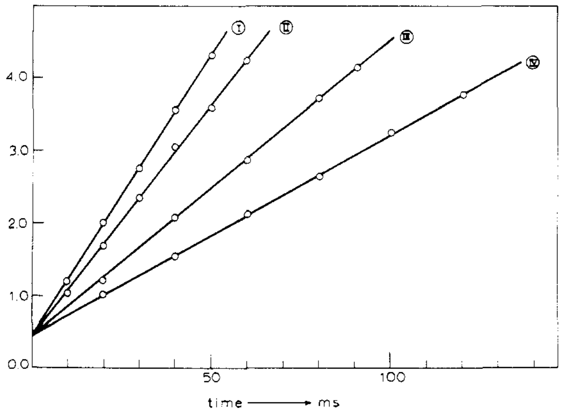

Figure 4. Plots of the equation $x_0/x - (k_2/k_{-1} - 1) \ln x = St + 1 - (k_2/k_{-1} - 1) \ln x_0$. All runs were 0.005 M in $[\mathrm{Eu^{II}}]_0$. I: $[\mathrm{Eu^{III}}]_0 = 0.180$ M, $[\mathrm{pyr}]_0 = 0.0005$ M, $[\mathrm{H^+}]_0 = 0.50$ M. II: $[\mathrm{Eu^{III}}]_0 = 0.500$ M, $[\mathrm{pyr}]_0 = 0.0020$ M, $[\mathrm{H^+}]_0 = 0.50$ M. III: $[\mathrm{Eu^{III}}]_0 = 0.180$ M, $[\mathrm{pyr}]_0 = 0.0010$ M, $[\mathrm{H^+}]_0 = 1.00$ M. IV: $[\mathrm{Eu^{III}}]_0 = 0.500$ M, $[\mathrm{pyr}]_0 = 0.0005$ M, $[\mathrm{H^+}]_0 = 1.00$ M.

reaction between $\mathrm{Cr^{II}}$ ion and pyruvic acid[1] this transformation is rate determining. In the reaction between $\mathrm{V^{II}}$ ion and pyruvic acid[2] the redox reaction is rate determining. The corresponding overall redox reaction of $\mathrm{Ti^{III}}$ ion is even slower.[8] The rates of these d ions correlate with their oxidation potentials:

$$\mathrm{Cr^{II}}\ (0.40\ \mathrm{V}) > \mathrm{V^{II}}\ (0.255\ \mathrm{V}) > \mathrm{Ti^{III}}\ (-0.04\ \mathrm{V})$$

On this scale f-donor $\mathrm{Eu^{II}}$ ion with an oxidation potential of 0.43 V is expected to react slightly faster than $\mathrm{Cr^{II}}$ ion. It does not. The explanation should not perhaps be sought in the redox reaction per se, but in the preceding complex formation (preequilibria, not depicted in the mechanism). It is reasonable to expect that complex formation via the d orbitals of $\mathrm{Cr^{II}}$ is more effective than formation via the f orbitals of $\mathrm{Eu^{II}}$ ion.

In the reaction of pyruvic acid with $\mathrm{V^{II}}$ ion the rate, in the range 0.5–2.5 M $\mathrm{HClO_4}$, is independent of hydrogen ion concentration. In the corresponding reaction of $\mathrm{Eu^{II}}$ ion a linear dependence on hydrogen ion concentration is observed. It can be argued that in both cases the rate-determining electron-transfer step is catalyzed by hydrogen ion, but in the case of the d-electron donor $\mathrm{V^{II}}$ ion the dependence on hydrogen ion concentration is canceled out by the inverse dependence in the preceding complex formation. This does not seem to be the case with $\mathrm{Eu^{II}}$ ion.

Registry No. $\mathrm{Eu^{2+}}$, 16910-54-6; pyr, 127-17-3; lactic acid, 50-21-5.

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[8] Unpublished results of the present authors.

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Kinetics and Mechanisms of the Cleavage of the Chromium–Carbon Bond in (Ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetato)(hydroxyalkyl)chromium(III) Complexes

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Kinetic measurements of the cleavage of the Cr–C bond in (ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetato)(hydroxyalkyl)chromium(III) complexes, $[\mathrm{Cr(CR_1R_2OH)(EDTA)}]^{2-}$ ($\mathrm{R_1,R_2}$ = H or $\mathrm{CH_3}$), to give $[\mathrm{Cr(EDTA)(H_2O)}]^-$ were made at ionic strength of 1.0 ($\mathrm{LiClO_4}$). The reactions obeyed the rate law $-d[\mathrm{complex}]/dt = (k_0 + k_1[\mathrm{H^+}])[\mathrm{complex}]$ for the $\mathrm{CH_2OH}$ and $\mathrm{C(CH_3)_2OH}$ complexes and the rate law $-d[\mathrm{complex}]/dt = [(k_0 + k_1[\mathrm{H^+}])/(1 + Q[\mathrm{H^+}])][\mathrm{complex}]$ for the $\mathrm{CH(CH_3)OH}$ complex. The rate constants at 25.0 °C were $k_0 = (2.52 \pm 0.22) \times 10^{-4}\ \mathrm{s^{-1}}$ and $k_1 = 256 \pm 3\ \mathrm{M^{-1}\ s^{-1}}$ for $[\mathrm{Cr(CH_2OH)(EDTA)}]^{2-}$, $k_0 = (1.35 \pm 0.11) \times 10^{-3}\ \mathrm{s^{-1}}$ and $k_1 = 73.5 \pm 4.2\ \mathrm{M^{-1}\ s^{-1}}$ for $[\mathrm{Cr(CH(CH_3)OH)(EDTA)}]^{2-}$, and $k_0 = (1.38 \pm 0.03) \times 10^{-2}\ \mathrm{s^{-1}}$ and $k_1 = 176 \pm 3\ \mathrm{M^{-1}\ s^{-1}}$ for $[\mathrm{Cr(C(CH_3)_2OH)(EDTA)}]^{2-}$. The activation parameters of these reactions were also determined. The value of Q was determined to be $2 \times 10^3\ \mathrm{M^{-1}}$ at 25.0 °C. Comparison of the kinetic parameters with those of the corresponding (hydroxyalkyl)pentaaqua complexes indicates that the uncoordinated carboxylic acid group of the coordinated EDTA acts as an internal electrophile to the chromium-bound carbon atom.

Introduction

Schmidt et al. reported the preparation of (hydroxyalkyl)pentaaquachromium(III) complexes ($[\mathrm{CrR(H_2O)_5}]^{2+}$) and the kinetics of the acid hydrolyses of $[\mathrm{CrR(H_2O)_5}]^{2+}$ to $[\mathrm{Cr(H_2O)_6}]^{3+}$.[1] It was found, in the present work, that analogous reactions in the presence of ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate afforded (ethylenediaminetetraacetato)(hydroxyalkyl)chromium(III) complexes (hereafter abbreviated as $[\mathrm{CrR(EDTA)}]^{2-}$), in which the R ligands were $\mathrm{CH_2OH^-}$, $\mathrm{CH(CH_3)OH^-}$, and $\mathrm{C(CH_3)_2OH^-}$. This paper describes the preparation of $[\mathrm{CrR(EDTA)}]^{2-}$ and the kinetic results of the cleavage reactions of the Cr–C bonds in these complexes. Through the comparison of the kinetic behaviors of the $[\mathrm{CrR(EDTA)}]^{2-}$ complexes with those of the corresponding $[\mathrm{CrR(H_2O)_5}]^{2+}$ complexes, a unique effect of the EDTA ligand on the rate of the Cr–C bond cleavage will be discussed.

Experimental Section

Materials. Redistilled water was used to prepare all the solutions. The solutions of $[\mathrm{Cr(H_2O)_6}](\mathrm{ClO_4})_2$ were prepared by the reduction of $[\mathrm{Cr(H_2O)_6}](\mathrm{ClO_4})_3$ solutions with zinc amalgam. The $[\mathrm{Cr^{II}(EDTA)(H_2O)}]^{2-}$ solutions were prepared by the addition of the $[\mathrm{Cr(H_2O)_6}]^{2+}$ solutions into solutions containing excess EDTA. An aqueous hydrogen peroxide solution (30%) was used without further purification and standardized against potassium permanganate solutions. The alcohols, methanol, ethanol, and 2-propanol, were purified by distillation. The solution of $\mathrm{LiClO_4}$ was prepared as reported previously.[2] In most experiments, the solutions of $[\mathrm{CrR(EDTA)}]^{2-}$ complexes were prepared as follows. The $[\mathrm{Cr(H_2O)_6}]^{2+}$ solution was injected into a solution containing appropriate amounts of $\mathrm{H_2O_2}$, EDTA, and alcohol (methanol, ethanol, or 2-propanol) under a nitrogen or argon atmosphere. The initial concentrations of the reagents

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Table I. Electronic Absorption Maxima (λ/nm) and Molar Absorptivities (ϵ/M^{-1} cm^{-1}) for $[Cr(CR_1R_2OH)(EDTA)]^{2-}$ and $[Cr(CR_1R_2OH)(H_2O)_5]^{2+}$

complex	λ (ε)	λ (ε)	λ (ε)	ref
$[Cr(CH_2OH)(EDTA)]^{2-}$	270 sh (2000)[a]	385 (270)	540 (130)	this work
$[Cr(CH_2OH)(EDTA)]^{2-}$	*b*	388 (290)[c]	540 (100)[c]	this work
$[Cr(CH(CH_3)OH)(EDTA)]^{2-}$	280 sh (2600)[a]	392 (330)	540 (170)	this work
$[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$	295 sh (2000)[a]	385 (360)	540 (180)	this work
$[Cr(CH_2OH)(H_2O)_5]^{2+}$	282 (2400)	392 (570)	*d*	3
$[Cr(CH(CH_3)OH)(H_2O)_5]^{2+}$	296 (2800)	396 (690)	*d*	3
$[Cr(C(CH_3)_2OH)(H_2O)_5]^{2+}$	311 (2500)	407 (700)	*d*	3

[a] sh means shoulder. [b] Not measured. [c] $[Cr(CH_2OH)(EDTA)]^{2-}$ was prepared by the reaction of $[Cr(CH_2OH)(H_2O)_5]^{2+}$ with EDTA. [d] The band in the visible region is too weak to be studied effectively by the pulse radiolytic technique.[3]

were $[[Cr(H_2O)_6]^{2+}]_0 = 4.00 \times 10^{-4}–3.85 \times 10^{-3}$ M, $[EDTA]_0 = 6.00 \times 10^{-3}–6.00 \times 10^{-2}$ M, $[H_2O_2]_0 = 1.99 \times 10^{-4}–1.99 \times 10^{-3}$ M, and [alcohol] = 0.18–1.98 M. An identical solution resulted when the $[Cr^{II}(EDTA)(H_2O)]^{2-}$ solution was mixed with a solution containing H_2O_2 and the corresponding alcohol or when H_2O_2 was added into a solution containing $[Cr^{II}(EDTA)(H_2O)]^{2-}$ and the alcohol.

Kinetic Procedures. Kinetic measurements were made under a nitrogen or argon atmosphere at $I = 1.0$ ($LiClO_4$) unless otherwise stated. The hydrogen ion concentrations were adjusted with EDTA solutions as buffer solutions and measured with a Toa HM-20B pH meter calibrated with standard perchloric acid solutions at $I = 1.0$ ($LiClO_4$). The cleavage of the Cr–C bond in $[CrR(EDTA)]^{2-}$ was monitored by following the decrease in absorbance at 340–370 nm with a Union-Giken SM401 recording spectrophotometer.

Results

Formation of $[CrR(EDTA)]^{2-}$. Schmidt et al.[1] prepared $[CrR(H_2O)_5]^{2+}$ by the oxidation of $[Cr(H_2O)_6]^{2+}$ with hydrogen peroxide in the presence of aliphatic alcohols. When $[Cr(H_2O)_6]^{2+}$ is replaced by $[Cr^{II}(EDTA)(H_2O)]^{2-}$, the formation of $[CrR(EDTA)]^{2-}$ may be expected by the following mechanism analogous to that for the formation of $[CrR(H_2O)_5]^{2+}$:

$$[Cr^{II}(EDTA)(H_2O)]^{2-} + H_2O_2 + H^+ \rightarrow [Cr^{III}(EDTA)(H_2O)]^- + \cdot OH + H_2O \quad (1)$$

$$HCR_1R_2OH + \cdot OH \rightarrow \cdot CR_1R_2OH + H_2O \quad (2)$$

$$[Cr^{II}(EDTA)(H_2O)]^{2-} + \cdot CR_1R_2OH \rightarrow [Cr(CR_1R_2OH)(EDTA)]^{2-} + H_2O \quad (3)$$

On the assumption that the stoichiometry of the reaction of $[Cr(EDTA)(H_2O)]^{2-}$ with H_2O_2 in the presence of alcohol is expressed as eq 4, the electronic spectra were depicted. The

$$2[Cr^{II}(EDTA)(H_2O)]^{2-} + HCR_1R_2OH + H_2O_2 + H^+ = [Cr^{III}(EDTA)(H_2O)]^- + [Cr^{III}(CR_1R_2OH)(EDTA)]^{2-} + 3H_2O \quad (4)$$

spectral data thus obtained are given in Table I and show that each complex gives a shoulder band around 270–295 nm (molar absorptivity $\epsilon \sim 2000$ M^{-1} cm^{-1}) and a band around 390 nm ($\epsilon \sim 300$ M^{-1} cm^{-1}). These data are quite similar to the reported spectral features of the complexes containing Cr–C bond.[1,3–13] For the comparison, the spectral data of some $[CrR(H_2O)_5]^{2+}$ complexes determined by the pulse radiolytic technique[3] are given also in Table I.

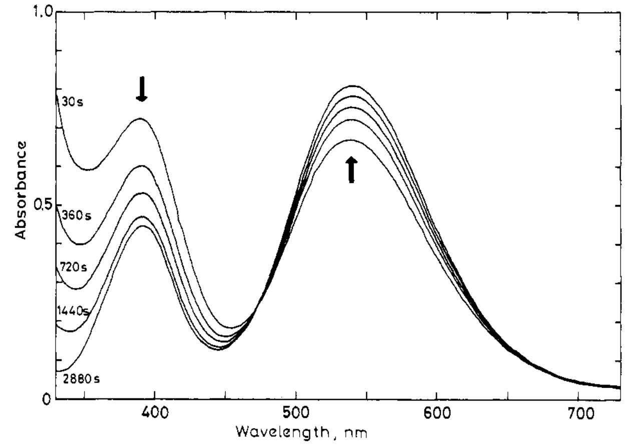

Figure 1. Changes in visible absorption spectrum for the Cr–C bond cleavage of $[Cr(CH_2OH)(EDTA)]^{2-}$ at $I = 1.0$ ($LiClO_4$) and 25.0 °C: $[H^+] = 4.51 \times 10^{-6}$ M, $[Cr(II)]_0 = 3.85 \times 10^{-3}$ M, $[EDTA]_{tot} = 6.00 \times 10^{-2}$ M, $[H_2O_2]_0 = 1.99 \times 10^{-3}$ M, $[CH_3OH] = 0.18$ M.

Additional evidence for the formation of a Cr–C bond was obtained by the following experiment. When EDTA was added to the solution containing $[Cr(CH_2OH)(H_2O)_5]^{2+}$ prepared by the method of Schmidt et al.,[1] spectral change occurred and was complete within the time of mixing (<30 s). This spectral change was consistent with reaction 5. On

$$[Cr(CH_2OH)(H_2O)_5]^{2+} + EDTA^{4-} \rightarrow [Cr(CH_2OH)(EDTA)]^{2-} + 5H_2O \quad (5)$$

the basis of eq 5, spectral data of $[Cr(CH_2OH)(EDTA)]^{2-}$ were estimated. The values are given in Table I. The satisfactory agreement is seen between the spectral data of $[Cr(CH_2OH)(EDTA)]^{2-}$ obtained from two independent sources.

Kinetic measurements were made for the oxidation of $[Cr^{II}(EDTA)(H_2O)]^{2-}$ to $[Cr^{III}(EDTA)(H_2O)]^-$ by H_2O_2. The rate constant was 3×10^5 M^{-1} s^{-1} at $[H^+] = 1 \times 10^{-6}$ M, $I = 1.0$ M ($LiClO_4$), and 25.0 °C. Under the same condition, kinetic measurements were made for the reaction of $[Cr^{II}(EDTA)(H_2O)]^{2-}$ with H_2O_2 in the presence of alcohol to form $[CrR(EDTA)]^{2-}$ and gave a rate constant of 3×10^5 M^{-1} s^{-1}. The results may indicate that the rate-determining step in the conversion process of $[Cr^{II}(EDTA)(H_2O)]^{2-}$ to $[CrR(EDTA)]^{2-}$ is reaction 1.

Cleavage Reaction of the Cr–C Bond. Figure 1 shows the spectral change of the solution containing $[Cr(CH_2OH)(EDTA)]^{2-}$. There is an isosbestic point at 472 nm, and no intermediate species was detected. Similar spectral changes were observed for $[Cr(CH(CH_3)OH)(EDTA)]^{2-}$ and $[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$. The final spectra were identical with that of $[Cr(EDTA)(H_2O)]^-$. The product solutions were ex-

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Table V. Rate Constants and Q Values (Equation 9) for the Cr–C Bond Cleavage of $[Cr(CR_1R_2OH)(EDTA)]^{2-}$

complex	$k_0/10^{-3}$ s^{-1}	$k_1/10^2$ M^{-1} s^{-1}	$Q/10^3$ M^{-1}	temp/ °C
$[Cr(CH_2OH)(EDTA)]^{2-}$	0.117	1.19		19.7
	0.252	2.56		25.0
	0.502	5.70		31.2
	0.996	17.7		40.0
	1.36	28.0		43.8
$[Cr(CH(CH_3)OH)(EDTA)]^{2-}$	0.302	0.136	0.7	12.1
	0.658	0.341	1	19.0
	1.35	0.735	2	25.0
	2.60	1.39	2	30.8
	5.20	2.26	0.7	37.0
$[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$	1.99	0.343		9.4
	3.65	0.652		14.8
	6.81	1.14		20.0
	13.8	1.76		25.0
	21.7	3.29		30.4

amined with QAE-Sephadex A-25 (Cl^- form) column chromatography, and it was confirmed that the chromium product was $[Cr(EDTA)(H_2O)]^-$. The product analyses and the spectral changes indicate that the reaction can be expressed as the cleavage of the Cr–C bond in $[CrR(EDTA)]^{2-}$ (eq 6).

$$[CrR(EDTA)]^{2-} \xrightarrow{H_2O \text{ and/or } H_3O^+} [Cr(EDTA)(H_2O)]^- + \text{organic product(s)} \quad (6)$$

Attempts to identify the organic product(s) were not made, but the main product is considered to be RH.

The cleavage of the Cr–C bond in $[CrR(EDTA)]^{2-}$ obeyed the pseudo-first-order kinetics within 3–4 half-lives when the initial concentration of $[CrR(EDTA)]^{2-}$ was $\sim 0.2 \times 10^{-3}$ M. The pseudo-first-order rate constants, k_{obsd}, were determined from the slope of the ln $|A_t - A_\infty|$ vs. t plots, where A_t and A_∞ denote the absorbances at time t and inifinity, respectively. At higher complex concentrations ($[[CrR(EDTA)]^{2-}]_0 = \sim 2 \times 10^{-3}$ M), however, the ln $|A_t - A_\infty|$ vs. t plots showed slight deviations from linearity at the initial portion of the reaction. One example is shown in Figure 2.[14] The slope of the plots which corresponds to the latter portion of the reaction was identical with that of the plots obtained at the lower complex concentrations. The kinetic pattern at the higher complex concentrations fitted the rate equation consisting of the parallel first-order and second-order kinetic terms which was derived by Chao and Espenson.[15] However, the details of this kinetic behavior were not investigated further, and most kinetic measurements were made at the complex concentrations of $\sim 0.2 \times 10^{-3}$ M.

Kinetic data for the Cr–C bond cleavage of $[CrR(EDTA)]^{2-}$ are given in Tables II–IV.[14] The observed rate constants were not affected by the concentration changes of EDTA, H_2O_2, and alcohol, as well as the presence of oxygen. The k_{obsd} values for $[Cr(CH_2OH)(EDTA)]^{2-}$ and $[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$ complexes increased linearly with the increase in the hydrogen ion concentrations as shown in Figures 3 and 4.[14] Therefore, the rate law can be expressed as eq 7 and 8.

$$-d \ln [[CrR(EDTA)]^{2-}]/dt = k_{obsd} \quad (7)$$

$$k_{obsd} = k_0 + k_1[H^+] \quad (8)$$

As shown in Figure 5, however, the k_{obsd} values for the $[Cr(CH(CH_3)OH)(EDTA)]^{2-}$ complex do not fit eq 8 but fit eq 9. If the condition $1 \gg Q[H^+]$ is satisfied, eq 9 is simplified

$$k_{obsd} = (k_0 + k_1[H^+])/(1 + Q[H^+]) \quad (9)$$

to eq 8. The values of Q, k_0, and k_1 were determined by the procedure given in Appendix.[14] The results are summarized in Table V. The solid lines in Figure 5 indicate the curves calculated by using the values of Q, k_0, and k_1.

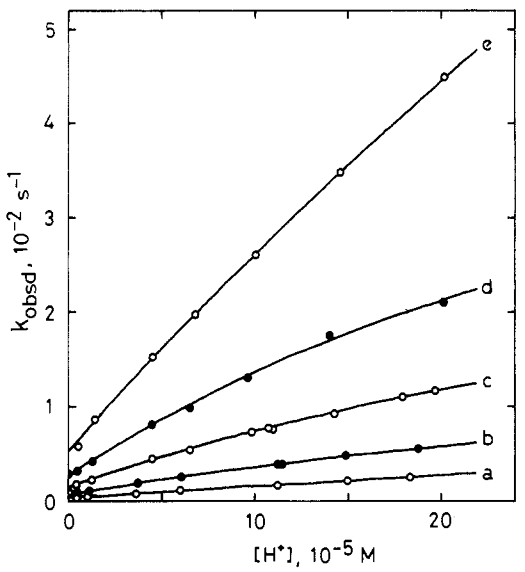

Figure 5. $[H^+]$ dependence of the pseudo-first-order rate constants, k_{obsd}, for the Cr–C bond cleavage reaction of $[Cr(CH(CH_3)OH)(EDTA)]^{2-}$ at $I = 1.0$ ($LiClO_4$) and at 12.1 °C (a), 19.0 °C (b), 25.0 °C (c), 30.8 °C (d), and 37.0 °C (e).

Table VI shows the kinetic parameters of the Cr–C bond cleavage reactions of $[Cr(CR_1R_2OH)(EDTA)]^{2-}$ complexes along with those reported for $[Cr(CR_1R_2OH)(H_2O)_5]^{2+}$ complexes.[1]

Discussion

The hydrogen abstraction from alcohols by ·OH radicals (eq 2) might compete with reactions 10–13. The rate constant

$$H_2O_2 + \cdot OH \xrightarrow{k_{10}} O_2H + H_2O \qquad k_{10} = 4.5 \times 10^7 \ M^{-1} \ s^{-1} \quad (10)^{16}$$

$$EDTA + \cdot OH \xrightarrow{k_{11}} EDTA\cdot + H_2O \qquad k_{11} = 4.0 \times 10^8 \ M^{-1} \ s^{-1} \quad (11)^{17}$$

$$[Cr^{II}(EDTA)(H_2O)]^{2-} + \cdot OH + H^+ \xrightarrow{k_{12}} [Cr^{III}(EDTA)(H_2O)]^- + H_2O \quad (12)$$

$$[Cr(EDTA)(H_2O)]^{-/2-} + \cdot OH \xrightarrow{k_{13}} [Cr(EDTA\cdot)(H_2O)]^{n-} + H_2O \quad (13)$$

of reaction 2 has been determined to be 5×10^8–2×10^9 M^{-1} s^{-1}.[16] Therefore, the contribution of the reactions 10 and 11 to the reaction 2 may be small under the present experimental conditions because the concentrations of the alcohols are 1000–10 000 times higher than $[H_2O_2]_0$ and 3–30 times higher than $[EDTA]_0$. The rate constant of the oxidation of $[Cr(H_2O)_6]^{2+}$ by ·OH radicals is known to be 1.2×10^{10} M^{-1} s^{-1}.[18] Therefore, the k_{12} value may be estimated to be $\sim 10^{10}$ M^{-1} s^{-1}. The contribution of reaction 12 for the disappearance of ·OH radicals may also be small because the rate constant of the hydrogen abstraction from alcohols (eq 2) is (0.5–2) $\times$ 10^9 M^{-1} s^{-1}[16] and the concentrations of the alcohols are 50–500 times higher than those of $[Cr(EDTA)(H_2O)]^{2-}$. It was reported that the rate of the hydrogen abstraction from EDTA

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[14] Supplementary material.

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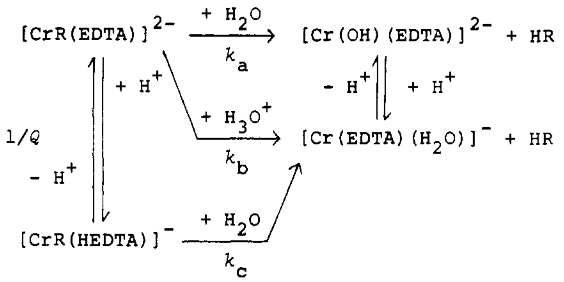
Table VI. Rate Constants at 25 °C and Activation Parameters for the Acid Hydrolyses of the Chromium–Carbon Bond in $[Cr(CR_1R_2OH)L]^{(n-2)-}$ ($I = 1.0$)

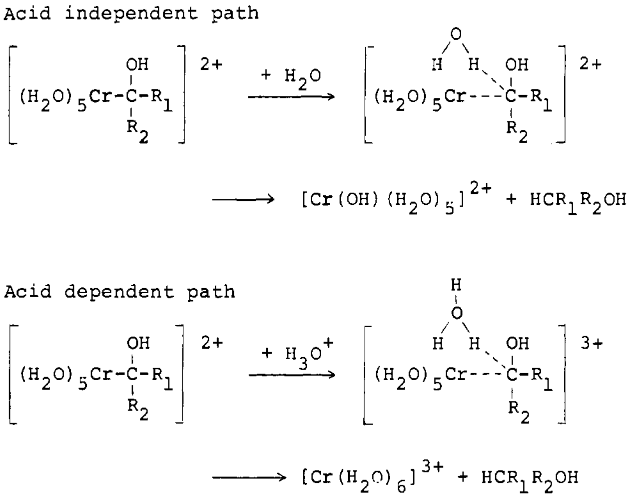
complex	$k_0{}^a/s^{-1}$	$\Delta H_0{}^‡$/kJ mol^{-1}	$\Delta S_0{}^‡$/J K^{-1} mol^{-1}	ref
$[Cr(CH_2OH)(EDTA)]^{2-}$	$(2.52 \pm 0.22) \times 10^{-4}$	74.2 ± 6.8	-65 ± 22	this work
$[Cr(CH(CH_3)OH)(EDTA)]^{2-}$	$(1.35 \pm 0.11) \times 10^{-3}$	81.9 ± 2.0	-25 ± 7	this work
$[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$	$(1.38 \pm 0.03) \times 10^{-2}$	80.9 ± 4.2	-10 ± 14	this work
$[Cr(CH_2OH)(H_2O)_5]^{2+}$	$(7.0 \pm 0.2) \times 10^{-4}$			1
$[Cr(CH(CH_3)OH)(H_2O)_5]^{2+}$	$(1.90 \pm 0.05) \times 10^{-3}$			1
$[Cr(C(CH_3)_2OH)(H_2O)_5]^{2+}$	$(3.3 \pm 0.1) \times 10^{-3}$	71.5 ± 2.9	-46 ± 8	1
complex	$k_1{}^b/M^{-1}\ s^{-1}$	$\Delta H_1{}^‡$/kJ mol^{-1}	$\Delta S_1{}^‡$/J K^{-1} mol^{-1}	ref
$[Cr(CH_2OH)(EDTA)]^{2-}$	$(2.56 \pm 0.03) \times 10^2$	98.6 ± 0.8	132 ± 3	this work
$[Cr(CH(CH_3)OH)(EDTA)]^{2-}$	$(7.35 \pm 0.42) \times 10$	81.8 ± 5.5	65 ± 18	this work
$[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$	$(1.76 \pm 0.03) \times 10^2$	72.9 ± 2.7	43 ± 10	this work
$[Cr(CH_2OH)(H_2O)_5]^{2+}$	$(3.2 \pm 0.2) \times 10^{-4}$			1
$[Cr(CH(CH_3)OH)(H_2O)_5]^{2+}$	$(1.22 \pm 0.04) \times 10^{-3}$			1
$[Cr(C(CH_3)_2OH)(H_2O)_5]^{2+}$	$(4.7 \pm 0.3) \times 10^{-3}$	81.2 ± 3.3	-21 ± 8	1

[a] $k_0 = k_a$. [b] $k_1 = k_b + k_cQ$ for $[CrR(EDTA)]^{2-}$ complexes.

Scheme I



Scheme II



in $[Zn(EDTA)]^{2-}$ is about 10 times faster than the rate of the hydrogen abstraction from the free EDTA.[17] If a similar relation holds between reactions 11 and 13, the k_{13} value is estimated to be $4 \times 10^9\ M^{-1}\ s^{-1}$. The contribution of reaction 13 to reaction 2 may be again small. As the result, reaction 2 is the major reaction path for the disappearance of the ·OH radicals.

Equation 9 is consistent with Scheme I. This scheme leads to the relations $1/Q = [H^+][[CrR(EDTA)]^{2-}]/[[CrR(HEDTA)]^-$, $k_0 = k_a$, and $k_1 = k_b + k_cQ$. If this mechanism is correct, the reciprocal of Q corresponds to the acid dissociation constant of $[Cr(CH(CH_3)OH)(HEDTA)]^-$. The p$K$ value of this complex is estmated to be 2.8–3.3. This value is comparable in magnitude with the pK values of the complexes of the $[CrX(HEDTA)]^{(n-3)-}$ type: 1.8 for $[Cr(HEDTA)(H_2O)]$[19] and 3.4 for $[Cr(NCS)(HEDTA)]^-$.[19] The pK values for both $[Cr(CH_2OH)(EDTA)]^{2-}$ and $[Cr(C(CH_3)_2OH)(EDTA)]^{2-}$ complexes were estimated to be less than 2.5.

The rate law of the acid hydrolyses of $[CrR(H_2O)_5]^{2+}$ to $[Cr(H_2O)_6]^{3+}$ conformed to eq 14.[1] The mechanism shown

$$-d \ln [[CrR(H_2O)_5]^{2+}]/dt = k_{obsd} = k_0 + k_1[H^+] \qquad (14)$$

in Scheme II was proposed for the reaction. The acid-independent path (k_0 path) and the acid-dependent path (k_1 path) correspond to the H_2O- and H_3O^+-assisted heterolytic cleavages of the Cr–C bond, respectively.[1]

Kinetic results in Table VI indicate that the rate constants of the acid-independent path of $[CrR(EDTA)]^{2-}$ (k_0 values) are quite similar to the k_0 values of the corresponding $[CrR(H_2O)_5]^{2+}$. Therefore, replacement of five water ligands in $[CrR(H_2O)_5]^{2+}$ by $EDTA^{4-}$ shows little influence on the rate of the cleavage of the Cr–C bond. The aquation and anation reactions of $[CrX(EDTA)]^{n-}$ studied previously (X = acetate, thiocyanate, etc.) were 10^7–10^9 times faster than those of pentaaquachromium(III) complexes.[19,20] The enhanced lability has been interpreted by a postulate that the uncoordinated NCH_2COO^- group in the Cr–EDTA complex acts as an internal nucleophile and assists the ligand substitution at the sixth coordination position of the Cr(III) center. As the Cr–C bond is cleaved by the electrophilic attack of a water molecule, the rate of the Cr–C bond cleavage is not affected by the presence of the uncoordinated NCH_2COO^- group in the Cr–EDTA complex. In other words, the cleavage of Cr–C bond in $[CrR(EDTA)]^{2-}$ is analogous to that of $[CrR(H_2O)_5]^{2+}$. The following observations also reflect this. The k_0 values of $[CrR(EDTA)]^{2-}$ complexes increase in the following order with the nature of the R ligands: $CH_2OH < CH(CH_3)OH < C(CH_3)_2OH$. This order is the same as that found for the k_0 values of $[CrR(H_2O)_5]^{2+}$ complexes. An electron-donating substituent on the Cr–C bond makes the carbon more negative and the electrophilic attack of a water molecule easier. The attacking mode mentioned above is supported also by the similarity between the $\Delta H_0{}^*$ values of the $[CrR(EDTA)]^{2-}$ and $[CrR(H_2O)_5]^{2+}$ complexes. The negative entropies of activation are consistent with the mechanism.

The k_1 values of $[CrR(EDTA)]^{2-}$ are strikingly different from those of the corresponding $[CrR(H_2O)_5]^{2+}$ complex; the former values are 10^4–10^6 times larger than the latter values. If the acid-dependent path of $[CrR(EDTA)]^{2-}$ proceeds via the electrophilic attack by an external H_3O^+ on the chromium-bound carbon atom, the k_1 path of $[CrR(EDTA)]^{2-}$ corresponds to the k_b path shown in Scheme I and is the reaction analogous to the k_1 path of $[CrR(H_2O)_5]^{2+}$. The magnitude of the k_b values is expected to be very similar to that of the k_1 values of $[CrR(H_2O)_5]^{2+}$ because the k_0 values for both

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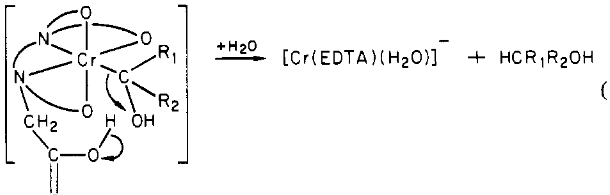
systems are very similar to each other. The large difference between the k_1 values of $[\mathrm{CrR(EDTA)}]^{2-}$ and $[\mathrm{CrR(H_2O)_5}]^{2+}$ may suggest that the k_c path predominates over the k_b path in the reaction of $[\mathrm{CrR(EDTA)}]^{2-}$. The intimate mechanism of the k_c path would be expressed as eq 15. In this mechanism, the uncoordinated $\mathrm{CH_2COOH}$ group acts as an internal electrophile to the chromium-bound carbon atom and supplies the proton to the hydroxyalkyl ligand in the same complex.



(15)

Registry No. $[\mathrm{Cr(CH_2OH)(EDTA)}]^{2-}$, 79391-91-6; $[\mathrm{Cr(CH(CH_3)OH)(EDTA)}]^{2-}$, 79391-92-7; $[\mathrm{Cr(C(CH_3)_2OH)(EDTA)}]^{2-}$, 79391-93-8.

Supplementary Material Available: Table II (kinetic data for $[\mathrm{Cr(CH_2OH)(EDTA)}]^{2-}$), Table III (kinetic data for $[\mathrm{Cr(CH(CH_3)OH)(EDTA)}]^{2-}$), Table IV (kinetic data for $[\mathrm{Cr(C(CH_3)_2OH)(EDTA)}]^{2-}$), Figure 2 (plots of ln $|A_t - A_\infty|$ vs. t at different concentrations of $[[\mathrm{Cr(CH_2OH)(EDTA)}]^{2-}]_0$), Figure 3 (relation between k_{obsd} and $[\mathrm{H^+}]$ for the $[\mathrm{Cr(CH_2OH)(EDTA)}]^{2-}$ system), Figure 4 (relation between k_{obsd} and $[\mathrm{H^+}]$ for the $[\mathrm{Cr(C(CH_3)_2OH)(EDTA)}]^{2-}$ system), and the Appendix (procedure for the determination of the Q, k_0, and k_1 values) (7 pages). Ordering information is given on any current masthead page.

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Ligand Substitution of (Ethylenediaminediacetato)vanadium(V) with Nitrilotriacetate Ions

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Kinetics studies of ligand substitution of ethylenediaminetetraacetate (EDTA) or ethylenediaminediacetate (EDDA) by nitrilotriacetate ions (NTA) in vanadium(V) complexes have been carried out by stopped-flow spectrophotometry in solution at pH 4–6, $\mu = 3$ ($\mathrm{NaClO_4}$), and 25 °C. We took into account that the general mechanism of reaction could proceed, for each chelate, by three paths: direct, $\mathrm{H^+}$-induced dissociation followed by formation of the NTA chelate, and direct attacks by NTA species. The results show that there is no reaction via the direct dissociative path, only via the $\mathrm{H^+}$-induced dissociative path; there exist possibilities of direct attacks of $\mathrm{VO_2EDTA^{3-}}$ by $\mathrm{H(NTA)^{2-}}$, of $\mathrm{VO_2EDTA^{3-}}$ by $\mathrm{H_2NTA^-}$, of $\mathrm{VO_2H(EDTA)^{2-}}$ by $\mathrm{H(NTA)^{2-}}$, of $\mathrm{VO_2EDDA^-}$ by $\mathrm{H(NTA)^{2-}}$, and of $\mathrm{VO_2EDDA^-}$ by $\mathrm{H_2NTA^-}$. The direct attacks of the NTA species would be fast formations of outer-sphere complexes followed by aminocarboxylate ligand interchanges, which are the rate-determining steps. This mechanism differs from the generally proposed one in the fact that there is no inner water molecule bonded to the metal in the reactant chelates.

Many studies have reported on kinetic mechanisms of substitution of metal chelates with multidentate aminocarboxylate ligands in aqueous solutions.[1-11] In these papers, one multidentate ligand displaces another from a metal ion, usually $\mathrm{Ni^{2+}}$, $\mathrm{Cu^{2+}}$, $\mathrm{Co^{2+}}$, or $\mathrm{Zn^{2+}}$. The proposed mechanism of the exchange reactions shows the substitution proceeding through an intermediate in which the metal atom is bonded with both the leaving and the entering multidentate ligands. The complete displacement is then obtained by a "chain of reactions" with bond ruptures between the metal and the leaving ligand and bond formations between the metal and the entering ligand. The first attack of the entering multidentate ligand can occur either by displacement of water molecules bonded to the metal or by displacement of one of the very weak bonds of the leaving ligand. Thence we can distinguish between the chelates with a multidentate ligand, which has a number of chelating groups inferior to the number of the available coordination sites of the metal, and the chelates without such a ligand. In the first case the metal is simultaneously bonded to chelating groups and water molecules. In the second case some of the chelating groups of the multidentate ligand could be either very weakly bonded to the metal or not bonded and replaced by water molecules. Conformational and steric effects also lead to this hypothesis, which explains the formation of an inner mixed complex during the reactions of substitution of one multidentate ligand by another, which have been studied.

The present paper describes ligand-exchange reactions (eq 1 and 2) with vanadium(V) as the metal (previous results have

$$\sum_{i=0}^{2} \mathrm{VO_2H_\mathit{i}EDTA}^{(3-i)-} + \sum_{j=0}^{4} \mathrm{H_\mathit{j}NTA}^{(3-j)-} \rightarrow \mathrm{VO_2NTA^{2-}} + \sum_{k=0}^{6} \mathrm{H_\mathit{k}EDTA}^{(4-k)-} \quad (1)$$

$$\mathrm{VO_2EDDA^-} + \sum_{i=0}^{4} \mathrm{H_\mathit{i}NTA}^{(3-i)-} \rightarrow \mathrm{VO_2NTA^{2-}} + \sum_{j=0}^{4} \mathrm{H_\mathit{j}EDDA}^{(2-j)-} \quad (2)$$

shown the complexation of $\mathrm{VO_2^+}$ as the central ion[15]), where

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