$_3$TPP)$^+$ intermediate, which can really alkylate DMF itself. The reactivity of the Pd(II) may be highly dependent on the ligands in the first coordination sphere, which may vary under the conditions used to study the reaction. The proposal that dealkylation of Pd(*N*-CH$_3$TPP)$^+$ could be fast relative to the rate of its formation in dimethylformamide is reasonable in view of the fact that the rate of dealkylation of Ni(*N*-CH$_3$TPP)$^+$ is competitive with the complexation rate[7] and that the dealkylation rate of Pd(*N*-CH$_3$TPP)$^+$ is faster than that of Ni(*N*-CH$_3$TPP)$^+$ under comparable conditions (3.0×10^{-3} and 2.8×10^{-4} M^{-1} s^{-1},[4b] respectively, at 25 °C in acetonitrile with di-*n*-butylamine as nucleophile).

The overall mechanism for formation of PdTPP from Pd(II) and *N*-CH$_3$HTPP in several solvents appears to be as in eq 1–5.

$$\mathrm{Pd^{II}L_4{}^{2+} + \mathit{N}\text{-}CH_3HTPP \rightarrow L_4Pd{:}\mathit{N}\text{-}CH_3HTPP^{2+}} \quad (1)$$

$$\mathrm{L_4Pd{:}\mathit{N}\text{-}CH_3HTPP^{2+} \rightarrow L_3Pd(\mathit{N}\text{-}CH_3HTPP)^{2+} + L} \quad (2)$$

$$\mathrm{L_3Pd(\mathit{N}\text{-}CH_3TPP)^{2+} \rightarrow L_2Pd(\mathit{N}\text{-}CH_3HTPP)^{2+} + L} \quad (3)$$

$$\mathrm{L_2Pd(\mathit{N}\text{-}CH_3HTPP)^{2+} \rightarrow LPd(\mathit{N}\text{-}CH_3TPP)^{+} + H^{+} + L} \quad (4)$$

$$\mathrm{LPd(\mathit{N}\text{-}CH_3TPP)^{+} + nu \rightarrow PdTPP + CH_3nu^{+} + L} \quad (5)$$

In all cases, ion-dipole formation (step 1) can be considered rapid. In acetonitrile all steps principally involving loss of ligands from Pd(II) (2–4) are rapid, and step 5, the nucleophilic displacement of PdTPP from the methyl group, is rate determining. If the formation of LPd(*N*-CH$_3$TPP)$^+$ is highly favorable, as is typical for *N*-methylporphyrin complexes in the absence of acid, [Pd] $\gg$ [*N*-CH$_3$HTPP], and equilibria 1–4 are established rapidly; the overall reaction rate should be dependent on the amine concentration but not the palladium(II) concentration. In dimethyl sulfoxide, it appears that steps 3 and 4 are relatively slow. They are distinguishable, with step 3 occurring about 2 orders of magnitude faster than step 4. Once the Pd(*N*-CH$_3$TPP)$^+$ complex is formed in dimethyl sulfoxide, it is rapidly dealkylated (step 5). Typical half-lives for the overall reaction at 25 °C are 5 min in acetonitrile (1 M di-*n*-butylamine), 100 min in dimethyl sulfoxide, and 20 min in dimethylformamide. Both the formation of an *N*-methylporphyrin complex (1–4) and the dealkylation reaction (5) are expected to be slower in solvents that form better complexes and have higher dielectric constants, the former because complexation rates tend to parallel ligand exchange rates[7,31] and the latter because better solvation of the reactants retards bimolecular nucleophilic displacement reactions, including the dealkylation of *N*-methylporphyrins.[32] Thus, the order of rates in the solvents studied CH$_3$CN > DMF > Me$_2$SO, appears reasonable.

The nature of the rate-determining step as well as the overall rate of formation of a non-N-methylated palladium(II) porphyrin complex from Pd(II) and an *N*-methylporphyrin depends on the solvent medium. In strongly complexing solvent media, which are nucleophilic with respect to alkyl groups, dealkylation can occur rapidly with respect to complexation. Rates of complexation are more rapid in poorly complexing solvents.

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Registry No. Pd, 7440-05-3; *N*-CH$_3$HTPP, 51552-53-5.

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Effect of pH and Acetate on the Rate of Hydrolysis of the Chromium–Carbon Bond in (α-Hydroxyalkyl)chromium(III) Complexes

HAIM COHEN*† and DAN MEYERSTEIN*‡

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The kinetics of the hydrolysis of [(H$_2$O)$_5$CrC(CH$_3$)$_2$OH]$^{2+}$ in the pH range 0.0–5.6 are reported. The results indicate that the hydrolysis reaction is faster for [(H$_2$O)$_{5-n}$(OH)$_n$CrC(CH$_3$)$_2$OH]$^{2-n}$. Furthermore, the rate of hydrolysis of [(H$_2$O)$_5$CrCR$_1$R$_2$OH]$^{2+}$ is accelerated by acetate anions. The mechanistic implications of these results are discussed in detail.

Introduction

The mechanism of metal–carbon bond cleavage in alkylchromium(III) and (substituted alkyl)chromium(III) complexes in aqueous solutions has been recently studied extensively.[1,2] The interest in this mechanism arose as it serves as a model system for the behavior of metal–carbon σ bonds in aqueous solutions and as these complexes are relatively easily attainable.[1,3] Two mechanisms of decomposition of CrR^{2+}

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† Nuclear Research Centre Negev.
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complexes in aqueous solutions in the absence of electrophilic or redox reagents were reported:

The first is homolysis,[4] i.e.

$$(H_2O)_5Cr^{III}\text{–}R \rightleftarrows Cr(H_2O)_6^{2+} + \cdot R \qquad (1)$$

This mechanism prevails for $\cdot R = \cdot CH_2C_6H_5$, $\cdot CH_2C_5H_4NH^+$,[5,6] and analogous compounds and contributes to the mechanism of decomposition, in solutions containing a low concentration of $Cr(H_2O)_6^{2+}$, for R = $\cdot CH(CH_3)_2$, $\cdot c\text{-}C_5H_9$, $\cdot C(CH_3)_2OH$, $\cdot C(CH_3)_2CN$, $\cdot C(CH_3)_2\text{–}O\text{-}i\text{-}C_3H_7$, and analogous compounds.[3d,7]

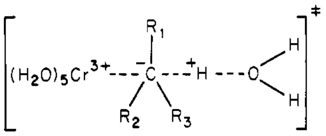
The second mechanism reported is heterolytic hydrolysis, usually referred to as acidolysis:

$$(H_2O)_5Cr^{III}\text{–}R \xrightarrow{H_2O} Cr(H_2O)_6^{3+} + RH \qquad (2)$$

Reaction 2 generally obeys a rate law of the form

$$\frac{-d[(H_2O)_5CrR^{2+}]}{dt} = (k_1 + k_2[H_3O^+])[(H_2O)_5CrR^{2+}] \qquad (3)$$

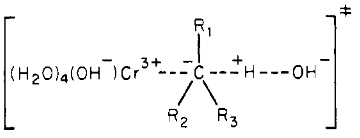
In some cases k_1 or k_2 values are negligible.[1,8] This rate law is in agreement with the suggestion that the mechanism involves an electrophylic attack on the carbon atom of the Cr–C bond. Activated complexes of the type



I

have been suggested[1] and corroborated by the large H/D solvent isotope effect.[9,10] For aliphatic residues, ·R, with α-hydroxyl groups, hydrogen bonding of the attacking water molecule to this group was also suggested.[11]

With the exception of $(H_2O)_5CrCHI_2^{2+}$ [12] no inverse acid pathway for the decomposition of CrR^{2+} complexes was reported.[13] It was argued that such a pathway would not be expected for organometallic complexes as the carbanion, :R⁻, is not a suitable leaving group. However, if the attacking water molecule is not coordinated to the cis position of the chromium and thus becomes less acidic in $(H_2O)_4(OH)CrR^+$, then one would expect that the rate of decomposition via II would be faster than via III. This effect is expected to be more pronounced if the water molecule is hydrogen bonded to an α-hydroxyl as in IV. Indeed it is known[1] that in more alkaline solutions CrR^{2+} complexes decompose rapidly to yield $Cr(OH)_3$. We decided therefore to extend the study of the kinetics of decomposition of $(H_2O)_5Cr\text{–}CR_1R_2OH^{2+}$, where R_1, R_2 = H or CH_3, to higher pH values as studies to date were limited to pH ≤2.0.



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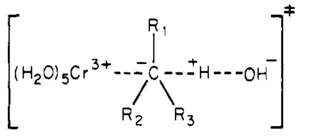

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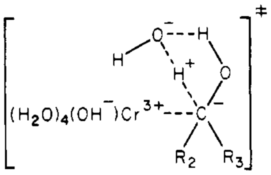

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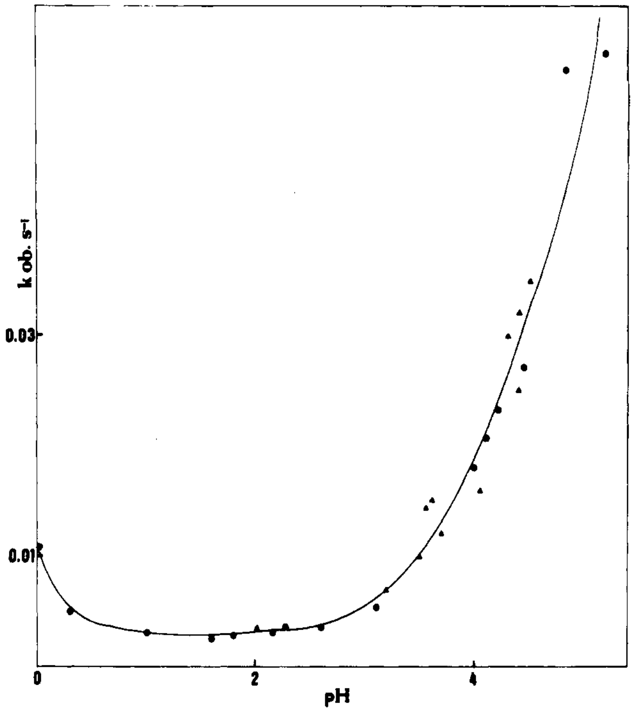

Figure 1. pH dependence of the rate of decomposition of the $Cr^{III}\text{–}C(CH_3)_2OH$ bond (measured at 390 nm): ●, measured in a spectrophotometer; ▲, measured at the Linac.

The results reported here indeed indicate that the rate of hydrolysis of $Cr\text{–}CR_1R_2OH^{2+}$ complexes increases with increasing pH in the range 2 ≤ pH ≤ 5.6. Furthermore it was found that the reaction is also catalyzed by acetate anions; such a catalysis was reported to date only for the decomposition of $(H_2O)_5CrCH_2C_6H_5^{2+}$.[14]

Experimental Section

Materials. Chromous solutions were prepared by dissolving high-purity grade chromium powder in 1 M perchloric acid under continuous bubbling of vanadous-scrubbed argon. All other chemicals were of analytical grade and were used without further treatment. All water used was triply distilled.

Irradiation. Short electron pulses from the linear accelerator at the Hebrew University of Jerusalem were used. The dose per pulse was in the range 5×10^2–4×10^3 rd/pulse. The kinetics were followed spectrophotometrically.

The experimental techniques used throughout this study, the experimental setups, and the techniques used for evaluating the results have been described earlier in detail.[8]

Results

Nitrous oxide saturated solutions containing 0.1 M 2-propanol in the pH range 0–5.6 and 1×10^{-3} M Cr_{aq}^{2+} were

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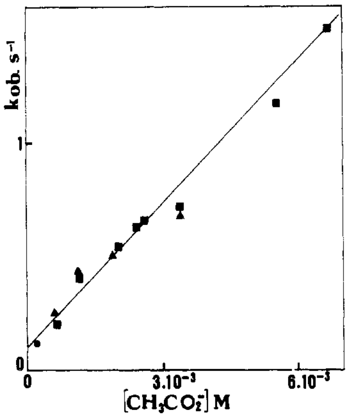

Figure 2. $[CH_3CO_2^-]$ dependence of the rate of decomposition of the $Cr^{III}-C(CH_3)_2OH$ bond in the presence of acetate buffer in the pH range 3.4–5.4 (measured at 390 nm): ●, total acetate concentration 9×10^{-4} M; ▲, total acetate concentration 4.5×10^{-3} M; ■, total acetate concentration 1.0×10^{-2} M.

irradiated by a short electron pulse from the linear accelerator. The rate of formation and decomposition of the Cr–C bond was measured by following the formation and bleaching of the absorption at 310 nm. The specific rate of reaction $k(Cr(H_2O)_6^{2+} + \cdot C(CH_3)_2OH = (5 \pm 1) \times 10^7$ M^{-1} s^{-1} was found to be independent of 2-propanol and acid concentrations in full agreement with previous results.[8] The rate of decomposition was found to be independent of Cr^{2+} and 2-propanol concentrations but pH dependent. The observed rates of decomposition are plotted in Figure 1. The spectrum of the transient is identical, within the experimental error limit, with that of $(H_2O)_5Cr-C(CH_3)_2OH^{2+}$.

Nitrous oxide saturated solutions containing 0.01–2 M 2-propanol in the pH range 0–6.2 (the pH was adjusted by perchloric acid), (1–15) × 10^{-4} M Cr_{aq}^{2+}, and (9–100) × 10^{-4} M total[15] acetate were irradiated. Formation of an absorption due to a transient was observed. The spectrum of the transient is composed of two absorption bands of λ_{max} (ϵ_{max}) 310 nm (2900 M^{-1} cm^{-1}) and 396 nm (800 M^{-1} cm^{-1}), in agreement with the spectrum of $(H_2O)_5CrC(CH_3)_2OH^{2+}$. The rate of formation of the transient was found to be independent of 2-propanol, total acetate, and acid concentrations and was first order in Cr_{aq}^{2+} concentration ($k(Cr^{2+} + \cdot(CH_3)_2COH) = (5 \pm 1) \times 10^7$ M^{-1} s^{-1}. The rate of decomposition of the transient was found to be independent of wavelength and 2-propanol and Cr_{aq}^{2+} concentration but was dependent on the pH and acetate concentration. The dependence of the rate of decomposition on acetate ion concentration is plotted in Figure 2. The dependence of the rate of decomposition on pH at a constant total acetate concentration is plotted in Figure 3.

The effect of changing the solvent from H_2O to 99.8% D_2O in buffered acetate solutions decreased the rate of decomposition of the transient. In N_2O-saturated solutions containing 1 × 10^{-2} M total acetate and 0.1 M 2-propanol, the rate of decomposition at pH 3.75 and 4.3 was 0.11 and 0.25 s^{-1}, respectively.

Nitrous oxide saturated solutions containing 0.01–2 M methanol or ethanol in the pH range 0–6.2, (1–20) × 10^{-4} M Cr_{aq}^{2+} and (9–100) × 10^{-4} M total acetate were irradiated by short electron pulses from the linear accelerator. Formation of typical absorptions of chromium-substituted alkyl complexes was observed. The rate of formation was found to be independent of organic solute, total acetate and acid concentrations, and wavelength and was first order in Cr_{aq}^{2+}: $k(R\cdot + Cr^{2+}) = (2 \pm 0.2) \times 10^8$ and $(1.0 \pm 0.15) \times 10^8$ M^{-1} s^{-1} for $R\cdot = \cdot CH_2OH$ and $CH_3\dot{C}HOH$, respectively. The rates of decomposition of the (α-hydroxyalkyl)chromium(III) complexes were found to be independent of wavelength and alcohol and Cr_{aq}^{2+} concentrations, but they depended on pH and acetate concentration. The results are summarized in Table I.

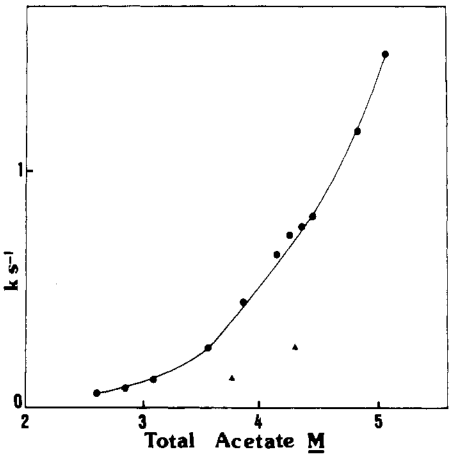

Figure 3. pH dependence of the rate of decomposition of the $Cr^{III}-C(CH_3)_2OH$ bond in solutions containing 1 × 10^{-2} M total acetate. For the ▲ points the solvent was 99.8% D_2O.

Table I. Effect of pH and Acetate on the Rate of Decomposition of (α-Hydroxyalkyl)chromium(III) Complexes

[alcohol], M	$[Cr^{2+}]$, M	$[OAc^-]$ + [OHAc], M	pH	k, s^{-1}
		CH_3OH		
0.1	2×10^{-4}	9×10^{-3}	5.65	0.20
0.1	2×10^{-4}	9×10^{-3}	5.00	0.18
0.11	1.4×10^{-4}	1.0×10^{-2}	4.80	0.145
0.90	5×10^{-4}	9×10^{-4}	4.70	0.025
0.95	3.65×10^{-4}	9.5×10^{-4}	4.80	0.029
		CH_3CH_2OH		
0.1	5×10^{-4}	9×10^{-3}	4.95	0.72
0.1	5×10^{-4}	9×10^{-4}	5.5	0.78
0.9	3.6×10^{-4}	9×10^{-4}	4.7	0.097
0.9	7.7×10^{-4}	9×10^{-4}	4.6	0.081
		$(CH_3)_2CHOH$		
1	5×10^{-4}	1.0×10^{-2}	5.05	1.5
1	5×10^{-4}	1.0×10^{-2}	4.45	0.81
1	1.2×10^{-3}	1.0×10^{-2}	4.45	0.79
0.1	5×10^{-4}	1.0×10^{-2}	4.85	1.2
1	5×10^{-4}	9×10^{-4}	4.35	0.29
1	5×10^{-4}	4.5×10^{-3}	4.35	0.47
1	5×10^{-4}	1.0×10^{-2}	4.25	0.73

Discussion

The production of (α-hydroxyalkyl)chromium(III) complexes in our system is based on the reaction sequence[8] (4)–(8).

$$H_2O \xrightarrow{\gamma,\, e} e_{aq}^-, \cdot H, \cdot OH, H_2, H_2O_2, H_3O^+ \tag{4}$$

$$e_{aq}^- + N_2O \xrightarrow{H_2O} N_2 + \cdot OH \tag{5}$$

$$e_{aq}^- + H_3O^+ \rightarrow \cdot H \tag{6}$$

$$\cdot H/\cdot OH + HCR_1R_2OH \rightarrow \cdot CR_1R_2OH + H_2/H_2O \tag{7}$$

$$Cr(H_2O)_6^{2+} + \cdot CR_1R_2OH \rightarrow (H_2O)_5Cr-CR_1R_2OH^{2+} \tag{8}$$

The addition of acetate has little effect on these reactions as the specific rates of reactions 9 are considerably lower than

$$\cdot H/\cdot OH + CH_3CO_2^- \rightarrow \cdot CH_2CO_2^- + H_2/H_2O \tag{9}$$

those of reactions 7[16] and as the acetate concentrations used

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[15] The solutions contained a mixture of free acetate ion and acetic acid. The total concentration of $[CH_3CO_2^-]$ + $[CH_3CO_2H]$ is denoted as total acetate.

are much lower than those of the alcohols. Furthermore, the transients in this study have spectra identical with those of $(H_2O)_5CrCR_1R_2OH^{2+}$ in acidic solutions within experimental error.[8]

It should be noted that complexes of acetate with $Cr(H_2O)_6^{2+}$ are known,[17] but their stability constants are relatively low and under our experimental conditions over 95% of the chromous ions present are $Cr(H_2O)_6^{2+}$.

The kinetics of decomposition of $(H_2O)_5Cr{-}CR_1R_2OH^{2+}$ in this study always obeyed a first-order rate law with a rate independent of $[Cr(H_2O)_6^{2+}]$ and wavelength of measurement. These results prove that the mechanism of decomposition does not change from hydrolysis to homolysis due to the change in pH. The rate of decomposition of $(H_2O)_5{-}Cr{-}C(CH_3)_2OH^{2+}$ in the pH range 0.0–2.0 (Figure 1) is in agreement with the reported rate law (3).[8,11] However, the increase in the rate of decomposition at pH >2.0 clearly indicates that further terms have to be included in this rate law. Such an effect is probably due to an equilibrium of the type

$$(H_2O)_5Cr{-}C(CH_3)_2OH^{2+} \rightleftarrows (H_2O)_4(OH)Cr{-}C(CH_3)_2OH^{+} + H_3O^{+} \quad (10)$$

where the rate of decomposition of $(H_2O)_4(OH)Cr{-}C(CH_3)_2OH^{+}$ is faster than that of $(H_2O)_5Cr{-}C(CH_3)_2OH^{2+}$. If the observed effect would be due to one equilibrium reaction of this type, then one would expect a leveling of the observed rate of reaction above pK_{10} and a term proportional to $[H_3O^+]^{-1}$ at a pH considerably below the pK. The results in Figure 1 clearly do not conform with either of these predictions indicating a more complicated mechanism. This is not too surprising in view of the expectation that the pK's for the following proton losses, i.e. to form $(H_2O)_{5-n}(OH)_nCr{-}C(CH_3)_2OH^{2-n}$ where $n = 2$–4, are not far from pK_{10}. It should be noted that the increase in the rate of hydrolysis might partly be due to the larger gain in the free energy of reaction due to the stabilization of the product $Cr(H_2O)_{6-n}(OH)_n^{(3-n)+}$ relative to $Cr(H_2O)_6^{3+}$.[18a] The observed increase in the rate of the hydrolysis reaction of the chromium–carbon bond due to the pK of the inner-sphere hydration molecules,[18b] suggests that the attacking water molecule is not one of those cis coordinated to the chromium–carbon bond as their acidities, electrophilic properties, are expected to decrease due to the loss of protons from the other coordinated water molecules. We thus suggest that hydrolysis at least in the base-catalyzed path occurs via attack of a noncoordinated water molecule.

The results in the presence of acetate indicate a rate law of the form

$$k^{\mathrm{ac}}_{\mathrm{obsd}} = k^{0}_{\mathrm{obsd}} + k_{\mathrm{ac}}[CH_3CO_2^-] \quad (11)$$

where $k^{\mathrm{ac}}_{\mathrm{obsd}}$ is the observed rate of reaction and k^{0}_{obsd} is the rate observed at the same pH in the absence of acetate. From Figure 2, $k_{\mathrm{ac}} = 210 \pm 20\ M^{-1}\ s^{-1}$ is calculated for the hydrolysis of $(H_2O)_5Cr{-}C(CH_3)_2OH^{2+}$. Due to the large value of k_{ac}, the dependence of k^{0}_{obsd} on pH does not show a deviation from the straight line in Figure 2. The effect of the acetate is probably due to the reaction sequence[19] (12) and (13) where

$$(H_2O)_5Cr{-}C(CH_3)_2OH^{2+} + CH_3CO_2^- \rightleftarrows (H_2O)_4(CH_3CO_2)Cr{-}C(CH_3)_2OH^{+} \quad (12)$$

$$(H_2O)_4(CH_3CO_2)Cr{-}C(CH_3)_2OH^{+} \xrightarrow{H_2O} Cr(H_2O)_5(CH_3CO_2)^{2+} + CH(CH_3)_2OH \quad (13)$$

k_{13} is considerably larger than k_2. The rate observed thus probably corresponds to $K_{12}k_{13} = 210 \pm 10\ M^{-1}\ s^{-1}$. We estimate $K_{12} \sim 10\ M^{-1}$ and $k_{12} \sim 10^3\ M^{-1}\ s^{-1}$ as similar values are obtained[20] for the association of NCS^- to (α-hydroxyalkyl)chromium(III) complexes.[22] K_{12} has to be smaller than $5 \times 10^2\ M^{-1}$ as otherwise the plot in Figure 3 would deviate from the linear correlation at high $[CH_3CO_2^-]$. On the other hand, $[Cr^{III}CH_3CO_2^-]/[Cr^{3+}][CH_3CO_2^-] = 4.2 \times 10^4\ M^{-1}$ was reported.[23] Thus, $k_{13} \sim 20\ s^{-1}$ is estimated a value ca. 4 orders of magnitude higher than that for $(H_2O)_5Cr{-}C(CH_3)_2OH^{2+}$. This increase in rate of the hydrolysis reaction is in accord with reports[1,20] that NCS^- association accelerates this reaction though the effect is larger than expected. We note that acetate anions were shown to have a similar effect on the rate of hydrolysis of $(H_2O)_5CrCH_2C_6H_5^{2+}$.[14]

In parallel, we calculate from the results in Table I $K_{12}k_{13} = 140 \pm 15$ and $29 \pm 3\ M^{-1}\ s^{-}$ for the acceleration by acetate of the hydrolysis reaction of $(H_2O)_5CrCH(CH_3)OH^{2+}$ and $(H_2O)_5CrCH_2OH^{2+}$, respectively. It should be noted that we cannot rule out the possibility that the effect of acetate is due to direct attack on the chromium–carbon bond though this seems unlikely.[23]

The large effect of acetate coordination on the rate of the hydrolysis reaction is surprising as the rate of the pH-independent term for the hydrolysis of $[(edta)CrC(CH_3)_2OH]^{2-}$[24] equals that for $[(H_2O)_5CrC(CH_3)_2OH]^{2+}$. This apparent discrepancy might be explained if the acetate effect is a trans effect. It is known that in CrR complexes the trans ligand is labilized, and if the R group in $[(edta)CrR]^{2-}$ is trans to one of the nitrogen atoms bound to the chromium, the rate of hydrolysis might not be accelerated. The latter might be the case if in $[Cr(edta)H_2O]^{2-}$ the accessible position for attack by R· radicals is trans to a nitrogen atom or if both isomers are formed but that with ·R trans to a carboxylate decomposes too fast to be observed.

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Registry No. $(H_2O)_5CrC(CH_3)_2OH^{2+}$, 32108-93-3; $(H_2O)_5CrCH_2OH^{2+}$, 32108-95-5; $(H_2O)_5CrCH(CH_3)OH^{2+}$, 32108-94-4; Cr^{2+}, 22541-79-3; 2-propanol, 67-63-0; acetate, 71-50-1; methanol, 67-56-1; ethanol, 64-17-5.

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(16) (a) Anbar, M.; Bambenek, M.; Ross, A. B. *Nat. Stand. Ref. Data Ser. (U.S., Natl. Bur. Stand.)* **1973**, *NSRDS-NBS 43*. (b) Anbar, M.; Farhataziz, N.; Ross, A. B. *Ibid.* **1975**, *NSRDS-NBS 51*. (c) Farhataziz, N.; Ross, A. B. *Ibid.* **1977**, *NSRDS-NBS 59*.

(17) (a) Cannon, R. D.; Stillman, J. S. *Inorg. Chem.* **1975**, *14*, 2202. (b) Cannon, R. D.; Gholami, J. G. *J. Chem. Soc., Dalton Trans.* **1976**, 1574. (c) Cannon, R. D.; Gholami, J. G. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 594.

(18) (a) One of the reviewers pointed out that the stabilization of $Cr(H_2O)_{6-n}(OH)_n^{(3-n)+}$ over $Cr(H_2O)_6^{3+}$ in the pH range studied is not large. However, even an increase of several kilocalories, which exists, might contribute to an enhancement of the rate. (b) We cannot rule out the possibility that one of the pK's involved is that of the α-hydroxyl group of the alcohol. However, it is difficult to envisage why the latter pK should be so acidic and why it should increase the rate of the hydrolysis reaction.

(19) The reaction is written for the acidic form of the complex though clearly the alkaline forms of the type $(H_2O)_{5-n}(OH)_nCr{-}C(CH_3)_2OH^{(2-n)+}$ contribute also to the reaction sequence.

(20) (a) Bushey, W. R.; Espenson, J. H. *Inorg. Chem.* **1977**, *16*, 2772. (b) Bakac, A.; Espenson, J. H.; Miller, L. *Ibid.* **1982**, *21*, 1557.

(21) K_{12} has to be smaller than $5 \times 10^2\ M^{-1}$ as otherwise the plot in Figure 3 would deviate from the linear correlation of high $[CH_3CO_2^-]$. On the other hand, $[Cr^{III}{-}O_2CCH_3]/[Cr^{3+}][CH_3CO_2^-] = 4.2 \times 10^4\ M^{-1}$ was reported.[22]

(22) Tedesco, P. H.; Quintana, J. A. G. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2689.

(23) Such nucleophilic attack means an attack on the chromium, i.e., a seven-coordinated transition state as the ligand exchange of the cis aquo ligands is slow.[1,20] Furthermore, the D/H solvent isotope effect (Figure 3) indicates that a water molecule is bound to the 2-carbon in the transition state, a fact that causes steric hindrance to an attack on the chromium–carbon bond.

(24) Ogino, H.; Shimura, M.; Tanaka, N. *Inorg. Chem.* **1982**, *21*, 126.