Catalysis by Binuclear Zinc Ions in Ester Hydrolysis

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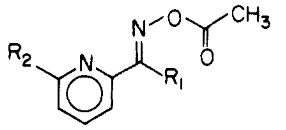
Abstract: The Zn(II)-catalyzed hydrolysis of 6-carboxy-*O*-(acetyloxy)-2-pyridinecarboxaldoxime (**3**) consists of two reaction paths. Rates of the paths were proportional to $[Zn(II)][OH^-]$ or to $[Zn(II)][OH^-]^2$. On the other hand, catalysis by the Cu(II) ion was not observed in the hydrolysis of **3**. The results were compared with those previously obtained for the Cu(II)- or Zn(II)-catalyzed hydrolysis of *O*-(acetyloxy)-2-pyridinecarboxaldoxime or 2-acetylpyridine *O*-(acetyloxy)ketoxime. The comparison revealed that the Zn(II)-catalyzed hydrolysis of **3** occurs through the participation of binuclear Zn(II) ions. The catalytic binuclear ions contain two Zn(II) and either one or two hydroxide ions. Binding of the binuclear species to **3** leads to intramolecular nucleophilic reactions.

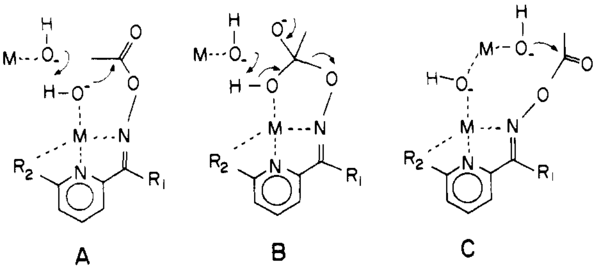
Some metal ions catalyze various organic reactions by participating as Lewis acids. Many kinetic studies have been performed for these reactions in order to elucidate the catalytic roles of the metal ions.[1-3] Determination of the roles of the metal ions is an important subject in the study of both inorganic and organic mechanisms. In addition, it provides valuable information on the possible roles of metal ions in metalloenzymes.

Our previous studies with metal ion catalysis in the ester hydrolysis of *O*-(acetyloxy)-2-pyridinecarboxaldoxime (**1**)[4,5] or 2-acetylpyridine *O*-(acetyloxy)ketoxime (**2**)[6] disclosed a new catalytic factor, the nucleophilic attack by metal-bound water molecules.



1: $R_1 = H, R_2 = H$
2: $R_1 = CH_3, R_2 = H$
3: $R_1 = H, R_2 = COOH$

In the Zn(II)-catalyzed hydrolysis of **2**, three reaction paths were observed.[6] The rate of one of the paths was proportional to $[Zn(II)]^2[OH^-]^2$, indicating the participation of two Zn(II) and two hydroxide ions in the rate-determining transition state. As the mechanism of this path, either A/B or C was proposed, taking other kinetic data into account. In mechanism A/B, two hydroxozinc(II) ions are involved, and one of them acts as a general base either in the formation (A) or in the breakdown (B) of the tetrahedral intermediate. In mechanism C, a dimeric hydroxozinc(II) ion participates as a catalytic unit.



R_1 = H or CH_3, R_2 = H or COO^-. Coordination of R_2 to M is possible only when R_2 is COO^-.

In order to differentiate mechanisms A/B and C, we studied the metal-ion catalyzed hydrolysis of 6-carboxy-*O*-(acetyloxy)-2-pyridinecarboxaldoxime (**3**). It was anticipated that the introduction of an additional five-membered chelate ring would exert different effects on the stability of the transition states for the two mechanisms. In this article, kinetic data and the mechanism of the Cu(II) or Zn(II)-catalyzed hydrolysis of **3** are described, and a novel catalytic factor, catalysis by binuclear metal ions in ester hydrolysis, is reported.

Experimental Section

6-Carboxy-*O*-(acetyloxy)-2-pyridinecarboxaldoxime (3). Ethyl 6-(hydroxymethyl)picolinate[7] (3.0 g) was refluxed with 1.0 g of selenium dioxide in 30 mL of dioxane for 3 h. After metallic selenium was removed by filtration, the volume of the mixture was reduced to 10 mL under reduced pressure. To the resulting mixture, hydroxylamine hydrochloride (1.7 g) dissolved in water (4 mL) was added at room temperature. After 30 min, the mixture was neutralized with 5 N sodium hydroxide solution. The resultant precipitates were dissolved in a minimal volume of 1 N sodium hydroxide solution, and then the mixture was stirred for 2 h. Acidification with 5 N hydrochloric acid to pH 2 precipitated 6-carboxy-2-pyridinecarboxaldoxime, which was recrystallized from ethanol, mp 230 °C dec. The oxime (1.5 g) was stirred with 1.1 g of acetic anhydride and 1.1 g of triethylamine in 15 mL of dry acetonitrile for 2 h at room temperature. Precipitates (**3**) formed during the reaction were separated and recrystallized from ethanol, mp 171-172 °C. As indicated in the previous reports,[5,6] syn configurations (the pyridyl ring and the oxime oxygen on the opposite sites) have been established[8-10] for **1** and the parent oximes of **1** and **2**. Since the configuration depends on the relative sizes of the pyridyl ring and the R_1 group indicated for the structures of **1-3**, it is very likely that **3** and its oxime have the same syn configuration.

Kinetic Measurements. Reaction rates were measured with a Beckman Model 5260 or 25 UV/vis spectrophotometer. The temperature (25 °C) was controlled to within ±0.1 °C with a Haake E52 circulator. Stock solutions of **3** were prepared in dimethyl sulfoxide, whose content in the reaction mixtures for kinetic studies was 0.8% (v/v). Kinetics were performed with 1×10^{-4} M **3** at an ionic strength of 1.0 adjusted with sodium chloride. Water was redistilled and deionized prior to the preparation of buffer solutions. Buffers used were acetate (pH 4) or 4-morpholinyl ethanesulfonate (pH 5.9-7.2). Zinc chloride and cupric chloride were prepared by reacting the corresponding oxides (Aldrich, "Gold" Label) with hydrochloric acid. Rates of the Zn(II)-catalyzed hydrolysis of **3** were measured with either 0.02 or 0.01 M buffer, but no appreciable rate difference was observed. Pseudo-first-order rate constants were calculated with the infinity absorbance values obtained. Quantitative production of 6-carboxy-2-pyridinecarboxaldoxime was evidenced by the UV spectra of the Zn(II)-containing product solutions.

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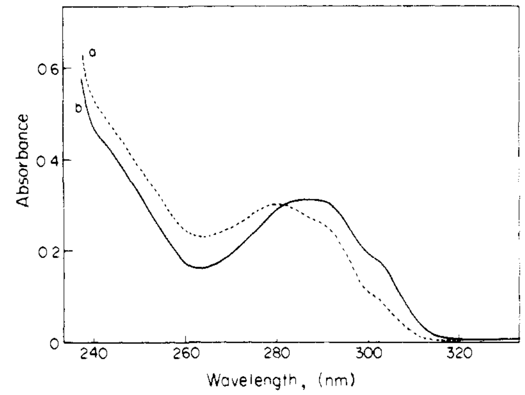


Figure 1. UV spectrum of **3** measured at pH 5.94 (a) in the absence of added Zn(II) and (b) in the presence of 2, 5, 10, or 20 mM Zn(II).

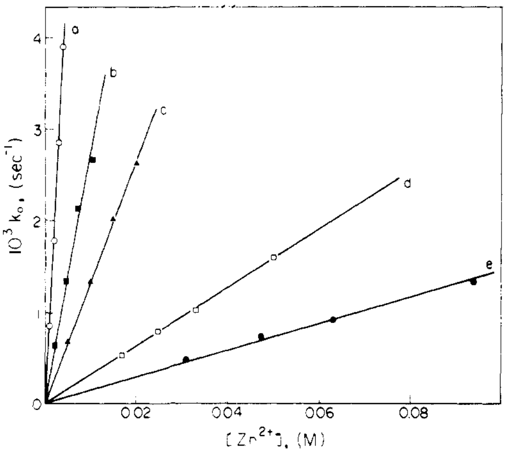


Figure 2. Plot of k_0 against [Zn(II)] for the Zn(II)-catalyzed hydrolysis of **3**: (a) pH 7.13, (b) pH 6.85, (c) pH 6.63, (d) pH 6.20, and (e) pH 5.94.

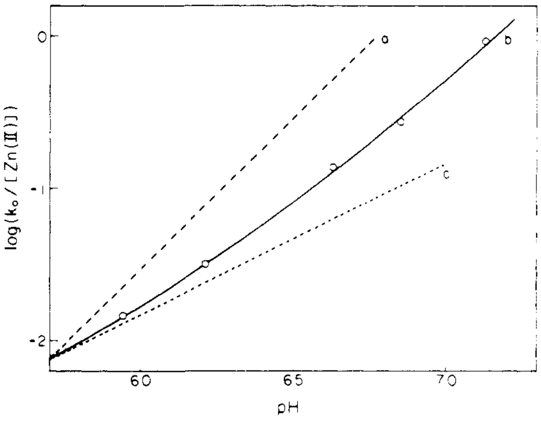


Figure 3. Plot of the logarithmic values of k_0/[Zn(II)] (slopes of the straight lines illustrated in Figure 2) against pH. Curve b was obtained by using eq 1 and the parameter values listed in Table I. Lines a and c are drawn with slopes 2.0 and 1.0, respectively.

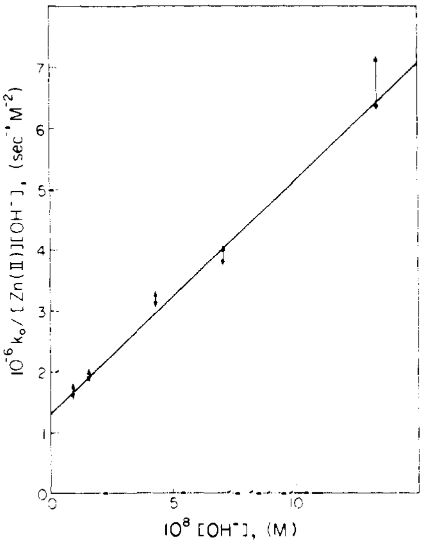


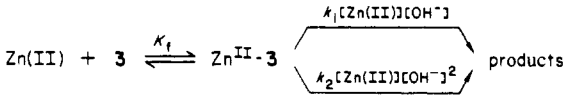
Figure 4. Plot of k_0/[Zn(II)][OH$^-$] (slopes of the straight lines illustrated in Figure 2 divided by hydroxide concentration) against [OH$^-$]. The straight line was obtained by the weighted linear regression of the data points.

Table I. Values of Kinetic Parameters for the Hydrolysis of **3**[a]

parameter	value
1. Zn(II)-catalyzed	
k_1	$(1.32 \pm 0.06) \times 10^6$ s^{-1} M^{-2}
k_2	$(3.91 \pm 0.28) \times 10^{13}$ s^{-1} M^{-3}
2. spontaneous alkaline	
k_{OH}[b]	8.0 ± 0.8 s^{-1} M^{-1}

[a] Measured at 25 °C and ionic strength of 1.0 in the presence of 0.8% (v/v) Me$_2$SO. [b] k_{OH} for **1** is 15 s^{-1} M^{-1} and that for **2** is 8.2 s^{-1} M^{-1} at 25 °C and ionic strength of 1.0.[6]

Scheme I



Results and Discussion

Rate Data. The UV spectra of **3** measured in the presence or absence of Zn(II) ion are illustrated in Figure 1. The free compound is represented by curve a and the Zn(II) complex by curve b. Since an identical spectrum was obtained at 2–20 mM Zn(II), complete complexation is achieved even at 2 mM Zn(II). Thus, the formation constant (K_f) for Zn^{II}-**3** is greater than 500 M^{-1}.

At a given pH, the pseudo-first-order rate constant (k_0) was proportional to [Zn(II)], as illustrated in figure 2. The logarithmic values of the slopes (k_0/[Zn(II)]) of the straight lines are plotted against pH in Figure 3. The experimental curve in Figure 3 deviates greatly from straight lines with slope 1 or 2. A straight line, however, is obtained when k_0/[Zn(II)][OH$^-$] is plotted against [OH$^-$], as illustrated in Figure 4. The linear dependence illustrated in Figure 4 leads to the rate expression of eq 1. Weighted linear regression of the data points of Figure 4 gave values of the rate parameters summarized in Table I.

$$k_0 = k_1[\mathrm{Zn(II)}][\mathrm{OH}^-] + k_2[\mathrm{Zn(II)}][\mathrm{OH}^-]^2 \qquad (1)$$

The simpliest kinetic scheme that is consistent with the very large formation constant of Zn^{II}-**3** and the rate expression of eq 1 is indicated by Scheme I. The rate equation derived for this scheme is eq 2, which becomes eq 1 when [Zn(II)] $\gg 1/K_f$. Since

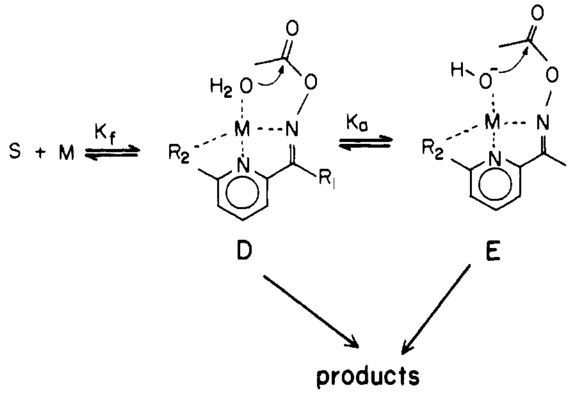
$$k_0 = (k_1[\mathrm{Zn(II)}][\mathrm{OH}^-] + k_2[\mathrm{Zn(II)}][\mathrm{OH}^-]^2)/(1 + 1/K_f[\mathrm{Zn(II)}]) \qquad (2)$$

K_f for Zn^{II}-**3** is very large, the Zn(II) ion needed for the complexation does not contribute to the overall rate expression of eq 1 at the concentrations of Zn(II) ion employed in the kinetic study. Instead, the observed rate expression reflects the molecularity of Zn(II) and hydroxide ions that participate in the conversion of Zn^{II}-**3** to the products.

The UV spectrum of **3** measured in the presence of 5–25 mM Cu(II) ion at pH 4 indicated complete complexation even at 5 mM [Cu(II)]. The hydrolysis of **3**, however, was not detected for 12 h at 25 °C when the reaction was followed in the presence of 25 mM Cu(II) ion.

Mechanism. The predominant reaction paths in the Cu(II)- or Zn(II)-catalyzed hydrolysis of **1** or **2** are indicated in Scheme II.[4-6,11]

Scheme II



For the Cu(II)-catalyzed hydrolysis of **1**, K_f was quite large (~50 M^{-1}), and both D and E contributed to the overall rate.[5] Even at pH 2–3, where the contribution of E to the rate was negligible, the half-life of Cu^{II}-**1** was about 30 s.[5] The reaction of Cu^{II}-**2** was even faster, with the half-life being less than 1 s at pH 2.[6]

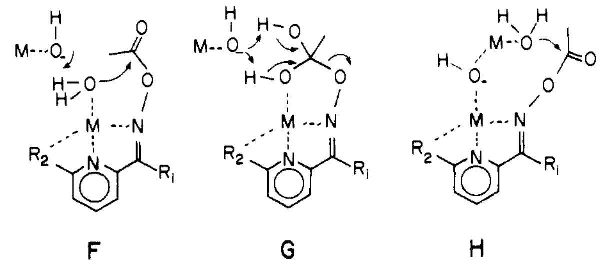
Although Cu^{II}-**3** was formed quantitatively, its hydrolysis was not detected over a period of 12 h at pH 4 in the present study. The extremely slow rate for Cu^{II}-**3** in contrast to Cu^{II}-**1** or Cu^{II}-**2** indicates that the introduction of the 6-carboxy substituent greatly destabilizes the transition states for the reactions of D and E.[12] As reflected by the rate of spontaneous alkaline hydrolysis (Table I), the 6-carboxy group exerts only small electronic effects. Instead, the destabilization of the transition state should be due to the steric effects exerted by the carboxy group which forms an additional five-membered chelate ring in the metal complex. If the mechanism of Scheme II is operative, the transition state for the reaction of Cu^{II}-**3** should contain three five-membered chelate rings.[13] The kinetic data for Cu^{II}-**3**, therefore, indicate that a considerable ring strain is involved in the transition states for Scheme II when the central metal ion is Cu(II).

Steric effects on the stability of chelate rings of the transition state have also been observed with **1** and **2**.[6] The methyl substituent of **2** should lower the reactivity of the carbonyl carbon if it exerts only electronic effects. The hydrolysis of M^{II}-**2** (M = Cu or Zn) was, however, much faster than that of M^{II}-**1**.[6] This was explained in terms of steric acceleration caused by the methyl substituent. When the hydrolysis occurs through the mechanism of Scheme II, a five-membered ring which is absent in the ground state is newly formed in the transition state, and a bulkier group substituted at R_1 could accelerate the reaction. Thus, introduction of the methyl substituent in **2** results in steric acceleration and that of the carboxy group in **3** leads to steric retardation for the reaction paths of Scheme II.

In the Zn(II)-catalyzed hydrolysis of **3**, the reaction path of D should result in a rate term independent of both [Zn(II)] and [OH^-] and that of E in a rate term proportional to [OH^-] but independent of [Zn(II)]. The contribution of these paths is represented by the intercept of the plot of k_0 against [Zn(II)] at a given pH. The data illustrated in Figure 1, however, demonstrate that the rate of D or E is negligible in the Zn(II)-catalyzed hydrolysis of **3**. At pH 6.63 in the presence of 0.02 M Zn(II), k_0 for the reaction paths of Scheme II was 0.0015 and 0.014 s^{-1} for **1** and **2**, respectively.[4,6] These are much greater than the intercept of line c of Figure 2.

Although **3** is fully complexed to Zn(II) ($K_f \gg 500$ M^{-1}) while extremely small portions of **1** and **2** are bound to Zn(II) ($K_f \ll 5$ M^{-1})[4,6] under the experimental conditions, the hydrolysis of **3** through the paths of Scheme II is much slower than that of **1** or **2**. Again, the extremely low reactivity of Zn^{II}-**3** in these paths indicates that a significant amount of ring strain is involved in the corresponding transition states. Thus, the structure containing the three five-membered chelate rings appears to be unstable when the central atom is the Zn(II) or Cu(II) ion.

In the Zn(II)-catalyzed hydrolysis of **3**, two reaction paths are observed. In the path whose rate is proportional to [Zn(II)][OH^-] (the first term of eq 1), the transition state of the rate-determining step contains two Zn(II) ions and one hydroxide ion. Possible mechanisms that meet this stoichiometric reqirement are F, G, and H. For the other path whose rate is proportional to [Zn(II)][OH^-]^2 (the second term of eq 1), the rate-determining transition state contains two Zn(II) and two hydroxide ions. Mechanisms A, B, and C agree with the observed rate expression. The transition states for mechanisms A, B, F, and G, however, involve the same unfavorable system of three five-membered chelate rings as those of D and E. These mechanisms, in which the second hydroxozinc(II) ion acts as a general base, therefore, can be excluded.[14]



The Zn(II)-catalyzed hydrolysis of **3** occurs through the participation of binuclear Zn(II) ions, as illustrated by C and H. These structures can be regarded as the complex of **3** bound to Zn–[μ-OH^-]–Zn–OH^- or Zn–[μ-OH^-]–Zn–OH_2. It is generally assumed that the metal ions in such dimers are bridged by μ-hydroxo or μ-oxo ligands.[15,16] The dimers may also contain two bridges. Other binuclear species such as Zn–[μ-O^{2-}]–Zn–OH_2 or Zn–[μ-OH^-]–Zn–OH_2, therefore, cannot be excluded as the complexing catalytic unit since they conform to the observed rate expression. In addition, hydrogen oxide ($OH^- \cdot OH_2$) has been recently found to be a bridging ligand in binuclear complexes.[17]

The lack of reactivity of **3** in the presence of Cu(II) ion indicates that the rate for the path of C or H is very slow for Cu^{II}-**3**. This may be ascribed either to the low concentrations or to the improper geometry of the intermediates containing binuclear Cu(II) ions.

Although many studies have been reported for binuclear complexes,[18] the behavior of dimeric hydroxo- or aquometal ions in

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(11) Chelate formation between the oxime ester and the metal ion is required for the catalysis. The hydrolysis of *O*-(acetyloxy)-3-pyridinecarboxaldoxime, for which the chelate formation is precluded, was not catalyzed by Zn(II) ion in contrast to the very efficient catalysis in the hydrolysis of **1**.[4] In addition, the saturation kinetic behavior observed in the Cu(II)-catalyzed hydrolysis of **1** was consistent with the complex formation between Cu(II) and **1** prior to the cleavage of the ester linkage.[5]

(12) The low reactivity of E may be attributed in part to the decrease in K_a of Scheme II caused by the introduction of the 6-carboxy group. Thus, the concentration of E at a given pH may be smaller for **3** than for **1**. For the Cu(II)-catalyzed hydrolysis of **1**, the k_0 value contributed to by E was 3×10^{-2} s^{-1} at pH 4. The extremely large difference in rate between **1** and **3** at pH 4 in the presence of Cu(II) ion, however, cannot be accounted for by the difference in K_a alone.

(13) Since the tetrahedral intermediates of transacylation reactions are much more unstable than the reactants or the products, transition states should resemble tetrahedral intermediates in accordance with Hammond's postulate (Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334). Therefore, the third five-membered chelate ring is formed to a significant extent in the transition state for **3** in the reaction paths of Scheme II.

(14) Exclusion of these mechanisms does not weaken the argument made previously on the results of the ^{18}O-exchange experiments of Carboxypeptidase A.[6] This is because breakdown of acylcarboxypeptidase A intermediates proceeds mainly through the water path[19] and because the attack of the Zn(II)-bound water molecule at the complexed model ester is catalyzed by general bases.[5]

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solution has been rarely investigated. A vast amount of literature is available for the metal ion catalysis in transacylation reactions.[1] Catalysis by binuclear metal ions, however, has not been reported. The present results indicate that the participation of the binuclear species could be a general phenomenon when the geometry of the transition state is appropriate.

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Registry No. 3, 100928-14-1; $ZnCl_2$, 7646-85-7; $CuCl_2$, 7447-39-4.

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Reaction of Chromium(VI) with Thiols: pH Dependence of Chromium(VI) Thio Ester Formation

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Abstract: The rates of ligand substitution reactions of chromium(VI) with cysteamine, cysteine, cysteine ethyl ester, homocysteine, 3-mercaptopropionic acid, *N*-acetylcysteine, and thioglycolic acid which result in the formation of chromium(VI) thio esters have been studied over a wide range of pH. The apparent second-order rate constants (k_1) for the formation of the chromium(VI) thio esters varied dramatically with pH. Analysis of the pH dependence of the rate constants revealed that (a) in the pH range of 5–10, the reaction of chromium(VI) with cysteine ethyl ester and cysteamine could be described by reaction of the chromium(VI) and aminothiol species having two of the three possible groups (oxo of chromium(VI), amine, or sulfhydryl) protonated, (b) in the pH range of 3–10, the reaction of chromium(VI) with cysteine and homocysteine could be described by the reaction of chromium(VI) and aminothiocarboxylic acid species having two, three, and four of the four possible groups (oxo of chromium(VI), amine, sulfhydryl, and carboxylate) protonated, (c) in the pH range of 2–10, the reaction of chromium(VI) with 3-mercaptopropionic acid and *N*-acetylcysteine could be described by the reaction of chromium(VI) and thiocarboxylic acid species having one, two, and three of the three possible groups (oxo of chromium(VI), sulfhydryl and carboxylate) protonated, and (d) in the pH range of 2–10, the reaction of chromium(VI) with thiolglycolic acid could be described by the reaction of chromium(VI) and thiocarboxylic acid species having two and three of the three possible groups protonated. Linear plots of log k_1 vs. pK_a of the thiol were obtained only for reaction of chromate or hydrogen chromate with species having the sulfhydryl group protonated. In these cases, log k_1 was inversely correlated with the thiol pK_a. Reaction of the thiols with hydrogen chromate was 10–100 times slower than with chromate. Protonation of carboxylate groups resulted in a ~1000 times increase in the apparent second-order rate constant for the reaction of chromate with the aminothiocarboxylic acids and thiocarboxylic acids. The rate of reaction of thioglycolic acid with chromium(VI) was anomalously high when compared to the other thiols and suggests a possible chelate effect or a more favorable geometry for proton transfer from –COOH to –CrOH. Our results indicate that ligand substitution reaction of chromium(VI) with thiols involves attack of chromate or hydrogen chromate by the protonated thiol with rate-determining proton transfer from the sulfhydryl to the chromium(VI).

The formation of chromium(VI) esters during the reaction of chromium(VI) with organic and inorganic acids has been well-documented.[2-5] Most studies of chromium(VI)–thiol reactions have been carried out under acidic conditions. Under these conditions, transient orange species (λ_{max} ~ 420–440 nm) have been observed and assigned as chromium(VI) thio esters on the basis of spectral features (the red shift in absorbance maximum compared to hydrogen chromate and large extinction coefficients).[6] Chromium(VI) thio esters have been detected upon reaction of chromium(VI) with cysteine,[7] penicillamine, glutathione, cysteamine,[6] thiourea,[8] hydrogen thiocyanate,[9] and hydrogen thiosulfate[10] under acidic conditions (eq 1). Although chromium(VI) is considered a *hard* acid and sulfur a *soft* base,[11] the equilibrium constants for the formation of chromium(VI) thio esters are several orders of magnitude greater than chromium(VI) oxy esters.[6]

$$RSH + HCrO_4^- \rightleftharpoons RSCrO_3^- + H_2O \qquad (1)$$

Our kinetic studies of the reaction of glutathione and other thiols with chromium(VI) at pH 7.4[12] and Kwong and Pennington's study of the reaction of cysteine with chromium(VI) at pH 7.0[13] showed that a general mechanism for the reaction of chromium(VI) with thiols involves the formation of a chromium(VI) thio ester (eq 2) followed by either a redox reaction involving a second molecule of thiol (eq 3) or a unimolecular redox reaction of the thio ester which leads to Cr(V) and a radical (eq 4) or Cr(IV) in the case of dithiols capable of forming an intramolecular disulfide bond (eq 5). We have obtained spectral and kinetic evidence at pH 7.4 for the formation of chromium(VI) thio esters upon the reaction of chromium(VI) with glutathione, cysteine ethyl

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