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EQUILIBRIUM AND KINETIC STUDIES OF THE REACTION OF N-2-HYDROXYETHYLETHYLENEDIAMINE-N,N',N'-TRIACETATOAQUACHROMIUM(III) WITH AZIDE ION

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The equilibrium constant (K) and the rate constants (k_f and k_b) of the reaction,

$$\mathrm{Cr(hedtra)(H_2O)} + \mathrm{N_3^-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Cr(N_3)(hedtra)^-} + \mathrm{H_2O}$$

were determined to be $113 \pm 9\ \mathrm{M^{-1}}$ for K, $19.9 \pm 1.1\ \mathrm{M^{-1}s^{-1}}$ for k_f and $0.176 \pm 0.010\ \mathrm{s^{-1}}$ for k_b at an ionic strength of 1.0 ($\mathrm{NaClO_4}$) and 25°C. The reaction is considered to proceed through an associative interchange mechanism.

It has been reported that the reaction of $\mathrm{CrY(H_2O)^{(n-3)-}}$ with acetate ($\mathrm{OAc^-}$),

$$\mathrm{CrY(H_2O)^{(n-3)-}} + \mathrm{OAc^-} \rightleftharpoons \mathrm{Cr(OAc)Y^{(n-2)-}} + \mathrm{H_2O} \tag{1}$$

is reversible and unexpectedly fast, where Y represents ethylenediamine-N,N,N',N'-tetraacetate(EDTA) or N-2-hydroxyethylethylenediamine-N,N',N'-triacetate (HEDTRA) and n is 4 for EDTA or 3 for HEDTRA.$^{1)}$ It would be worthwhile to investigate the reactions of $\mathrm{CrY(H_2O)^{(n-3)-}}$ with ligands other than acetate. This communication deals with the reaction of $\mathrm{Cr(hedtra)(H_2O)}$ with azide ion.

Upon the addition of an azide buffer solution to a solution of $\mathrm{Cr(hedtra)(H_2O)}$, the maxima of visible absorption spectrum shifted to longer wavelengths spontaneously. When this process was followed with time by use of a rapid scanning spectrophotometer (Hitachi RSP-2), isosbestic points were observed at 341 nm and 392 nm. This may indicate the occurrence of the rapid reaction,

$$\mathrm{Cr(hedtra)(H_2O)} + \mathrm{N_3^-} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{Cr(N_3)(hedtra)^-} + \mathrm{H_2O} \tag{2}$$

All measurements were carried out spectrophotometrically at an ionic strength of 1.0 ($\mathrm{NaClO_4}$) and 25°C. The pH of the solution was adjusted with hydrazoic acid - sodium azide buffer solutions.

Equilibrium Study   If reaction (2) takes place, the following equation may be obtained$^{1)}$:

$$\frac{1}{\bar{\varepsilon} - \varepsilon_1} = \frac{1}{\varepsilon_2 - \varepsilon_1} + \frac{1}{\varepsilon_2 - \varepsilon_1} \times \frac{1}{K[\mathrm{N_3^-}]} \tag{3}$$

where ε_1 and ε_2 represent the molar extinction coefficients of $\mathrm{Cr(hedtra)(H_2O)}$ and $\mathrm{Cr(N_3)(hedtra)^-}$ respectively, $K = [\mathrm{Cr(N_3)(hedtra)^-}]/\{[\mathrm{Cr(hedtra)(H_2O)}][\mathrm{N_3^-}]\}$, and $\bar{\varepsilon} = D/[\mathrm{Cr(III)}]_T$. The symbol D denotes the absorbance of chromium(III)-HEDTRA in an azide buffer soltuion for unit cell length.

It was confirmed that plots of $1/(\bar{\varepsilon} - \varepsilon_1)$ vs. $1/[\mathrm{N_3^-}]$ gave linear relations. The K values determined at two pH's were essentially identical. In Table 1, the K value is compared with those obtained for the related reactions. The equilibrium constant of the reaction of $\mathrm{Cr(hedtra)(H_2O)}$ with azide is 7 times larger than that of the corresponding reaction with acetate. The trend is similar to that observed in $\mathrm{Cr(edta)(H_2O)^-}$ complex.$^{1)}$

Table 1. Equilibrium and Kinetic Data for Cr(III)-HEDTRA and Cr(III)-EDTA Complexes at 25°C and an Ionic Strength of 1.0 ($NaClO_4$)

Reaction	K/M^{-1}	$k_f/M^{-1}s^{-1}$	k_b/s^{-1}
$Cr(hedtra)(H_2O) + N_3^- \rightleftharpoons Cr(N_3)(hedtra)^- + H_2O$ a)	113 ± 9 b)	19.9 ± 1.1 c)	0.176 ± 0.010 c)
$Cr(hedtra)(H_2O) + OAc^- \rightleftharpoons Cr(OAc)(hedtra)^- + H_2O$ d)	16.9 ± 0.9	7.60 ± 0.61	0.450 ± 0.030
$Cr(edta)(H_2O)^- + N_3^- \rightleftharpoons Cr(N_3)(edta)^{2-} + H_2O$ d)	5.9 ± 0.3	——	——
$Cr(edta)(H_2O)^- + OAc^- \rightleftharpoons Cr(OAc)(edta)^{2-} + H_2O$ d)	0.62 ± 0.03	3.3 ± 0.4	5.4 ± 0.6

a) This work. b) At pH's 4.37 and 5.18. c) At pH 4.37 - 5.23. d) From ref. 1.

Kinetic Study Rate measurements were carried out at 420 nm by stopped-flow technique under the pseudo first order conditions. The following rate equation can be derived for reaction (2):

$$2.303 \log \frac{D_0 - D_\infty}{D_t - D_\infty} = k_0 t = (k_f[N_3^-] + k_b)t \qquad (4)$$

where D_0, D_t, and D_∞ represent absorbancies at time 0, t, and infinity, respectively. The plots of log $|D_t - D_\infty|$ vs. time gave straight lines, from whose slopes the k_0 values were determined. The k_0 values were independent of the change in pH within the range of 4.37 - 5.23. The values of k_f and k_b were determined as reported previously.[1)]

The rate constant, k_f, was independent of the concentrations of azide. This fact indicates that the forward reaction in equation (2) is strictly of second order. The data obtained in this and in the previous work[1)] are summarized in Table 1. The k_f value of the reaction of $Cr(hedtra)(H_2O)$ with azide is 2.6 times larger than that of the reaction of $Cr(hedtra)(H_2O)$ with acetate. This would be a significant result, because the rates of the anation reactions depend on the nature of the entering ligands. This is compatible with the results of recent investigations that chromium(III) substitution reactions proceed through an associative interchange mechanism.[2,3)] In the previous paper[1)], the mechanism was proposed as that the transient coordination of free $-CH_2CH_2OH$ group in $Cr(hedtra)(H_2O)$ labilizes the sixth coordination position of chromium(III) ion. Therefore, the associative substitution reaction of $Cr(hedtra)(H_2O)$ by X is catalyzed with the free $-CH_2CH_2OH$ group. This interpretation would be also applicable to the chromium(III)-EDTA system because of similarities between the two systems.

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