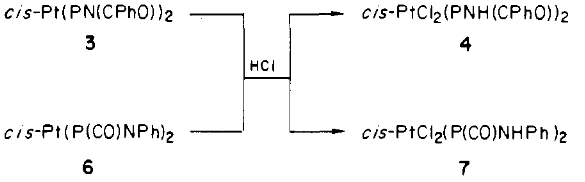
plexes *cis*-$PtCl_2(PNH(CPhO)_2$ (**4**) and *cis*-$PtCl_2(P(CO)NHPh)_2$ (**7**) (eq 6), and indeed this method of synthesis is the preferred



(6)

one for complex **7**. Complexes **3**, **5**, **6**, **10**, and **11** do not undergo substitution reactions by added chloride ion; therefore, the initial step in their reactions with HCl must involve protonation at nitrogen. For the platinum amido complexes the stereochemistry is retained, but the reaction of either the cis or the trans isomer of $Pd(P(CO)NPh)_2$ with HCl gives only a single product, $PdCl_2(P(CO)NHPh)_2$ **9** ($\delta_P$ 19.2). The spectral properties of **4** and **7** are respectively $\delta_P$ 2.3 ($^1J(PtP)$ = 3646 Hz) and $\delta_P$ 7.6 ($^1J(PtP)$ = 3737 Hz). NMR and IR spectral data for the complexes are collected in Table V.

Like the trans analogues **1** and **2**, the cis complexes **4** and **7** react with base to give the N-bonded amido complexes. In contrast, however, reaction of **4** or **7** with Dabco in acetonitrile solvent *rapidly* gives the amido complexes at ambient temperature. The respective products **3** and **6** are formed with retention of stereochemistry. This relative ease of intramolecular chloride ion substitution by the amido anion in the cis isomers over the trans ones is a consequence of the higher trans influence of the phosphine ligand.

**Registry No.** **1**, 91410-06-9; **2**, 98838-49-4; **3**, 91410-08-1; **4**, 91464-49-2; **5**, 98838-50-7; **6**, 98919-88-1; **7**, 98919-89-2; **8**, 91410-15-0; **9**, 98838-51-8; **10**, 98838-52-9; **11**, 98919-90-5; P(O)NHBz, 98821-87-5; PNHBz, 91410-00-3; PCNHPh, 91410-01-4; PNH(CPhO), 91409-99-3; P(CO)NHPh, 91410-02-5; P(O)NH-c-$C_5$, 98821-88-6; P(O)NH-c-$C_6$, 98821-89-7; *o*-$Ph_2PC_6H_4CH$=NPh, 98821-90-0; *o*-$Ph_2P(O)C_6H_4NH_2$, 23081-74-5; PhCHO, 100-52-7; $Ph_2SiH_2$, 775-12-2; *o*-$Ph_2PC_6H_4CHO$, 50777-76-9; $PhNH_2$, 62-53-3; *o*-$Ph_2PC_6H_4NH_2$, 65423-44-1; PhC(O)Cl, 98-88-4; *o*-$Ph_2PC_6H_4CO_2H$, 17261-28-8; $K_2PtCl_4$, 10025-99-7; $Na_2PdCl_4$, 13820-53-6.

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Contribution from the Chemistry Departments, Ben-Gurion University of the Negev, Beer-Sheva, Israel,
and Nuclear Research Center Negev, Beer-Sheva, Israel

# Mechanism of Hydrolysis of the Metal–Carbon Bond in α-Hydroxyalkyl–Chromium(III) Complexes. Effect of Nonparticipating Ligands

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The specific rates of reaction of the free radicals $\cdot CH_2OH$, $\cdot CH(CH_3)OH$, and $\cdot C(CH_3)_2OH$ with $[Cr^{II}(edta)]^{2-}$, $[Cr^{II}(nta)]^-$, and *trans*-$[(1,4,8,12\text{-tetraazacyclopentadecane})(H_2O)_2Cr^{II}]^{2+}$ are reported and compared with the analogous reactions with $Cr(H_2O)_6^{2+}$. The spectra of the α-hydroxyalkyl-chromium(III) complexes thus formed are reported and discussed. The rates of hydrolysis of the latter complexes are reported as well as that of *cis*-$[(nta)(H_2O)Cr^{III}-CH_3]^-$. The results point out that the electrophile in these hydrolysis reactions is a solvent water molecule and not a cis aqua ligand as earlier suggested. The effects of the pH of the solution and the addition of acetate on the hydrolysis reactions are reported and discussed.

The relative stability of alkyl–chromium(III) complexes in aqueous solutions allows the detailed study of their decomposition mechanisms.[2] The large range of stabilities of these complexes and variety of mechanisms of decomposition resulted in extensive studies[2] aimed at elucidating the factors affecting the mechanisms and rates of these reactions, which are model reactions to the decomposition of other complexes with σ metal–carbon bonds in protic media.

Pentaaqua(α-hydroxyalkyl)chromium(III) complexes were shown to decompose in acidic solutions via two pathways.

The first is a homolytic decomposition:[3]

$$[(H_2O)_5Cr^{III}-CR_1CR_2OH]^{2+} \overset{H_2O}{\rightleftharpoons} Cr(H_2O)_6^{2+} + \cdot CR_1R_2OH \quad (1)$$

This mechanism is important only in the presence of scavengers of $Cr(H_2O)_6^{2+}$ and/or $\cdot CR_1R_2OH$, as $K_1 >> 1$.

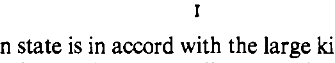
The second pathway is a heterocyclic hydrolysis reaction:[2,4]

$$[(H_2O)_5Cr^{III}-CR_1R_2OH]^{2+} \xrightarrow{H_2O} Cr^{III}_{aq} + HCR_1R_2OH \quad (2)$$

This reaction obeys in acidic solutions the rate law

$$-\frac{d[[(H_2O)_5Cr^{III}-CR_1R_2OH]^{2+}]}{dt} = (k_{H_2O} + k_{H_3O^+}[H_3O^+])[[(H_2O)_2Cr^{III}-CR_1R_2OH]^{2+}] \quad (3)$$

When the measurements were carried out in $D_2O$ instead of $H_2O$ it was found that both $k_{H_2O}$ and d $k_{H_3O^+}$ have large kinetic H/D isotope effects.[5] For the $[H_3O^+]$-dependent term the following transition state is commonly accepted

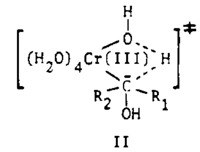


I

This transition state is in accord with the large kinetic isotope effect and with the observation that bulky $R_1$ and $R_2$ substituents decrease $k_{H_3O^+}$.[3]

For the [acid]-independent term, $k_{H2O}$, two different transition states were proposed.

1. It was suggested[2] that the attacking water molecule is the ligand bound to the chromium cis to the α-hydroxyalkyl ligand:



II

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[1] (a) Ben-Gurion University of the Negev. (b) Nuclear Research Centre Negev.

[2] Espenson, J. H. "Advances in Inorganic and Bioinorganic Mechanisms"; G. Sykes, Ed.; Academic Press: London, 1982; Vol. 1, p 1.

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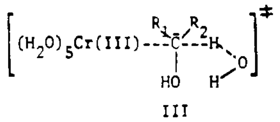
The arguments in favor of this transition state are as follows:[2]

a. The water molecule bound as a ligand is a stronger acid than the solvent water molecules.

b. No steric effect of bulky $R_1$ and $R_2$ substituents is observed.[c]

c. $k_{H_2O}$ for the hydrolysis of $[(edta)Cr^{III}-CR_1R_2OH]^{2-}$ is similar to that of $[(H_2O)_5Cr^{III}-CR_1R_2OH]^{2+}$ though $k_{H_3O^+}$ for the former is ca. $10^5$ faster than for the latter.[2,6] The effect of edta as a ligand on $k_{H_3O^+}$ is attributed to the considerably larger stability of $Cr^{III}(edta)$ than that of $Cr^{3+}_{aq}$.[2] The absence of an analogous effect on $k_{H_2O}$ was attributed to the lack of a cis water ligand in the edta complex, which compensates the expected effect.[2]

2. On the other hand, it was suggested[7] that the transition state for the [acid]-independent term is analogous to that of the [acid]-dependent term, i.e.



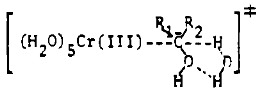
III

The arguments in favor of this transition state are as follows:

a. It was found that the rate of hydrolysis of $[(H_2O)_5Cr^{III}-CR_1R_2OH]^{2+}$ increases with increasing pH above pH 2.0.[7] This effect was attributed to the formation of *trans*-$[(H_2O)_4(OH)Cr^{III}-CR_1R_2OH]^+$ and $[(H_2O)_3(OH)_2Cr^{III}-CR_1R_2OH]$. It is clear that the remaining cis aqua ligands in the latter complexes are less acidic than those in $[(H_2O)_5Cr^{III}-CR_1R_2OH]^{2+}$. It is therefore more plausible that the attacking water molecule is one from the solvent.

b. The term $k_{H_2O}$ for *trans*-$[(H_2O)_4(CH_3CO_2^-)Cr-CR_1R_2OH]^+$ is considerably larger than for $[(H_2O)_5Cr^{III}-CR_1R_2R_3]^{2+}$.[7] This effect is, as that described for the pH effect (see previous paragraph), easier to explain by assuming that the attacking water molecule is one from the solvent.

c. The ratio of $k_{H_2O}/k_{H_3O^+}$ is considerably larger for the hydrolysis of the $[(H_2O)_5Cr^{III}-CR_1R_2OH]^{2+}$ complexes than for the hydrolysis of the $[(H_2O)_5Cr^{III}CR_1R_2R_3]^{2+}$ complexes. This effect was attributed[2,4a] to stabilization of the transition state by hydrogen bonding in the former case, i.e.



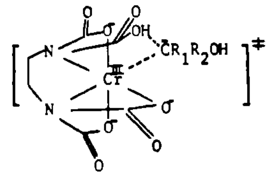
IV

Such an effect is not expected if the attacking water molecule is one of the cis ligands.

d. According to this mechanism the increase in $k_{H_3O^+}$ for the $[(edta)Cr^{III}-CR_1R_2OH]^{2-}$ complexes is due to an intramolecular acid attack,[6] i.e.

$$[(edta)Cr^{III}-CR_1R_2OH]^{2-} + H_3O^+ \rightleftarrows [(Hedta)Cr^{III}-CR_1R_2OH]^- \quad (4)$$

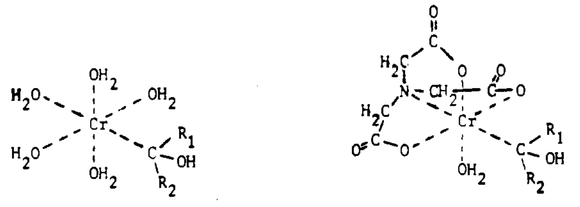
where the acidic form decomposes considerably faster than the alkaline form due to a transition state of the form



V

In order to analyze the plausible role of the cis water ligand we decided to study the mechanism of hydrolysis of the complexes *cis*-$[(nta)(H_2O)Cr^{III}-CR_1R_2OH]^-$ and *trans*-$[([15]ane-N_4)(H_2O)Cr^{III}-CR_1R_2OH]^{2+}$ as both complexes have one water molecule as a ligand, but due to the structure of the chelating ligand this water molecule is cis to the α-hydroxyalkyl ligand in the former complex and trans to it in the lattter (nta ≡ nitrilotriacetate and [15]ane-$N_4$ ≡ 1,4,8,12-tetraazacyclopentadecane). The results clearly point out that a cis aqua ligand has no major role in the mechanism of hydrolysis of α-hydroxyalkyl–chromium(III) complexes.

**Chart I.** Structures of the Complexes Studied

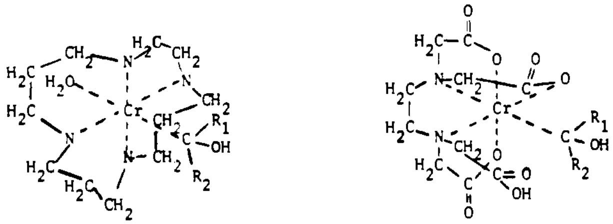


$(H_2O)_5Cr:CR_1R_2OH^{2+}$

cis+trans water

*cis*-$NTACr(H_2O):CR_1R_2OH^-$

cis water



trans [15] ane$N_4Cr(H_2O):CR_1R_2OH^{2+}$

trans water

$(EDTA)Cr(H_2O):CR_1R_2OH^{2-}$

no water coordination

## Experimental Section

**Materials.** All solutions were prepared from AR grade chemicals, which were used without further treatment, and from distilled water, which was further purified by passing through a milli Q Millipore setup so that its final resistivity was >10 MΩ/cm.

$Cr(H_2O)_6^{2+}$ 0.5 M solutions were prepared by dissolving superpure (BDH) chromium powder in 1.0 M $HClO_4$ solution continuously purged with Ar or He. The gases were first purified from traces of dioxygen by being bubbled through a washing bottle containing $VSO_4$ in dilute $H_2SO_4$ over Zn amalgam.

Solutions of *trans*-$[(H_2O)([15]ane-N_4)Cr^{II}]^{2+}$ were prepared by mixing deaerated solutions of $Cr(H_2O)_6^{2+}$ and the free ligand. The ratio of the free ligand concentration to $[Cr(H_2O)_6^{2+}]$ was always ≥1.1. The solutions were kept for 0.5 h before irradiation; thus over 95% of the $Cr^{2+}$ was complexed by the ligand.[21]

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

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

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(11) (a) Anbar, M.; Bambenck, M.; Ross, A. B. *Natl. 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*.

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(13) Misckei, K.; Debreczeni, F.; Nogypal, I. *J. Chem. Soc., Dalton Trans.* **1983**, 1335.

(14) Perin, D. D. "Stability Constants of Metal Ion Complexes, Part B"; Wheaton, and Co.: Oxford, England, 1979; p 449.

(15) Matheson, M. S.; Dorfman, L. M. "Pulse Radiolysis"; MIT Press: Cambridge, MA, 1969; Chapter 6.

(16) In solutions containing $C_2H_5OH$ and $CH(CH_3)_2OH$ ca. 13% of the free radicals formed are $\cdot CH_2CH_2OH$ and $\cdot CH_2CH(OH)CH_3$, respectively.[17a] The corresponding alkyl–chromium complexes decompose via a fast β-elimination process[17b] and thus did not interfere in this study.

(17) (a) Asmus, K. D.; Mockel, H.; Henglein, A. *J. Phys. Chem.* **1973**, *77*, 1218. (b) Cohen, H.; Meyerstein, D., submitted for publication.

(18) See, for example: Buxton, G. V.; Sellers, R. M.; McCracken, D. R. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1464. Jubran, N.; Ginzburg, G.: Cohen, H.; Koresh, Y.; Meyerstein, D. *Inorg. Chem.* **1985**, *24*, 251.

(19) $k_{OH+CH_3CHO}$ has not been reported; however, $k_{OH+CH_2(OH)_2} = 2 \times 10^9$ $M^{-1}$ $s^{-1}$,[11] and $k_{OH+CH_3CH_2CH_2CHO} = 3.5 \times 10^9$ $M^{-1}$ $s^{-1}$.[11]

(20) This the rate for $e_{aq}^- + Cr(edta)^-$;[11] the rate for the nta complex might be slightly larger.

(21) Samuels, G. J.; Espenson, J. H. *Inorg. Chem.* **1982**, *21*, 126.

All solutions containing $Cr(H_2O)_6^{2+}$ and/or $L_5Cr^{III}–CR_1R_2OH$ complexes were handled by the syringe technique in order to avoid contact with dioxygen.

**Techniques.** Spectrophotometric measurements were carried out with a Spectronic 2000 Bausch and Lomb spectrophotometer.

pH determinations of solutions containing $Cr(H_2O)_6^{2+}$ were carried out by immersing the combined electrode into the syringe while Ar was bubbled through the solution.

The concentration of $Cr(H_2O)_6^{2+}$ solutions was determined by oxidation to $Cr(H_2O)_6^{3+}$ and measurement of the optical density at 408 nm where $\epsilon(Cr(H_2O)_6^{3+}) = 15.6\ M^{-1}\ cm^{-1}$.[8] In dilute solutions the concentration of chromium was determined with an atomic absorption spectrophotometer.

Pulse-radiolysis experiments were carried out at the linear electron accelerator facility of the Hebrew University of Jerusalem; 0.2–1.5-μs, 5-MeV, and 200-mA pulses were used. The dose per pulse was in the range 500–4000 rad/pulse. The experimental setup as well as the techniques used for evaluating the results has been described elsewhere in detail.[4,9]

**Preparation of the α-Hydroxyalkyl–Chromium(III) Complexes.** Two general methods were used to prepare the α-hydroxyalkyl–chromium(III) complexes. The key reaction in both methods is[4]

$$L_5Cr^{II}H_2O + \cdot CR_1R_2OH \rightarrow [L_5Cr^{III}–CR_1R_2OH] + H_2O \qquad (5)$$

Thus both methods are aimed at producing $\cdot CR_1R_2OH$ free radicals in the presence of $L_5Cr^{II}H_2O$. The difference between the two techniques is mainly their time resolution.

**The Modified Fenton Reagent.** This technique was used for the study of the kinetics of decomposition of α-hydroxyalkyl–chromium complexes with a half-life longer than 2 min, i.e. of the $[(nta)(H_2O)Cr^{III}–CR_1R_2OH]^-$ complexes.

A deaerated solution containing $Cr(H_2O)_6^{2+}$, nta, $CH_3CO_2Na$, and $HCR_1R_2OH$ at the required pH is mixed in a syringe with a deaerated solution containing $H_2O_2$. Upon mixing the following reactions occur:

$$[Cr^{II}(nta)(H_2O)_2]^- + H_2O_2 \xrightarrow{H_2O} [Cr^{III}(nta)(H_2O)_2] + \cdot OH \qquad (6)$$

or[10]

$$\begin{gathered} Cr(H_2O)_6^{2+} + H_2O_2 \rightarrow Cr^{III}{}_{aq} + \cdot OH \\ \cdot OH + HCR_1R_2OH \rightarrow H_2O + \cdot CR_1R_2OH \\ k_7 > 8 \times 10^8\ M^{-1}\ s^{-1}\ \text{[11]} \end{gathered} \qquad (7)$$

$$[Cr^{II}(nta)(H_2O)_2]^- + \cdot CR_1R_2OH \rightarrow [(nta)(H_2O)Cr^{III}–CR_1R_2OH]^- \qquad (8)$$

$$Cr(H_2O)_6^{2+} + \cdot CR_1R_2OH \rightarrow [(H_2O)_5Cr^{III}–CR_1R_2OH]^{2+} \qquad (9)$$

In order to avoid reactions 10 and 11 the concentration ratios $[HCR_1R_2OH] \geqslant 10[CH_3CO_2^-]$ and $[HCR_1R_2OH] > 30[nta]$ have to be kept:

$$\begin{gathered} \cdot OH + CH_3CO_2^- \rightarrow H_2O + \cdot CH_2CO_2^- \\ k_{10} = 8.5 \times 10^7\ M^{-1}\ s^{-1}\ \text{[11]} \end{gathered} \qquad (10)$$

$$\begin{gathered} \cdot OH + N(CH_2CO_2^-)_3 \rightarrow H_2O + N(CH_2CO_2^-)_2(\cdot CHCO_2^-) \\ k_{11} = 7.5 \times 10^8\ M^{-1}\ s^{-1} \text{ at pH } 4.0\text{[12]} \end{gathered} \qquad (11)$$

The stability constant of $[Cr(nta)(H_2O)_2^-]$ at $\mu = 1$ M was reported:

$$\begin{gathered} Cr(H_2O)_6^{2+} + nta^{3-} \rightleftarrows [Cr(nta)(H_2O)_2]^- \\ K = 3.2 \times 10^6\ M^{-1}\ \text{[13]} \end{gathered} \qquad (12)$$

At a lower ionic strength, as in this study, a considerably higher stability constant is expected. The p$K_a$'s for nta are p$K_{a_1} = 9.5$, p$K_{a_2} = 7.2$, and p$K_{a_3} = 1.7$.[14] From these values the apparent stability constants of $[Cr(nta)(H_2O)_2]^-$ at pH 4.0 and 5.0 are 10 and 100 $M^{-1}$, respectively. In order to avoid a competition of reaction 9 with reaction 8, very high concentrations of nta are required in this pH range. These concentrations are impractical due to the requirement that $[HCR_1R_2OH] > 30[nta]$. Thus under our experimental conditions reaction 9 competes with reaction 8. The $[(H_2O)_5Cr^{III}–CR_1R_2OH]^{2+}$ complex thus formed decomposes via two competing pathways:

$$\begin{gathered} [(H_2O)_5Cr^{III}–CR_1R_2OH]^{2+} \xrightarrow{H_2O} Cr^{III}{}_{aq} + HCR_1R_2OH \\ k > 3 \times 10^{-2}\ s^{-1} \text{ at pH } >4.0\text{[7]} \end{gathered} \qquad (2)$$

$$[(H_2O)_5Cr^{III}–CR_1R_2OH]^{2+} + nta^{3-} \rightarrow [(nta)(H_2O)Cr^{III}–CR_1R_2OH]^- \qquad (13)$$

followed by

$$\begin{gathered} [(nta)(H_2O)Cr^{III}–CR_1R_2OH]^- \xrightarrow{H_2O} [Cr^{III}(nta)(H_2O)_2] + HCR_1R_2OH \\ k_{14} < 2.5 \times 10^{-3}\ s^{-1} \text{ (see below)} \end{gathered} \qquad (14)$$

From these data it is clear that reaction 2 did not interfere with our measurement of the specific rates of reaction 14. As in many experiments, see below, the nta concentration was relatively low, and it is clear that $k_{13}[nta^{3-}] > k_2$, in analogy to similar reports for the edta system.[6]

**Pulse-Radiolysis Experiments.** This technique was used for measuring the specific rates of reaction 8 and the rates of decomposition of $[L_5Cr^{III}–CR_1R_2OH]$ complexes with short lifetimes. This technique was also used to determine the molar absorption coefficients of the $[L_5Cr^{III}–CR_1R_2OH]$ complexes and for measuring the absorption spectrum of $[([15]ane\ N_4)(H_2O)Cr^{III}–C(CH_3)_2OH]^{2+}$.

The radiolysis of water and dilute aqueous solutions can be summed up by[15]

$$H_2O \xrightarrow{\gamma,\, e^-} e_{aq}^-, \cdot H, \cdot OH, H_2, H_2O_2, H_3O^+ \qquad (15)$$

The yields of these products are $G_{e_{aq}^-} = 2.65$, $G_{OH} = 2.65$, $G_H = 0.60$, $G_{H_2} = 0.45$ and $G_{H_2O_2} = 0.75$. ($G$ is defined as the number of molecules of each product per 100 eV absorbed in the solution.[15]) In concentrated solutions the yield of the primary free radicals is often somewhat higher and that of $H_2$ and $H_2O_2$ somewhat lower.[15]

In neutral $N_2O$-saturated solutions, $[N_2O] = 2.2 \times 10^{-2}$ M, the following reaction occurs:

$$N_2O + e_{aq}^- \xrightarrow{H_2O} N_2 + \cdot OH \qquad k = 8.7 \times 10^9\ M^{-1}\ s^{-1}\ \text{[11]} \qquad (16)$$

thus all the primary free radicals aretransformed into ·OH and ·H free radicals. The ·OH radicals react in the systems studied via reactions 7, 10, and 11 and the ·H atoms via

$$\begin{gathered} \cdot H + HCR_1R_2OH \rightarrow H_2 + \cdot CR_1R_2OH \\ k > 1.6 \times 10^6\ M^{-1}\ s^{-1}\ \text{[11]} \end{gathered} \qquad (17)$$

$$\cdot H + CH_3CO_2^- \rightarrow H_2 + \cdot CH_2CO_2^- \qquad k = 3.5 \times 10^5\ M^{-1}\ s^{-1}\ \text{[11]} \qquad (18)$$

$$\begin{gathered} \cdot H + N(CH_2CO_2^-)_3 \rightarrow H_2 + N(CH_2CO_2^-)_2(\cdot CHCO_2^-) \\ k = 7.5 \times 10^6\ M^{-1}\ s^{-1}\ \text{[11]} \end{gathered} \qquad (19)$$

Thus in $N_2O$-saturated solutions, under our experimental conditions, all the free radicals are transformed into the desired $\cdot CR_1R_2OH$ free radicals.[16]

We observed that when solutions containing $[Cr(nta)(H_2O)_2]^-$ are saturated with $N_2O$ their color changes from blue to violet; i.e., the complex is oxidized to $Cr(nta)(H_2O)_2$ probably via

$$[Cr^{II}(nta)(H_2O)_2]^- + N_2O \xrightarrow{H_2O} [(H_2O)(nta)Cr^{IV}{=}O]^- + N_2 \qquad (20)$$

followed by

$$[(H_2O)(nta)Cr^{IV}{=}O]^- + [Cr^{II}(nta)(H_2O)_2]^- + 2H_3O^+ \rightarrow 2[Cr^{III}(nta)(H_2O)_2] \qquad (21)$$

in analogy to the reaction mechanism of $N_2O$ with other reducing complexes.[18] The specific rate of reaction 20 in solutions containing $1 \times 10^{-2}$ M $Cr^{2+}$, $(1.6–8.4) \times 10^{-2}$ M nta, and $(0.9–3.0) \times 10^{-2}$ M $CH_3CO_2Na$ in the pH range 5.0–6.0 was found to be $k_{20} = 1.35 \pm 0.35\ M^{-1}\ s^{-1}$.

Therefore $N_2O$ could not be used as the hydrated electron scavenger in the Cr–nta system. We used two alternative approaches.

a. When $\cdot C(CH_3)_2OH$ or $\cdot CH(CH_3)OH$ radicals were required, $(CH_3)_2CO$ or $CH_3CHO$, respectively, was used for scavenging the hydrated electrons:

$$\begin{gathered} e_{aq}^- + (CH_3)_2CO \xrightarrow{H_3O^+} \cdot C(CH_3)_2OH \\ k_{22} = 7.6 \times 10^9\ M^{-1}\ s^{-1}\ \text{[11]} \end{gathered} \qquad (22)$$

$$\begin{gathered} e_{aq}^- + CH_3CHO \xrightarrow{H_3O^+} \cdot CH(CH_3)OH \\ k_{23} = 3.5 \times 10^9\ M^{-1}\ s^{-1}\ \text{[11]} \end{gathered} \qquad (23)$$

The concentration of the acetone and acetaldehyde has to be high enough so that $e_{aq}^-$ would not react with $Cr(H_2O)_6^{2+}$[11] but low enough so that the ·OH radicals would not react with them ($k_{OH+(CH_3)_2CO} = 7 \times 10^7\ M^{-1}\ s^{-1}$; $k_{OH+CH_3CHO} \simeq 2 \times 10^9\ M^{-1}\ s^{-1}$[19]). The relatively large molar absorption coefficients of $(CH_3)_2CO$ and $CH_3CHO$ in the near-UV inhibits the measurement of the spectra of $[(nta)(H_2O)Cr^{III}–CR_1R_2OH]^-$ in this region.

**Table I.** Specific Rates of Formation, $k_8$, of Various $\alpha$-Hydroxoalkyl Complexes

| complex | $k$, $M^{-1}\ s^{-1}$ |
|---|---|
| $[(H_2O)_5Cr–CH_2OH]^{2+}$ | $1.6 \times 10^{8}$ [a] |
| $[(H_2O)_5Cr–CH(CH_3)OH]^{2+}$ | $7.9 \times 10^{7}$ [a] |
| $[(H_2O)_5Cr–C(CH_3)_2OH]^{2+}$ | $5.1 \times 10^{7}$ [a] |
| *trans*-$[([15]ane\text{-}N_4)(H_2O)Cr–CH_2OH]^{2+}$ | $(1.2 \pm 0.2) \times 10^{8}$ |
| *trans*-$[([15]ane\text{-}N_4)(H_2O)Cr–C(CH_3)_2OH]^{2+}$ | $(4.9 \pm 0.5) \times 10^{7}$ |
| *cis*-$[(nta)(H_2O)Cr–CH_2OH]^-$ | $(2.2 \pm 0.2) \times 10^{8}$ |
| *cis*$[(nta)(H_2O)Cr–CH(CH_3)OH]^-$ | $(1.0 \pm 0.1) \times 10^{8}$ |
| *cis*$[(nta)(H_2O)Cr–C(CH_3)_2OH]^-$ | $(8.4 \pm 0.8) \times 10^{7}$ |
| $[(edta)Cr–CH(CH_3)OH]^{2-}$ | $(3.9 \pm 0.5) \times 10^{7}$ |
| $[(edta)Cr–C(CH_3)_2OH]^{2-}$ | $(2.6 \pm 0.4) \times 10^{7}$ |

[a] Taken from ref 4.

b. As $CH_2O$ is present in neutral solutions as $CH_2(OH)_2$, it is a poor $e_{aq}^-$ scavenger. We therefore used $[Cr^{III}(nta)(H_2O)_2]$ as a scavenger:

$$[Cr^{III}(nta)(H_2O)_2] + e_{aq}^- \rightarrow [Cr^{II}(nta)(H_2O)_2]^- \qquad k = 2.6 \times 10^{10}\ M^{-1}\ s^{-1}\,{}^{20} \tag{24}$$

The concentration of $[Cr^{III}(nta)(H_2O)_2]$ has to be at least 10 times larger than that of $[Cr^{II}(nta)(H_2O)]^-$ so that the latter will not scavenge the hydrated electrons. (On the other hand, when the concentration ratio $[Cr^{III}(nta)(H_2O)_2]/[Cr^{II}(nta)(H_2O)_2]^-$ was too high, some of the $\cdot CR_1R_2OH$ radicals reacted with the tervalent complex. These reactions are out of the scope of the present study and will not be discussed further.) Finally due to the strong absorption bands of $[Cr^{III}(nta)(H_2O)_2]$, only measurements around 325 nm, where it has an optical window, were possible.

**Measurement of the Spectra of the $[(nta)(H_2O)Cr^{III}–CR_1R_2OH]^-$ Complexes.** Due to the above mentioned experimental limitations the pulse-radiolytic technique could not be used for the measurement of these spectra. It was however used for determining the molar absorption coefficients at a given wavelength. The spectra of samples prepared by the modified Fenton reagent technique were recorded. These samples contain also $[Cr^{III}(nta)(H_2O)_2]$, and their concentration is not constant during the measurement due to reaction 14. Therefore the spectra were calculated by using the following data: (a) the measured spectra, (b) the spectra of the solutions after reaction 14 ended, (c) the absorption spectrum of $[Cr^{III}(nta)(H_2O)_2]$ measured separately, (d) the molar absorption coefficient of $[(nta)(H_2O)Cr^{III}–CR_1R_2OH]^-$ at a given wavelength, and (e) the measured rate of reaction 14 (see below).

## Results

$N_2O$-saturated solutions containing 1.0 M of the required alcohol, $(0.16–1.0) \times 10^{-3}$ M $Cr(H_2O)_6^{2+}$, $(0.2–11.0) \times 10^{-3}$ M $[15]ane\text{-}N_4$, and $(0–9) \times 10^{-3}$ M total acetate (the solutions contain both $CH_3CO_2^-$ and $CH_3CO_2H$ the sum of their concentrations is denoted as total acetate) in the pH range 4.4–5.3 were irradiated. The specific rates of the reaction

$$trans\text{-}[(H_2O)_2Cr^{II}([15]ane\text{-}N_4)]^{2+} + \cdot CR_1R_2OH \rightarrow trans\text{-}[(H_2O)([15]ane\text{-}N_4)Cr^{III}–CR_1R_2OH]^{2+} \tag{25}$$

were measured by following the appearance of the absorption due to the ($\alpha$-hydroxyalkyl)chromium complex at 320 nm, which always obeyed a pseudo-first-order rate law. The results are summed up in Table I. The spectrum of *trans*-$[(H_2O)([15]ane\text{-}N_4)Cr^{III}–C(CH_3)_2OH]^{2+}$ is plotted in Figure 1.

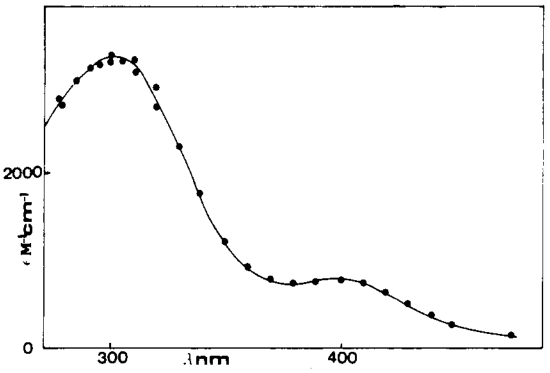


**Figure 1.** Absorption spectrum of *trans*-$[(H_2O)([15]ane\text{-}N_4)Cr–C(CH_3)_2OH]^{2+}$ at pH 5.0.

The observed first-order rates of the heterolytic hydrolysis reaction 2 for *trans*-$[(H_2O)([15]ane\text{-}N_4)Cr^{III}–CR_1R_2OH]^{2+}$ under different conditions are summed up in Table II. This reaction always obeyed a first-order rate law, the rate of reaction being independent of the pulse intensity, wavelength, and the concentration of $Cr^{2+}$, ([15]ane $N_4$), and $HCR_1R_2OH$, but dependent on pH and acetate concentration. The latter dependence is plotted in Figure 2. From the figure it is evident that up to $7 \times 10^{-2}$ M acetate reaction 2 is pseudo first order in acetate, but at higher concentrations a saturation effect is observed and $k_2$ approaches a limiting value.

Helium-saturated solutions containing $(0.42–1.00) \times 10^{-3}$ M $Cr^{2+}{}_{aq}$, $5.5 \times 10^{-2}$ M nta, and $9 \times 10^{-3}$ M total acetate in the pH range 5.0–6.4 plus 2.1 M $CH(CH_3)_2OH$ and 0.12 M $(CH_3)_2CO$ or 1.8 M $C_2H_5OH$ and 0.16 M $CH_3CHO$ were irradiated. The specific rate of reaction 8 was calculated from the rate of appearance of the absorption due to the *cis*-$[(nta)(H_2O)Cr^{III}–$

**Table II.** Observed Rates of Decomposition of *trans*-$[(H_2O)([15]ane\text{-}N_4)Cr–CR_1R_2OH]^{2+}$ Complexes at pH 4.4–5.3 at Different Acetate Concentrations[a]

| expt | $:CR_1R_2OH$ | $10^3[[15]ane\text{-}N_4]$, M | $10^3[Cr^{2+}]$, M | $10^3$[total acetate], M | $10^3$[acetate], M | pH | $k_{obsd}$, $s^{-1}$ |
|---|---|---|---|---|---|---|---|
| 1 | $:C(CH_3)_2OH$ | 1.10[c] | 1.08 | | | 4.4 | 0.023 |
| 2 | | 1.00[c] | 1.08 | 9.00 | 2.80 | 4.4 | 0.85 |
| 3 | | 1.00[c] | 1.08 | 27.00 | 8.40 | 4.4 | 1.16 |
| 4 [b] | | 1.10 | 1.00 | 1.00 | 0.47 | 4.7 | 0.23 |
| 5 | | 0.36 | 0.30 | 90.00 | 47.90 | 4.8 | 2.08 |
| 6 | | 0.36 | 0.30 | 70.00 | 37.20 | 4.8 | 2.00 |
| 7 | | 0.36 | 0.30 | 30.00 | 16.00 | 4.8 | 1.88 |
| 8 | | 0.36 | 0.30 | 45.00 | 23.90 | 4.8 | 1.92 |
| 9 | | 0.36 | 0.30 | 9.00 | 5.30 | 4.9 | 1.04 |
| 10 | | 1.10 | 1.00 | | | 5.0 | 0.09 |
| 11 [b] | | 1.10 | 1.00 | | | 5.0 | 0.11 |
| 12 [b] | | 1.10 | 1.00 | 6.00 | 3.86 | 5.0 | 0.39 |
| 13 | | 0.36 | 0.30 | 4.50 | 3.12 | 5.0 | 0.79 |
| 14 [b] | | 1.10 | 1.00 | 0.45 | 0.31 | 5.1 | 0.16 |
| 15 [b] | | 1.10 | 1.00 | 3.00 | 2.08 | 5.1 | 0.30 |
| 16 | | 0.70 | 0.51 | | | 5.3 | 0.30 |
| 17 | | 0.70 | 0.60 | 5.00 | 3.91 | 5.3 | 0.62 |
| 18 | | 0.70 | 0.56 | 2.00 | 1.56 | 5.3 | 0.53 |
| 19 | $:CH(CH_3)OH$ | 0.70 | 0.58 | | | 4.7 | $\leqslant 0.04$ |
| 20 | | 0.70 | 0.60 | 9.00 | 4.5 | 4.7 | 0.77 |
| 21 | $:CH_2OH$ | 0.70 | 0.56 | | | 4.7 | $\leqslant 0.02$ |
| 22 | | 0.70 | 0.61 | 9.00 | 4.5 | 4.7 | 0.13 |

[a] Measured at 325 nm; a Corning 053 filter was introduced to prevent photodecomposition. [b] Measured at 410 nm with a Corning 3-75 filter. [c] These solutions contained higher Cr(II) concentration than that of the ligand.

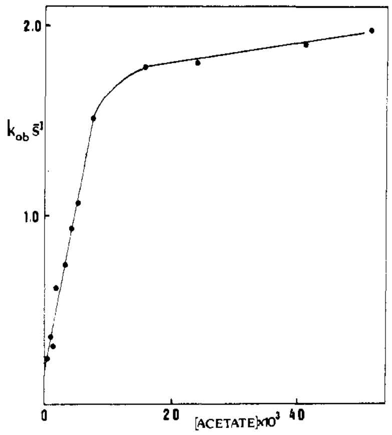


**Figure 2.** Dependence of the rate of hydrolysis of *trans*-$[(H_2O)([15]\text{ane-}N_4)Cr{-}C(CH_3)_2OH]^{2+}$ on $[CH_3CO_2^-]$. The value of $[CH_3CO_2^-]$ is calculated from the pH and total acetate concentration data taken from Table II.

**Table V.** pH and [Acetate] Dependence of the Rate of Decomposition of *cis*-$[(nta)(H_2O)Cr{-}C(CH_3)_2OH]^-$ [a]

| $10^3$ × [nta], M | $10^3$ × [$Cr^{2+}$], M | $10^3$ × [$H_2O_2$], M | $10^3$[total acetate], M | $10^3$ × [acetate], M | pH | $10^3$ × $k_{obsd}$, $s^{-1}$ |
|---|---|---|---|---|---|---|
| 14.6 | 12.2 | 1.0 | 7.2 | 1.6 | 4.2 | 3.3 |
| 6.3 | 1.7 | 0.7 | 1.7 | 0.4 | 4.2 | 2.8 |
| 7.4 | 7.0 | 0.7 | 9.2 | 2.4 | 4.3 | 3.3 |
| 5.4 | 4.5 | 0.9 | | | 4.4 | 2.0 |
| 7.4 | 7.0 | 2.9 | 9.2 | 3.6 | 4.6 | 4.3 |
| 7.4 | 7.0 | 5.0 | 9.6 | 4.0 | 4.7 | 7.0 |
| 7.7 | 4.0 | 1.1 | | | 4.8 | 4.2 |
| 5.4 | 4.5 | 0.9 | 9.2 | 5.4 | 4.9 | 4.0 |
| 10.8 | 4.5 | 0.9 | 9.2 | 5.4 | 4.9 | 3.7 |
| 5.4 | 4.5 | 0.9 | | | 4.9 | 2.8 |
| 4.6 | 4.0 | 0.9 | 9.6 | 6.2 | 5.0 | 6.1 |
| 7.4 | 6.7 | 2.2 | 9.2 | 6.8 | 5.2 | 6.8 |
| 7.4 | 5.6 | 2.2 | 46.0 | 36.0 | 5.3 | 12.2 |
| 7.4 | 4.8 | 2.2 | 4.8 | 3.8 | 5.3 | 5.3 |
| 7.4 | 5.6 | 2.2 | 9.2 | 7.2 | 5.3 | 7.0 |
| 7.4 | 6.7 | 2.2 | 9.2 | 7.5 | 5.4 | 7.1 |
| 7.4 | 6.7 | 2.2 | 9.2 | 7.8 | 5.5 | 7.4 |
| 4.6 | 3.8 | 0.8 | 9.6 | 8.2 | 5.5 | 4.0 [b] |
| 4.6 | 4.0 | 0.9 | 9.2 | 7.8 | 5.5 | 9.0 |
| 4.6 | 3.8 | 0.7 | 9.6 | 4.9 | 5.6 | 9.1 |
| 7.4 | 7.0 | 2.2 | 9.2 | 8.3 | 5.7 | 11.0 |
| 7.4 | 4.4 | 2.2 | 9.2 | 8.5 | 5.8 | 8.9 |
| 7.4 | 4.4 | 2.2 | 9.2 | 8.5 | 5.8 | 14.0 [c] |
| 7.4 | 4.4 | 2.2 | 9.2 | 8.5 | 5.8 | 19.0 [d] |
| 7.4 | 4.4 | 2.2 | 9.2 | 8.5 | 5.8 | 15.6 [e] |
| 7.4 | 6.7 | 2.2 | 9.2 | 8.6 | 5.9 | 10.3 |
| 7.4 | 6.2 | 2.2 | 9.2 | 8.7 | 6.0 | 9.1 |

[a] [2-proponal] = 0.70–0.96 M; rates measured at 402 nm. [b] $[Cr^{III}(nta)(H_2O)_2]_0 = 1.8 \times 10^{-2}$ M. [c] $[NaClO_4] = 1.84 \times 10^{-2}$ M. [d] $[NaClO_4] = 0.18$ M. [e] $[NaClO_4] = 0.37$ M.

$CR_1R_2OH]^-$ complexes, which obeyed a pseudo-first-order rate law, the rate being proportional to *cis*-$[(nta)Cr(H_2O)_2]^-$ and independent of pulse intensity, wavelength, and pH. The results are summed up in Table I. Analogous experiments with edta replacing nta were carried out. The results are also summed up in Table I.

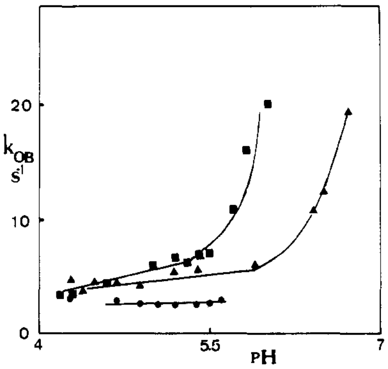


**Figure 3.** pH effect on the rate of hydrolysis of *cis*-$[(nta)(H_2O)Cr^{III}{-}CR_1R_2OH]^-$ complexes: (●) :$CH_2OH$; (▲) :$CH(CH_3)OH$; (■) :$C(CH_3)_2OH$. Data were taken from Tables III–V.

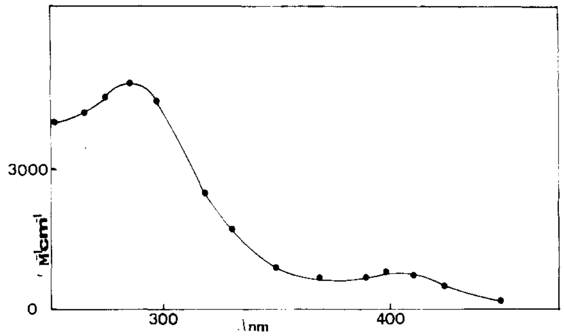


**Figure 4.** Absorption spectrum of *cis*-$[(nta)(H_2O)Cr{-}CH(CH_3)OH]^-$ at pH 5.0.

Helium-saturated solutions containing 1.0 × $10^{-3}$ M $[(nta)Cr^{III}(H_2O)_2]$, 5.5 × $10^{-2}$ M nta, 9 × $10^{-3}$ M total acetate, and (2–5) × $10^{-4}$ M $Cr^{2+}_{aq}$ at pH 5.6 plus 2.2 M $CH_3OH$ or 2.1 M $CH(CH_3)_2OH$ were irradiated. The specific rate of reaction 8 was calculated from the rate of formation of *cis*-$[(nta)(H_2O)Cr^{III}{-}CR_1R_2OH]^-$; the results for the 2-propanol system were identical with those observed in the system described above.

The kinetics of decomposition of the *cis*-$[(nta)(H_2O)Cr^{III}{-}CR_1R_2OH]^-$ complexes were measured by following the rate of bleaching of their absorption in samples prepared by the modified Fenton reagent technique. In all cases the kinetics obeyed first-order rate laws, the rate of reaction being independent of wavelength and the concentration of $Cr^{2+}_{aq}$, nta, $H_2O_2$, and alcohol. Also, ionic strength had nearly no effect on the rates. The rates depend slightly on the acetate concentration and on pH; the latter dependence is plotted in Figure 3. The results are summed up in Tables III–V (Tables III and IV are as supplementary material).

The spectra of the *cis*-$[(nta)(H_2O)Cr^{III}{-}CR_1R_2OH]^-$ complexes were calculated from the results as described in the Experimental Section. The data are summed up in Tabler VI; a typical spectrum is plotted in Figure 4. It should be noted that for the nta complexes two isomers might be formed in the pulse-radiolytic experiments, one with the α-hydroxyalkyl group trans to the nitrogen

**Table VI.** Absorption Maxima and Molar Extinction Coefficients of $[L_5Cr^{III}{-}CR_1R_2OH]$ Complexes

| $[L_5CrCR_1R_2OH]$ | $\lambda_1$, nm | $\epsilon_1$, $M^{-1}$ $cm^{-1}$ | $\lambda_2$, nm | $\epsilon_2$, $M^{-1}$ $cm^{-1}$ | ref |
|---|---|---|---|---|---|
| $[([15]\text{ane-}N_4)(H_2O)Cr{:}C(CH_3)_2OH]^{2+}$ | 305 ± 5 | 3350 ± 350 | 400 ± 5 | 480 ± 50 | this work |
| $[(nta)Cr(H_2O){:}CH_2OH]^-$ | 255 ± 5 | 3800 ± 380 | 400 ± 5 | 320 ± 35 | this work |
| $[(nta)Cr(H_2O){:}CH(CH_3)OH]^-$ | 285 ± 5 | 4850 ± 500 | 400 ± 5 | 800 ± 80 | this work |
| $[(nta)Cr(H_2O){:}C(CH_3)_2OH]^-$ | 295 ± 5 | 7750 ± 780 | 410 ± 5 | 1150 ± 120 | this work |
| $[(H_2O)_5Cr{:}CH_2OH]^{2+}$ | 282 | 2400 | 392 | 570 | 4 |
| $[(H_2O)_5Cr{:}CH(CH_3)OH]^{2+}$ | 296 | 2800 | 396 | 690 | 4 |
| $[(H_2O)_5Cr{:}C(CH_3)_2OH]^{2+}$ | 311 | 2500 | 407 | 700 | 4 |
| $[(edta)Cr{:}CH_2OH]^{2-}$ | 270 | 2000 | 385 | 270 | 6 |
| $[(edta)Cr{:}CH(CH_3)OH]^{2-}$ | 280 | 2600 | 392 | 330 | 6 |
| $[(edta)Cr{:}C(CH_3)_2OH]^{2-}$ | 295 | 2000 | 385 | 360 | 6 |

**Table VII.** Specific Rates of Hydrolysis of Several $[L_5Cr^{III}–CR_1R_2OH]$ Complexes[a]

| nonparticipating ligands | $k_{H_2O}$, $s^{-1}$ | $k_{Ac} = k_{31}K_{30}$, $M^{-1}\ s^{-1}$ | $k_{H_3O^+}$, $M^{-1}\ s^{-1}$ | $:CR_1R_2OH$ |
|---|---|---|---|---|
| $(H_2O)_5$ | $6.6 \times 10^{-4}$ [b] | 29[d] | $4.65 \times 10^{-4}$ [b] | $:CH_2OH$ |
| *cis*-nta($H_2O$) | $2.5 \times 10^{-3}$ | ≤0.18 | | |
| *trans*-([15]ane-$N_4$)($H_2O$) | | ~25 | | |
| edta | $2.25 \times 10^{-4}$ [c] | | $2.56 \times 10^{2}$ [c] | |
| $(H_2O)_5$ | $1.9 \times 10^{-3}$ [b] | 140[d] | $1.22 \times 10^{-3}$ [b] | $:CH(CH_3)OH$ |
| *cis*-nta($H_2O$) | $3.4 \times 10^{-3}$ | ≤0.3 | | |
| *trans*-([15]ane-$N_4$)($H_2O$) | | ~170 | | |
| edta | $1.35 \times 10^{-3}$ [c] | ≤0.1 | $7.35 \times 10$ [c] | |
| $(H_2O)_5$ | $3.3 \times 10^{-3}$ [b] | 210[d] | $4.9 \times 10^{-3}$ [b] | $:C(CH_3)_2OH$ |
| *cis*-nta($H_2O$) | $3.8 \times 10^{-3}$ | ≤0.6 | | |
| *trans*-([15]ane-$N_4$)($H_2O$) | $2.0 \times 10^{-3}$ | 150 | | |
| edta | $1.38 \times 10^{-2}$ [c] | ≤0.1 | $1.76 \times 10^{2}$ [c] | |

[a] $k_{H_2O}$ is the [acid]-independent term; $k_{H_3O^+}$ is the [acid]-dependent term; $k_{Ac}$ is the [acetate]-dependent term in the region where the rate increases linearly with acetate concentration. [b] Taken from ref 22. [c] Taken from ref 6. [d] Taken from ref 7.

ligand, the other with the α-hydroxyalkyl group trans to one of the carboxylate groups of nta. Due to reasons discussed below we believe that the complexes prepared by the modified Fenton reagent and observed in the spectrophotometer have the structure of the former isomer. Therefore the absolute absorption coefficients as determined from the pulse-radiolytic experiments might include a small systematic error.

**Kinetics of Decomposition of *cis*-$[(nta)(H_2O)Cr^{III}–CH_3]^-$.** Helium-saturated solutions containing $1.0 \times 10^{-2}$ M $[(nta)Cr^{III}(H_2O)_2]$, $2 \times 10^{-2}$ M nta, 1.2 M $(CH_3)_2SO$, and $5 \times 10^{-4}$ M *cis*-$[(nta)Cr^{II}(H_2O)_2]^-$, at pH 5.0 were irradiated. Under these conditions the following reactions occur:

$$(CH_3)_2SO + \cdot OH \rightarrow (CH_3)_2\dot{S}O(OH) \qquad k = 7.0 \times 10^9\ M^{-1}\ s^{-1}\ {}^{22} \tag{26}$$

$$(CH_3)_2\dot{S}O(OH) \rightarrow CH_3SO_2H + \cdot CH_3 \qquad k = 1.5 \times 10^7\ s^{-1}\ {}^{22} \tag{27}$$

$$[(nta)Cr^{II}(H_2O)_2]^- + \cdot CH_3 \rightarrow cis\text{-}[(nta)(H_2O)Cr^{III}–CH_3]^- \tag{28}$$

The maximum of the absorption band of $(H_2O)_5Cr–CH_3^{2+}$ is at 258 nm;[23] nta causes a blue shift of the absorption bands (see below). Thus only a small signal in the optical accessible window, 315–335 nm, under the experimental conditions, was obtained. However the rate of hydrolysis under these conditions could be measured

$$cis\text{-}[(nta)(H_2O)Cr^{III}–CH_3]^- \rightarrow cis\text{-}[(nta)Cr^{III}(H_2O)_2] + CH_4 \qquad k_{29} = (2.5 \pm 0.7) \times 10^{-2}\ s^{-1} \tag{29}$$

This rate is over 2 orders of magnitude greater than that reported for $[(H_2O)_5Cr^{III}–CH_3]^{2+}$.[2]

## Discussion

**Spectra of α-Hydroxyalkyl–Chromium(III) Complexes.** All complexes with chromium(III)–carbon bonds, where the organic group is an aliphatic one, have three typical absorption bands.

a. The first is a weak band at 516–560 nm attributed to a d–d transition. Due to the low concentrations of the complexes in this study these bands were not observed.

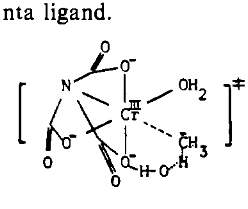
b. The second is a band in the 380–410-nm region with molar absorption coefficients in the range 100–1000 $M^{-1}\ cm^{-1}$, attributed to a d–d transition into which some charge-transfer character is mixed.[4] As can be seen from Table VI, exchanging the aqua ligands by nta, [15]ane-$N_4$, or edta has little effect on this band. This observation is in accord with the suggested assignment of this band.[4]

c. The third is an absorption band in the 250–310-nm region with large molar absorption coefficients attributed to a LMCT transition.[4] The results in Table VI clearly indicate that exchanging the aqua ligands by the stronger σ donor ligands, nta, edta, and ([15]ane $N_4$)), causes a blue shift of this band. This shift is in accord with the assignment of the band to a LMCT transition, as these ligands are expected to lower the redox potential of the $Cr^{II}/Cr^{III}$ couple; i.e., the electron affinity of the $Cr^{III}$ is lowered.

**Kinetics of Formation of the α-Hydroxyalkyl Complexes.** The results in Table I clearly indicate that the specific rates of reaction of $Cr(H_2O)_6^{2+}$, $[Cr^{II}(nta)(H_2O)_2]^-$, and $[Cr^{II}([15]ane\text{-}N_4)(H_2O)_2]^{2+}$ with the α-hydroxyalkyl free radicals are similar. The results seem to indicate that the nta complex is slightly more reactive than the other complexes. As in the nta and ([15]ane-$N_4$) complexes, less sites for attack are available; the results suggest that the decrease in the redox potential by the substituting ligands enhances the specific rates of formation of the chromium–carbon bonds. No steric factors seem to affect the observed rates. The decreased specific rates of reaction observed for the edta complexes, Table I, are attributed to the fact that no aqua ligand is present in the hexadentate $Cr^{II}$(edta) complex and only those complexes where the edta is pentacoordinated can react.

**Kinetics of Hydrolysis of the α-Hydroxyalkyl–Chromium(III) Complexes.** In Table VII are summed up the specific rates of the pH-independent terms, $k_{H_2O}$, of the hydrolysis reaction of the different complexes studied. (For comparison also the other terms are included in Table VII.) The values for the nta complexes are obtained by extrapolation from Figure 3, which causes the larger error limit. The results clearly point out that the presence of a cis aqua ligand, e.g. in $[(H_2O)_5Cr^{III}–CR_1R_2OH]^{2+}$ and *cis*-$[(nta)(H_2O)Cr^{III}–CR_1R_2OH]^-$, or its absence, e.g. in $[(edta)Cr^{III}–CR_1R_1OH]^{2-}$ and *trans*-$[([15]ane\text{-}N_4)(H_2O)Cr^{III}–Cr_1R_2OH]^{2+}$, has no effect on the specific rate of the hydrolysis reactions. This is true though the effects of edta and nta on the thermodynamic stability of the complexes, as judged from the energy of their LMCT bands, are similar. We therefore conclude that the attacking electrophilic water molecule is one from the solvent and not a cis ligand; i.e. the correct transition state description is III or probably IV.

The fact that $k_{H_2O}$ for $[(H_2O)_5Cr^{III}–CH_3]^{2+}$ is considerably lower than for $[(H_2O)_5Cr^{III}–Cr_1R_2OH]^{2+}$ has been attributed to the stabilization of the transition-state-complex IV by hydrogen bonding in the α-hydroxyalkyl–chromium(III) complexes.[4a] It is plausible that the enhanced rate of hydrolysis of *cis*-$[(nta)(H_2O)Cr^{III}–CH_3]^-$ in comparison to that of $[(H_2O)_5Cr^{III}–CH_3]^{2+}$ is due to a similar effect, i.e. that transition state VI is stabilized by hydrogen bonding to the "nonparticipating" nta ligand.



VI

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**pH Effects on the Rate of Hydrolysis of $\alpha$-Hydroxyalkyl–Chromium(III) Complexes.** The rate of the hydrolysis of *trans*-$[([15]\text{ane-N}_4)(H_2O)Cr^{III}\text{–}C(CH_3)_2OH]^{2+}$ increases with pH above pH 4.0 in a fashion similar to that reported for $[(H_2O)_5Cr^{III}\text{–}C(CH_3)_2OH]^{2+}$.[7] The effect in the former is slightly more pronounced. This observation is in accord with the suggestion[7] that the increased rate is due to the p$K_a$ of the trans aqua ligand.

The rate of hydrolysis of the *cis*-$[(\text{nta})(H_2O)Cr^{III}\text{–}CR_1R_2OH]^-$ complexes is nearly pH independent up to pH 5.5 and increases only at higher pHs, Figure 3. The latter increase is probably due to the deprotonation of the cis water molecule. The pH dependence, at lower pHs, of the rate of hydrolysis of $[(H_2O)_5Cr\text{–}C(CH_3)_2OH]^{2+}$ was also attributed in part to the p$K_a$ of the cis aqua ligands.[7] We could not extend the measurements to higher pHs due to precipitation. The higher pH region at which the effect is observed for the nta complexes is probably due to a shift in the p$K_a$ of the water molecule caused by the negative charge of the nta ligand.

**Acetate-Catalyzed Hydrolysis of $\alpha$-Hydroxyalkyl–Chromium(III) Complexes.** Acetate was shown to accelerate the rate of hydrolysis of the $[(H_2O)_5Cr^{III}\text{–}CR_1R_2OH]^{2+}$ complexes.[7,24] The results were interpreted as being due to a trans ligand exchange followed by fast hydroylsis.[7,24,25] We observe a similar effect of acetate on the rate of hydrolysis of *trans*-$[([15]\text{ane-N}_4)(H_2O)Cr^{III}\text{–}C(CH_3)_2OH]^{2+}$. The results in the latter system indicate that the increase in the rate of hydrolysis is pseudo first order in acetate up to a concentration of $1 \times 10^{-2}$ M and then levels off, Figure 2. The results fit a scheme similar to that suggested for the $[(H_2O)_5Cr^{III}\text{–}CR_1R_2OH]^{2+}$ system,[7,24] i.e.

$$\textit{trans}\text{-}[([15]\text{ane-N}_4)(H_2O)Cr^{III}\text{–}C(CH_3)_2OH]^{2+} + CH_3CO_2^- \overset{K_{30}}{\rightleftharpoons} \textit{trans}\text{-}[([15]\text{ane-N}_4)(CH_3CO_2)Cr^{III}\text{–}C(CH_3)_2OH]^{+} \quad (30)$$

$$\textit{trans}\text{-}[([15]\text{ane-N}_4)(CH_3CO_2)Cr^{III}\text{–}C(CH_3)_2OH]^{+} \xrightarrow[k_{31}]{H_2O} \textit{trans}\text{-}[([15]\text{ane-N}_4)(CH_3CO_2)Cr(H_2O)]^{2+} + CH(CH_3)_2OH \quad (31)$$

The rate of hydrolysis according to this scheme at high acetate concentration is $k_{\text{obsd}} = k_{H_2O} + k_{31}$. From the limiting value in Figure 2 we estimate that $k_{31} = 2 \pm 0.5\ s^{-1}$; $k_{H_2O}$ is clearly negligible. At lower acetate concentrations the expected rate is

$$k_{\text{obsd}} = k_{H_2O} + k_{31}K_{30}[CH_3CO_2^-]$$

The slope of the curve at low acetate concentrations in Figure 2 is $(150 \pm 60)\ M^{-1}\ s^{-1}$, and therefore $36 \leq K_{30} \leq 140\ M^{-1}$. These values are in good agreement with those estimated for the analogous $[(H_2O)_5Cr^{III}\text{–}C(CH_3)_2OH]^{2+}$ system.[7]

Almost no acetate effect was observed on the rate of hydrolysis of the *cis*-$[(\text{nta})(H_2O)Cr^{III}\text{–}CR_1R_2OH]^-$ complexes, Tables III–V. This is probably due to the fact that the acetate cannot substitute at the trans position. However we cannot rule out the possibility that the corresponding equilibrium constant to $K_{30}$ will be very small in the nta complexes due to the negative charge of the latter ligand.

Finally it should be pointed out again[7] that the large effect of a trans acetate ligand on the rate of hydrolysis suggests that in both $[(\text{edta})Cr^{III}\text{–}CR_1R_2OH]^{2-}$ and *cis*-$[(\text{nta})(H_2O)Cr^{III}\text{–}CR_1R_2OH]^-$ the $\alpha$-hydroxyalkyl ligand is bound to the chromium at a position trans to a nitrogen atom of the aminocarboxylate ligand, as depicted in the suggested structure of the complexes studied.

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**Registry No.** *trans*-$[([15]\text{ane-N}_4)(H_2O)Cr\text{–}CH_2OH]^{2+}$, 98737-23-6; *trans*-$[([15]\text{ane-N}_4)(H_2O)Cr\text{–}C(CH_3)_2OH]^{2+}$, 98737-24-7; *cis*-$[(\text{nta})(H_2O)Cr\text{–}CH_2OH]^-$, 96163-65-4; *cis*-$[(\text{nta})(H_2O)Cr\text{–}CH(CH_3)OH]^-$, 98737-25-8; *cis*-$[(\text{nta})(H_2O)Cr\text{–}C(CH_3)_2OH]^-$, 98760-07-7; $[(\text{edta})Cr\text{–}CH(CH_3)OH]^{2-}$, 98818-32-7; $[(\text{edta})Cr\text{–}C(CH_3)_2OH]^{2-}$, 79391-93-8; *trans*-$[(H_2O)([15]\text{ane-N}_4)Cr\text{–}CH(CH_3)OH]^{2+}$, 98737-26-9; $CH_3OH$, 67-56-1; $CH_3CH_2OH$, 64-17-5; $CH(CH_3)_2OH$, 67-63-0; $Cr(H_2O)_6^{2+}$, 20574-26-9; *cis*-$[Cr(\text{nta})(H_2O)_2]^-$, 96164-02-2; *trans*-$[Cr([15]\text{ane-N}_4)(H_2O)_2]^{2+}$, 70833-04-4; $[Cr(\text{edta})]^{2-}$, 12558-56-4; $(CH_3)_2SO$, 67-68-5; *cis*-$[(\text{nta})(H_2O)Cr\text{–}CH_3]^-$, 98737-27-0; *cis*-$[(\text{nta})Cr(H_2O)_2]$, 18042-08-5; *trans*-$[([15]\text{ane-N}_4)(CH_3CO_2)Cr(H_2O)]^{2+}$, 98737-28-1; $\cdot CH_2OH$, 2597-43-5; $\cdot CHCH_3OH$, 4422-54-2; $\cdot C(CH_3)_2OH$, 5131-95-3.

**Supplementary Material Available:** Tables III and IV, giving the observed rate of decomposition of *cis*-$[(\text{nta})(H_2O)Cr\text{–}CH_2OH]^-$ and *cis*-$[(\text{nta})(H_2O)Cr\text{–}CH(CH_3)OH]^-$ in analogy to Table V (2 pages). Ordering information is given on any current masthead page.

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