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KINETICS OF THE CLEAVAGE OF THE CHROMIUM-CARBON BOND IN *N*-2-HYDROXYETHYLETHYLENEDIAMINE-*N*,*N*',*N*'-TRIACETATO(HYDROXYMETHYL)-CHROMIUM(III) AND NITRILOTRIACETATO(HYDROXYMETHYL)AQUA-CHROMIUM(III)

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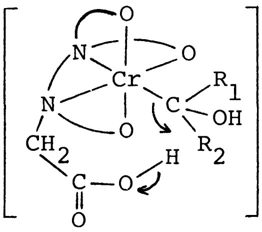
The hydrolysis of the Cr-C bond in *N*-2-hydroxyethylethylenediamine-*N*,*N*',*N*'-triacetato(hydroxymethyl)chromium(III) ($\underset{\sim}{1}$) obeyed the rate law, $-d[\underset{\sim}{1}]/dt = (k_0 + k_1[H^+])[\underset{\sim}{1}]$ at $I = 1.0$ ($LiClO_4$) and 25.0 °C, while the reaction of nitrilotriacetato(hydroxymethyl)-aquachromium(III) ($\underset{\sim}{2}$) obeyed $-d[\underset{\sim}{2}]/dt = \{(k_0 + k_0^L[L]) + (k_1 + k_1^L[L])[H^+]\}[\underset{\sim}{2}]$, where L denotes $H_n nta^{(3-n)-}$.

We have shown in a previous paper that the $edta^{4-}$ ligand greatly accelerates the cleavage of the Cr-C bond in $[Cr(CR_1R_2OH)(edta)]^{2-}$ (R_1, R_2 = H or CH_3) in aqueous solutions.[1)] It has been postulated that the $-CH_2COOH$ group of the pentadentate $edtaH^{3-}$ ligand serves as an electrophile to the Cr-C bond in the same molecule (Scheme 1). Our interest in such unique effect of the $edta^{4-}$ ligand brought us to examine the complexes containing aminopolycarboxylates other than $edta^{4-}$.



Scheme 1.

Aqueous solutions of $[Cr(CH_2OH)(hedtra)]^-$ ($hedtra^{3-}$ = *N*-2-hydroxyethylethylenediamine-*N*,*N*',*N*'-triacetate) ($\underset{\sim}{1}$) and $[Cr(CH_2OH)(nta)(H_2O)]^-$ ($\underset{\sim}{2}$) were prepared from either $[Cr^{II}(hedtra)(H_2O)]^-$ or $[Cr^{II}(nta)(H_2O)_2]^-$, H_2O_2, and methanol by a procedure similar to the preparation of $[Cr(CH_2OH)(edta)]^{2-}$.[1)] Kinetic measurements were made under a nitrogen atmosphere at ionic strength (I) of 1.0 ($LiClO_4$) and 25.0 °C by following the decrease in absorbance at 340 - 370 nm with a Union-Giken SM401 recording spectrophotometer. The hydrogen ion concentrations were controlled with $H_n hedtra^{(3-n)-}$ or $H_n nta^{(3-n)-}$ solutions as buffer solutions, and measured with a Toa HM20B pH meter calibrated with standard perchloric acid solutions at $I = 1.0$ ($LiClO_4$). The reactions obeyed first-order kinetics, and the observed rate constants (k_{obsd}) were determined by a standard method.

The reaction of $\underset{\sim}{1}$ followed the rate equation 1, which is

$$-d[\underset{\sim}{1}]/dt = (k_0 + k_1[H^+])[\underset{\sim}{1}] \qquad (1)$$

consistent with Eqs. 2 and 3.

$$\mathbf{1} + H_2O \xrightarrow{k_0} [Cr(hedtra)(H_2O)] + \text{organic products} \qquad (2)$$

$$\mathbf{1} + H_3O^+ \xrightarrow{k_1} [Cr(hedtra)(H_2O)] + \text{organic products} \qquad (3)$$

The reaction of **2**, on the other hand, followed Eq. 4, where [L] is the total

$$-d[\mathbf{2}]/dt = \{k_0 + k_0^L[L] + (k_1 + k_1^L[L])[H^+]\}[\mathbf{2}] \qquad (4)$$

concentrations of $H_n nta^{(3-n)-}$. The rate law implies that there are [L] dependent reaction pathways in addition to the simple hydrolysis reactions (Eqs. 5 and 6).

$$\mathbf{2} + H_2O \xrightarrow{k_0} [Cr(nta)(H_2O)_2] + \text{organic products} \qquad (5)$$

$$\mathbf{2} + H_3O^+ \xrightarrow{k_1} [Cr(nta)(H_2O)_2] + \text{organic products} \qquad (6)$$

The rate constants, k_0 and k_1, are summarized in Table 1.

Table 1. Rate constants for the chromium-carbon bond cleavage of the hydroxymethylchromium(III) complexes at 25.0 °C

	Complex	k_0/s^{-1}	$k_1/mol^{-1}\ dm^3\ s^{-1}$
1	$[Cr(CH_2OH)(hedtra)]^-$	$(3.42 \pm 0.14) \times 10^{-4}$	$(5.84 \pm 0.20) \times 10^{-1}$
2	$[Cr(CH_2OH)(nta)(H_2O)]^-$ a)	$(9.49 \pm 0.23) \times 10^{-4}$	$(3.35 \pm 0.49) \times 10^{-1}$
3	$[Cr(CH_2OH)(edta)]^{2-}$ b)	$(2.52 \pm 0.22) \times 10^{-4}$	$(2.56 \pm 0.03) \times 10^{2}$
4	$[Cr(CH_2OH)(H_2O)_5]^{2+}$ c)	$(7.0 \pm 0.2) \times 10^{-4}$	$(3.2 \pm 0.2) \times 10^{-4}$

a) $k_0^L = (7.00 \pm 0.47) \times 10^{-3}\ mol^{-1}\ dm^3\ s^{-1}$, $k_1^L = 17.5 \pm 1.0\ mol^{-2}\ dm^6\ s^{-1}$.

b) Ref. 1. c) Ref. 2.

The k_0 values of **1** and **2** are close to the k_0 of **4** as is the case for the reaction of **3**. The k_1 values of **1** and **2** are much smaller than **3**. This supports our postulate shown in Scheme 1, since the $hedtra^{3-}$ and nta^{3-} ligands in **1** and **2** do not have an acidic group to attack the Cr-C bond. The k_1 values of **1** and **2**, are significantly greater than k_1 for **4**. This may indicate more carbanion-like character of the CH_2OH group in **1** and **2** than in **4**. The negative charges of **1** and **2** should, in consequence, facilitate the approach of H^+ to the Cr-C bond.

The [L] dependent pathways for **2** can be attributed to free $H_n nta^{(3-n)-}$ ions which can replace the coordinated water molecule in **2** resulting in the accelerated Cr-C bond cleavage. Such mode of acceleration has been known for the reaction of organopentaaquachromium(III) complexes with carboxylates and other anions.[3,4]

References

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