The Kinetics of the Reaction between the Chromium(III) Ion and the Ethylenediamine-*N,N,N′,N′*-tetraacetate Ion in the Presence of Hydrogen Peroxide

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The rate of the reaction between chromium(III) ion and ethylenediamine-*N,N,N′,N′*-tetraacetate was found to be accelerated upon the addition of a large excess of hydrogen peroxide. Under such a condition the rate of $Cr^{III}(edta)(H_2O)^-$ formation shows a first-order dependence on the concentrations of hydrogen peroxide and chromium(III) ions, but is independent of the concentration of EDTA. The rate of $Cr^{III}(edta)(H_2O)^-$ formation catalyzed by the hydrogen peroxide increases with an increase in the pH and decreases with an increase in the acetate ion concentration. The kinetic study suggested that the initiation of the reaction takes place as follows: $Cr(III)+H_2O_2 \longrightarrow Cr(IV)+OH\cdot+OH^-$ The reaction mechanism of the hydrogen-peroxide catalysis is discussed in terms of the formation of the chromium(IV)- and /or the chronium(V)-EDTA complex in the course of the reaction. It was found that monohydroxochromium(III) is much more reactive than the chromium (III) ion toward hydrogen peroxide.

Though the reactivities of trivalent and sexavalent chromium ions with EDTA are very small at room temperature, Pribil *et al.*[1] and the present authors[2,3] have observed that $Cr^{III}(edta)(H_2O)^-$ was formed instantaneously when the chromium(VI) ion was reduced by reagents such as ascorbic acid in the presence of EDTA. This reaction was utilized for the spectrophotometric determination of the concentrations of reducing agents.[2,3]

Though the chemical properties of chromium(II), chromium(III), and chromium(VI) ions have been extensively investigated, those of chromium(IV) and chromium(V) ions are little known.[4]

Recently, Beck and Durham[5] investigated semiquantitatively the reduction of the chromium(VI) ion by hydrazine in the presence of EDTA; they suggested that chromium(IV)- and chromium(V)-EDTA complexes[6] act as intermediates in the course of the redox reaction.

The present authors found that the chromium(III) ion easily reacted with EDTA in the presence of hydrogen peroxide, as in the case of the reduction of the chromium(VI) ion by reducing agents in the presence of EDTA.

In this connection, a kinetic study of the formation of $Cr^{III}(edta)(H_2O)^-$ in the presence of hydrogen peroxide was carried out.

Experimental

Materials. A solution of chromium(III) perchlorate was prepared by the reduction of sodium dichromate in perchloric acid with hydrogen peroxide. The concentration of the chromium(III) ion was determined by the following procedure. A solution of the chromium(III) ion was heated with an excess of EDTA at 90 °C and pH 3.90 for 50 min. The concentration of the chromium(III) ion was calculated from the known molar extinction coefficient of $Cr^{III}(edta)(H_2O)^-$ at 550 nm. The stock solution of EDTA was standardized using calcium ions. The concentration of the reagent-grade hydrogen peroxide was determined by titration with a standard potassium permanganate solution. The pH and ionic strength of the reaction mixture were adjusted by the addition of an acetate buffer solution and sodium perchlorate respectively.

All the other chemicals were of a reagent grade.

Measurement of the Reaction Rate. To a chromium(III) ion solution in an Erlenmeyer flask we successively added the acetate buffer solution, the EDTA solution, and the hydrogen peroxide solution. Then this complete solution was transferred into a quartz spectrophotometer cell with a light path 1 cm in length. The temperature of the optical cells was controlled to 25±0.1 °C by circulating water through the cell holder. The kinetic measurements were carried out by recording the change in absorbance at 550 nm as a function of the time using a Hitachi EPS-3 type spectrophotometer. In every experiment hydrogen peroxide was present in a large excess relative to the concentrations of the chromium(III) ion and EDTA. The initial pH of the reaction solution was measured immediately after the initiation of the reaction with a Hitachi-Horiba F-5 pH meter. The variation in pH during the reaction was within 0.02 pH unit.

Results and Discussion

Reaction of the Chromium(III) Ion with EDTA in the Absence of Hydrogen Peroxide. The kinetics of the reaction of the chromium(III) ion with EDTA was studied by Hamm.[7] He found that the rate of the formation of $Cr^{III}(edta)(H_2O)^-$ did not depend upon the concentration of EDTA, and that it was very sensitive to the pH of the reaction mixture. Schwarzenbach and Biedermann[8] showed that one water molecule is contained in the first coordination sphere of the chromium(III)-EDTA complex. Moreover Ogino *et al.*[9,10] reported that the chromium(III)-EDTA complex was present as $Cr^{III}(edta)(H_2O)^-$ in the pH range from 3.6 to 5.3.

The dependence of the EDTA concentration on the formation rate was also examined in this work. The rate constant very slightly decreased with an increase in the EDTA concentration. The formation rate is independent of the acetate ion in the concentration range from 0.40 M to 0.05 M. Table 1 shows the first-order rate constants for the reaction between the chromium(III) ion and EDTA which were obtained in this work.

Reaction of the Chromium(III) Ion with EDTA in the Presence of Hydrogen Peroxide. The change in the absorption spectra of the chromium(III) ion solution

TABLE 1. CONDITIONAL RATE CONSTANTS k_{obsd} OF THE FORMATION OF $Cr^{III}(edta)(H_2O)^-$ AT 25 °C AND I=0.35 ($NaClO_4$)

pH	[CH_3COO^-] M	k_{obsd} a) $M^{-1}s^{-1}$	k b) s^{-1}
3.30	0.05	2.3×10^{-5}	
	0.10	1.5×10^{-5}	8.3×10^{-6}
	0.20	1.2×10^{-5}	
	0.35	1.1×10^{-5}	
3.52	0.05	3.6×10^{-5}	
	0.10	2.3×10^{-5}	1.4×10^{-5}
	0.20	1.9×10^{-5}	
	0.35	1.6×10^{-5}	
3.70	0.05	5.2×10^{-5}	
	0.10	3.3×10^{-5}	2.1×10^{-5}
	0.20	2.5×10^{-5}	
	0.35	2.0×10^{-5}	
4.00	0.05	1.1×10^{-4}	
	0.10	7.2×10^{-5}	3.8×10^{-5}
	0.20	5.1×10^{-5}	
	0.35	4.3×10^{-5}	
4.50	0.05	3.7×10^{-4}	
	0.10	2.1×10^{-4}	1.0×10^{-4}
	0.20	1.3×10^{-4}	
	0.35	9.1×10^{-5}	

a) The rate constants of the reaction between the chromium(III) ion and EDTA in the presence of hydrogen peroxide. b) The rate constants of th reaction between the chromium(III) ion and EDTA in the absence of hydrogen peroxide.

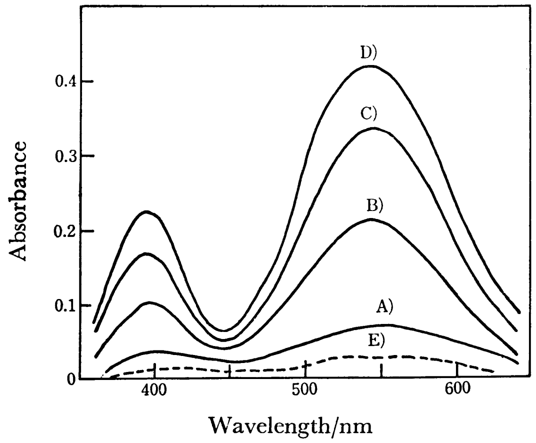

Fig. 1. The absorption spectral change of chromium (III) ion solution in the presence of EDTA upon the addition of hydrogen peroxide. [Cr^{3+}]=5.47×10^{-3} M, [EDTA]=6.40×10^{-3} M, [H_2O_2]=4.18 M, pH 4.10, [CH_3COO^-]=0.10 M, I=0.35, 25 °C.
A) 4 min, B) 15 min, C) 28 min, D) 45 min, E) 45 min (absence of H_2O_2) after the initiation of the reaction.

in the presence of EDTA upon the addition of a large excess of hydrogen peroxide is shown in Fig. 1. The change in the absorption spectra suggests that the reaction product of the chromium(III) ion is $Cr^{III}(edta)(H_2O)^-$. Curve E (45 min after the initiation of the reaction) in Fig. 1 is the absorption spectrum obtained in the absence of hydrogen peroxide. The rate of the formation of $Cr^{III}(edta)(H_2O)^-$ in the presence of hydrogen peroxide was found to be much larger than that in the absence of hydrogen peroxide.

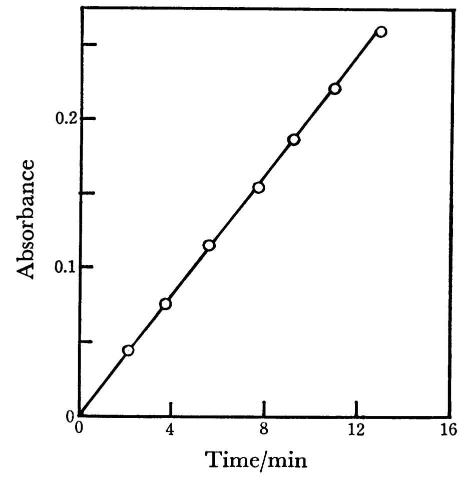

Fig. 2. Typical kinetic runs of the reaction between chromium(III) ion and EDTA in the presence of hydrogen peroxide.
[EDTA]=2.00×10^{-2} M, [H_2O_2]=5.05 M, [Cr^{3+}]=7.13×10^{-3} M, [CH_3COO^-]=0.10 M, pH 3.82, I=0.35, 25 °C, 550 nm.

The plot of the absorbance at 550 nm *vs.* the time were linear for at least 15% of the whole reaction (Fig. 2). Therefore, the zeroth-order rate constants of the formation of $Cr^{III}(edta)(H_2O)^-$ were determined from the initial slope of the absorbance *vs.* the time plots.

The formation rate of $Cr^{III}(edta)(H_2O)^-$ is independent of the order of the addition of the hydrogen peroxide and EDTA solutions to the chromium(III) solution.

Dependence of the Chromium(III)-ion and Hydrogen-peroxide Concentrations on the Formation Rate of $Cr^{III}(edta)(H_2O)^-$. The dependence of the concentration of the chromium(III) ion on the rate of the formation of $Cr^{III}(edta)(H_2O)^-$ was examined in the presence of a large excess of hydrogen peroxide at pH 3.82 and

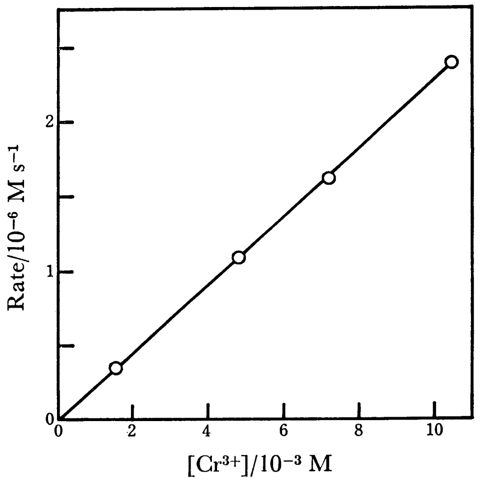

Fig. 3. The relation between the rate for the formation of $Cr^{III}(edta)(H_2O)^-$ and the concentration of chromium(III) ion.
[EDTA]=2.00×10^{-2} M, [H_2O_2]=5.05 M, pH 3.82, [CH_3COO^-]=0.10 M, I=0.35, 25 °C.

25 °C. As is shown in Fig. 3, the linear relationship between the chromium(III)-ion concentration and the formation rate indicates that the reaction rate has a first-order dependence with respect to the concentration of the chromium(III) ion. It was also found that the formation rate has a first-order dependence on the hydrogen peroxide in the concentration range 1.5 M to 5.0 M at a given pH and at a given acetate ion concentration.

Dependence of EDTA. The formation rate is independent of the EDTA concentration, as is shown in Fig. 4.

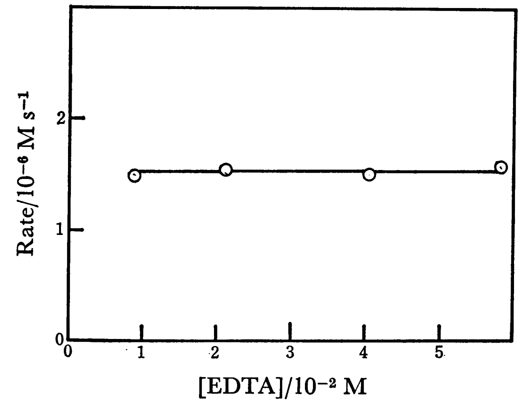

Fig. 4. The relation between the rate for the formation of $Cr^{III}(edta)(H_2O)^-$ and the concentration of hydrogen peroxide.
$[Cr^{3+}]=7.13\times10^{-3}$ M, $[EDTA]=2.00\times10^{-2}$ M, pH 3.82, $[CH_3COO^-]=0.10$ M, $I=0.35$, 25 °C.

The rate law for the hydrogen peroxide-catalyzed formation of $Cr^{III}(edta)(H_2O)^-$ is represented by Eq. 1:

$$\frac{d[Cr^{III}(edta)(H_2O)^-]}{dt} = k_{obsd}[Cr(III)][H_2O_2] \qquad (1)$$

where k_{obsd} represents the observed second-order rate constant under the given conditions.

Effects of the pH and the Acetate Ion on the Formation Rate of $Cr^{III}(edta)(H_2O)^-$. The formation rate of $Cr^{III}(edta)(H_2O)^-$ in the presence of hydrogen peroxide was found to increase with an increase in the pH in the pH range from 3.30 to 4.50. It was also found that the formation rate decreases with an increase in the acetate-ion concentration. The observed second-order rate constants under various experimental conditions are listed in Table 1. These data clearly indicate a linear relationship between k_{obsd} and reciprocal concentration of the acetate ions, with an intercept at any given pH. Thus, the conditional second-order rate constant may be expressed by Eq. 2:

$$k_{obsd} = k'_{obsd} + \frac{k''_{obsd}}{[CH_3COO^-]} \qquad (2)$$

The conditional rate constants, k'_{obsd} and k''_{obsd}, at the given pH are listed in Table 2.

The initiation of the reaction must take place by means of Reaction 3:

$$Cr(III) + H_2O_2 \xrightarrow{\text{slow}} Cr(IV) + OH\cdot + OH^- \qquad (3)$$

Table 2. Conditional rate constants, k'_{obsd} and k''_{obsd} of the formation of $Cr^{III}(edta)(H_2O)^-$ at 25 °C and I=0.35 ($NaClO_4$)

pH	k'_{obsd} $M^{-1}\,s^{-1}$	k''_{obsd} s^{-1}
3.30	8.9×10^{-6}	6.3×10^{-7}
3.52	1.4×10^{-5}	1.5×10^{-6}
3.70	1.6×10^{-5}	2.0×10^{-6}
4.00	3.0×10^{-5}	4.0×10^{-6}
4.50	5.0×10^{-5}	1.4×10^{-5}

For the subsequent reactions after Reaction 3 the following reaction paths are possible:

$$Cr(III) + OH\cdot \xrightarrow{\text{fast}} Cr(IV) + OH^- \qquad (4)$$

the rapid complex formation step of the chromium(IV)–EDTA complex,

$$Cr(IV) + EDTA \xrightarrow{\text{fast}} Cr(IV)\text{-}EDTA \qquad (5)$$

and the reduction of the chromium(IV)–EDTA complex by chromium(III) ion and/or hydrogen peroxide.

$$Cr(IV)\text{-}EDTA + Cr(III) \xrightarrow{\text{fast}} Cr^{III}(edta)(H_2O)^- + Cr(IV) \qquad (6)$$

$$Cr(IV)\text{-}EDTA + \frac{1}{2}H_2O_2 \xrightarrow{\text{fast}} Cr^{III}(edta)(H_2O)^- + \frac{1}{4}O_2 + \frac{1}{2}H_2O \qquad (7)$$

The possibility of the formation of chromium(V) and chromium(V)–EDTA can not be excluded. Therefore, Eqs. 8—11 may be added to Eqs. 4—7:

$$Cr(IV) + OH\cdot \xrightarrow{\text{fast}} Cr(V) + OH^- \qquad (8)$$

$$Cr(V) + EDTA \xrightarrow{\text{fast}} Cr(V)\text{-}EDTA \qquad (9)$$

$$Cr(V)\text{-}EDTA + Cr(III) \xrightarrow{\text{fast}} Cr(IV)\text{-}EDTA + Cr(IV) \qquad (10)$$

$$Cr(V)\text{-}EDTA + \frac{1}{2}H_2O_2 \xrightarrow{\text{fast}} Cr(IV)\text{-}EDTA + \frac{1}{4}O_2 + \frac{1}{2}H_2O \qquad (11)$$

No evolution of oxygen gas was observed up to about one half-life. Therefore, the possibility of Reactions 7 and 11 may be very small.

The predominant species of EDTA at pH 3.30 are H_2edta^{2-} (78%) and H_3edta^- (22%), while those at pH 4.50 are H_2edta^{2-} (97%) and $Hedta^{3-}$ (3%). Such a variation in species of EDTA does not affect the formation rate of $Cr^{III}(edta)(H_2O)^-$ in the presence of hydrogen peroxide, since the rate is independent of the EDTA concentration.

Although no detailed explanation of the effect of the acetate ion can be given, the interaction of the acetate ion with the chromium(III) ion through the formation of the hydrogen bond[11] may be one of the reasons for the retardation of the rate.

The chromium(III) ion was appreciably hydrolyzed to the monohydroxochromium(III) ion ($CrOH^{2+}$) under the present experimental conditions. Reaction 3 can be rewritten as Reaction 12:

$$\left\{\begin{matrix} \mathrm{Cr^{3+}} \\ K \downarrow\!\uparrow \mathrm{H^+} \\ \mathrm{CrOH^{2+}} \end{matrix}\right\} + \mathrm{H_2O_2} \longrightarrow \mathrm{Cr(IV)} + \mathrm{OH\cdot} + \mathrm{OH^-} \qquad (12)$$

Assuming the hydrolysis of the chromium(III) ion, the rate constant, k'_{obsd}, is represented by Eq. 13:

$$k'_{\mathrm{obsd}} = \frac{k[\mathrm{H^+}]+k_{\mathrm{OH}}K}{[\mathrm{H^+}]+K} \qquad (13)$$

where $K(K=[\mathrm{CrOH^{2+}}][\mathrm{H^+}]/[\mathrm{Cr^{3+}}])$ is the first hydrolysis constant of the chromium(III) ion and where k and k_{OH} are the second-order rate constants for the reactions involving a chromium(III) ion and a monohydroxochromium(III) ion respectively. If $k_{\mathrm{OH}}K \gg k[\mathrm{H^+}]$ is assumed, the reciprocal of k'_{obsd} is expressed as:

$$\frac{1}{k'_{\mathrm{obsd}}} = \frac{[\mathrm{H^+}]}{k_{\mathrm{OH}}K} + \frac{1}{k_{\mathrm{OH}}} \qquad (14)$$

A plot of $1/k'_{\mathrm{obsd}}$ *vs.* $[\mathrm{H^+}]$ shows a linear relationship. The values of k_{OH} and K are $6.2\times10^{-5}\ \mathrm{M^{-1}\,s^{-1}}$ and 8.3×10^{-5} M respectively at 25 °C and $I=0.35$. The value of K has been determined to be 1.3×10^{-4} M at 15 °C.[12] The slightly smaller value of K obtained in this work compared with that in the literature may be brought about by the differences in the experimental conditions and method.

The fact that the monohydroxochromium(III) ion is much more reactive than the chromium(III) ion toward hydrogen peroxide is very similar to the observation regarding the relative reactivity of the monohydroxomanganese(III) ion and the manganese(III) ion toward $\mathrm{N_2H_5^+}$,[13] and to that of the monohydroxocerium(IV) ion and the cerium(IV) ion toward $\mathrm{N_2H_5^+}$.[13] The H-atom transfer mechanism was proposed for the reaction between the monohydroxocerium(IV) ion and $\mathrm{N_2H_5^+}$.[14]

Though there is no reason for supposing that the mechanism for the reaction of the monohydroxochromium(III) ion with hydrogen peroxide is the H-atom transfer, the possibility of this mechanism can not necessarily be excluded.

Ogard and Taube[15] suggested that the chromium(IV) ion is very labile for the substitution on the basis of the kinetics of the dissociation reaction of $\mathrm{Cr(Cl)(H_2O)_5^{2+}}$ in the presence of an oxidizing agent.

The occurrence of the hydrogen peroxide-catalyzed reaction found in this work must be ascribed to the substitution lability of chromium(IV) or chromium(V), and the large oxidizing power and stability constant of chromium(IV)–EDTA or chromium(V)–EDTA.

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