reaction 1 occurs, in which thermal detrapping from the

$$e_m^- + \text{shallow trap} \rightleftarrows e_{st}^- \qquad (1)$$

shallow trap occurs at temperatures above 90°K. At 4 and 77°K reaction 1 occurs only in the forward direction and e_{st}^- apparently does not contribute to the epr spectrum of e_t^-. The lack of epr is rationalized below. Thus there is no temperature dependence for e_t^- photobleaching at 4 and 77°K. Above 77°K e_{st}^- is thermally detrapped and at least some of the e_m^- produced will be retrapped to form e_t^-. This back-reaction explains the negative temperature dependence. At higher temperatures more retrapping to form e_t^- occurs and decreases the net rate of e_t^- loss.

The fit to an Arrhenius plot in Figures 3 and 4 suggests that the average shallow trap depth is 1.2 kcal/mol (0.05 eV). The shallow-trap model implies that the photocurrent should show a positive temperature dependence corresponding to 0.05 eV. This has indeed been observed.[3] The photocurrent data also show that the density of shallow traps is radiation dose dependent and therefore suggest that the shallow trap is associated with O^-. If so, one might expect similar shallow traps to be associated with other holes in the alkaline ice matrix. Figure 3 shows the same negative temperature dependence for photobleaching of e_t^- from photoionization of ferrocyanide ion as for radiation-produced e_t^-. So, similar shallow traps appear to be associated with ferricyanide ion holes and O^- holes in the alkaline ice matrix. The epr spectrum of e_{st}^- could well be broadened beyond detection by spin-spin interaction with the holes.

Table I shows that the fraction of e_t^- that corresponds to O^- loss on prolonged optical bleaching is nearly independent of temperature and radiation dose. At 150°K dielectrons are not thermally stable.[18] Thus competition between e_t^- and O^- for e_m^- does not determine the fractions in Table I. Likewise the thermal instability of e_{st}^- precludes competition between O^- and shallow traps as the rationalization for Table I. The results seem to be tentatively explained by invoking two reactions of either e_m^- or e_{st}^- with O^- which have temperature independent rates. One reaction must lead to loss of both O^- and the electron species and the other reaction must lead to loss of only the electron species. The latter reaction may be regarded as analogous to the reaction of photobleached electrons with TMPD$^+$ in 3-methylpentane at 77°K which leads to loss of the electron optical spectrum but does not change the TMPD$^+$ optical spectrum.[19] The product of such a reaction is unknown in detail, but one possible model is a hole-electron charge pair.

Acknowledgment. This research was supported by the U. S. Atomic Energy Commission, by the Air Force Office of Scientific Research under Grant No. AFOSR-70-1852, and by Wayne State University.

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Metal-Ion Catalysis of Ethyl Oxalate Hydrolysis

Gordon L. Johnson[1a] and Robert J. Angelici*[1b]

Contribution from the Department of Chemistry,
Iowa State University, Ames, Iowa 50010. Received July 10, 1970

Abstract: The hydrolysis of ethyl oxalate, $^-O_2CCO_2Et(EtOx^-)$, is catalyzed by a variety of metal ions; the rate is given by the expression: rate = $k_3[EtOx^-][M^{2+}][OH^-]$. The values of k_3 (M^{-2} sec^{-1}) at 25° decrease with M^{2+} in the order Cu^{2+} (1.63×10^7) > Pb^{2+} (3.72×10^6) > Zn^{2+} (1.14×10^5) > Ni^{2+} (6.81×10^4) > Co^{2+} (4.15×10^4) > Mg^{2+} (1.02×10^3). The data have been interpreted in terms of a mechanism [$M^{2+} + EtOx^- \rightleftarrows MEtOx^+$ (K_f); $MEtOx^+ + OH^- \rightarrow M(C_2O_4) + EtOH$ (k)], in which the ester, which is coordinated to the metal ion in a prior rapid equilibrium, is attacked by OH^-. The experimental k_3 is then kK_f. Using estimated values of K_f, it is found that k for different metal ions follows the same trend as given above. The rate of OH^- attack on the ester is 2×10^5 larger when the ester is coordinated to Cu^{2+} than when free in solution. Activation parameters for the reaction indicate that an increase in ΔS^* is primarily responsible for the catalytic effect of the metal ions.

In recent years metal-ion catalysis of ester hydrolysis[2-4] has been of increasing interest. Our own investigations[5] have concentrated on the kinetics and mechanisms of amino acid ester hydrolysis. In the present paper we report the results of studies on the metal-ion catalysis of the hydrolysis of ethyl oxalate, $^-O_2CCO_2Et(EtOx^-)$, to oxalate, $C_2O_4^{2-}(Ox^{2-})$, according to the equation

$$M^{2+} + EtOx^- + H_2O \longrightarrow M(Ox) + H^+ + EtOH \qquad (1)$$

A less detailed study of this reaction as catalyzed by Cu(II) and Ni(II) was reported previously.[6]

Experimental Section

Materials. Potassium ethyl oxalate, $KO_2CCO_2Et(KEtOx)$, was prepared by half hydrolyzing diethyl oxalate.[7] The analytical

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Table I. Rates of Metal-Ion-Catalyzed Hydrolysis of Ethyl Oxalate[a]

pH_c	$[M^{2+}]$, mM	Temp, °C	10^4k_{obsd}, sec^{-1}
	No Metal Ion		
10.05		15.6	0.44
10.04		25.1	1.45
10.33		25.1	2.50
10.57		14.6	1.06
10.57		20.4	2.15
10.52		25.1	3.55
10.55		30.3	6.83
10.52		34.7	11.2
10.74		25.1	5.40
11.06		25.1	11.8
	Cu(II)		
4.91	8.35	25.0	1.90
5.03	8.35	15.4	0.792
5.02	8.35	20.4	1.48
5.03	1.25	25.0	0.388
5.03	2.09	25.0	0.555
5.03	4.18	25.0	1.08
5.03	8.35	25.0	2.22
5.03	16.7	25.0	5.18
5.03	25.1	25.0	7.80
5.03	33.4	25.0	11.4
5.03	8.35	30.2	4.72
5.03	8.35	35.0	7.85
5.03	8.35	39.8	13.0
5.03	8.35	45.0	20.3
5.17	8.35	25.0	3.08
5.35	8.35	25.0	4.16
5.46	8.35	25.0	6.57
5.66	8.35	25.0	9.32
	Pb(II)		
5.40	8.21	24.9	1.29
5.71	8.21	15.0	0.580
5.71	8.21	20.8	1.22
5.71	4.10	24.9	1.11
5.71	8.21	24.9	2.60
5.71	16.4	24.9	5.63
5.71	8.21	29.7	4.42
5.71	8.21	34.9	8.37
5.71	8.21	40.0	15.6
5.92	8.21	24.9	4.23
	Zn(II)		
6.64	8.41	24.9	0.663
6.96	8.41	14.7	0.282
6.96	8.41	20.3	0.635
6.96	4.21	24.9	0.648
6.96	8.41	24.9	1.40
6.96	16.8	24.9	3.33
6.96	8.41	30.1	2.83
6.96	8.41	35.1	6.18
6.96	8.41	39.7	15.0
7.16	8.41	24.9	2.18
	Ni(II)		
7.37	8.24	25.0	2.02
7.47	8.24	15.3	0.837
7.47	8.24	20.3	1.67
7.47	4.12	25.0	1.41
7.47	8.24	25.0	2.87
7.47	16.5	25.0	5.98
7.47	8.24	30.3	5.72
7.47	8.24	35.0	10.9
7.68	8.24	25.0	3.88
7.89	8.24	25.0	6.92
	Co(II)		
7.47	8.29	25.0	1.63
7.67	4.15	25.0	1.30
7.67	16.6	25.0	5.35
7.79	8.29	25.0	3.27
7.89	8.29	15.0	1.05
7.89	8.29	20.2	2.22
7.89	8.29	25.0	4.20
7.89	8.29	29.8	7.32
7.89	8.29	34.8	17.0
7.98	8.29	25.0	5.68
	Mg(II)		
8.50	8.22	25.1	0.437
9.00	8.22	15.4	0.338
9.00	8.22	20.4	0.672
9.00	4.11	25.1	0.745
9.00	8.22	25.1	1.46
9.00	16.4	25.1	2.70
9.00	8.22	29.6	2.43
9.00	8.22	35.1	5.53
9.00	8.22	39.5	9.38
9.53	8.22	25.1	4.52

[a] $\mu = 0.10\ M\ (KNO_3)$; $[EtOx] = 8 \times 10^{-4}\ M$.

reagent grade metal-ion salts were used in the following forms: $Cu(NO_3)_2 \cdot 3H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, KNO_3. Except for KNO_3, which was weighed out directly, aqueous solutions of the metal ions were standardized by titration with EDTA.[8] Doubly distilled water was used in all solutions.

pK_a of Ethyl Oxalate, HO_2CCO_2Et(HEtOx). Using a Radiometer TTTlc/SBR2/SBU1/TTTA31 pH meter recorder, syringe buret, and microtitration assembly, a solution of 0.08 M KEtOx and 0.08 M HNO_3 was titrated with NaOH. The ionic strength (μ) was adjusted to 0.4 M with KNO_3. The pH meter was calibrated in terms of H^+ concentration, pH_c (rather than H^+ activity, pH), using solutions of HCl and acetic acid[9] of known H^+ concentration. The pH at the midpoint of the titration yielded a value of 1.72 for the pK_a of HEtOx at 25.0° and $\mu = 0.4$. Under all conditions of the kinetic studies, the ethyl oxalate is unprotonated, *i.e.*, exists as $EtOx^-$.

Stability Constant, K_f, for the Coordination of Ethyl Oxalate by Cu(II). The stability constant of interest is for the reaction

$$Cu^{2+} + EtOx^- \overset{K_f}{\rightleftharpoons} Cu(EtOx)^+ \qquad (2)$$

It was estimated by measuring the H^+ displaced from HEtOx by Cu(II), according to the equilibrium

$$Cu^{2+} + HEtOx \overset{K_aK_f}{\rightleftharpoons} Cu(EtOx)^+ + H^+ \qquad (3)$$

Because K_f is small, it was necessary to use relatively concentrated solutions of Cu(II) and KEtOx. A solution containing 0.08 M Cu(II), 0.08 M KEtOx, 0.08 M HNO_3, and adjusted to an ionic strength of 0.4 with KNO_3, was titrated with NaOH. Above pH 1.53 precipitation (perhaps Cu(OH)(EtOx)) occurred; hence only data in the pH range 1.29–1.36 were used to estimate K_f. Using the H^+ concentration (pH_c) read from the pH meter as well as material balance expressions for total ethyl oxalate ($EtOx_{tot}$) and total Cu(II) (Cu_{tot})

$$Cu_{tot} = [Cu(II)] + [Cu(EtOx)^+]$$

$$EtOx_{tot} = [EtOx^-] + [HEtOx] + [Cu(EtOx)^+]$$

and substituting equilibrium expressions for K_a and K_f, an average value of 1.88 was obtained for log K_f at 25.0° and $\mu = 0.4$.[10] A

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value of 2.06 at $\mu = 0.1$ was obtained by correcting the activity coefficients (γ) of the species in the expression for K_f. The expression used for estimating the activity coefficients was

$$\log \gamma_{\pm} = -0.5Z_1Z_2\mu^{1/2}/(1 + \mu^{1/2}) + 0.2\mu$$

It should be emphasized that this value of K_f can only be regarded as approximate because of the small changes in pH_c observed in the titrations. This approximate value, however, will be of use in the interpretation of the kinetics of ester hydrolysis.

Rates of Ethyl Oxalate Hydrolysis. The rates of ester hydrolysis according to eq 1 were followed with the Radiometer pH-Stat unit mentioned previously.[11] The pH_c of the solution was maintained at a preset value by the automatic addition of 0.02 M NaOH. The amount of NaOH added corresponded to the amount of ester hydrolyzed. The amount of NaOH delivered was recorded as a percentage of the total capacity of the syringe buret. Pseudo-first-order rate plots of ($\%_{\text{end}} - \%_t$) *vs.* time (where $\%_{\text{end}}$ is the NaOH consumed at the end of the reaction and $\%_t$ is that consumed at any time t) were linear to at least 50% of reaction. Pseudo-first-order rate constants, k_{obsd}, were calculated from the slopes of these plots. Values of k_{obsd} determined at varying conditions of pH_c, metal-ion concentration, and temperature are given in Table I.

The initial concentration of KEtOx in most of the reactions was 8×10^{-4} M. Concentrations of 1.6×10^{-3} and 2.4×10^{-3} M KEtOx gave the same values of k_{obsd}. The concentration of the metal ions varied from 1.25×10^{-3} to 3.34×10^{-2} M. The ionic strength was held at 0.1 M with KNO_3.

Results and Discussion

Non-Metal-Ion-Catalyzed Hydrolysis. The values of k_{obsd} recorded in Table I indicate that the hydrolysis of ethyl oxalate in the absence of metal ions follows the rate law

$$\text{rate} = k_2[\text{EtOx}^-][\text{OH}^-] \qquad (4)$$

where $k_{\text{obsd}} = k_2[\text{OH}^-]$. To evaluate k_2, it was necessary to calculate $[\text{OH}^-]$ from pH_c and the expression $K_\omega = [\text{H}^+][\text{OH}^-]$. Values of K_ω at 0.10 ionic strength and various temperatures were obtained from standard references.[12] The average values of k_2 at different temperatures are 0.402 (14.6°), 0.540 (20.4°), 0.687 (25.1°), 0.821 (30.3°), and 1.00 (34.7°) M^{-1} sec^{-1}. A literature value[13] of 0.743 M^{-1} sec^{-1} at 25° and 0.087 M (KNO_3) ionic strength compares favorably with our result at the same temperature and similar ionic strength. From a plot of log k_2 *vs.* $1/T$, the activation energy, E_a, was calculated to be 7.7 kcal/mol. The enthalpy, ΔH^*, and entropy, ΔS^*, of activation at 25° are 7.1 ± 0.3 kcal/mol and −35.5 ± 2 eu, respectively.

Metal-Ion-Catalyzed Hydrolysis. As required by the data in Table I, the metal-ion-catalyzed hydrolysis of ethyl oxalate follows the rate law

$$\text{rate} = k_3[\text{EtOx}^-][\text{M}^{2+}][\text{OH}^-] \qquad (5)$$

where $k_{\text{obsd}} = k_3[\text{M}^{2+}][\text{OH}^-]$. From k_{obsd}, pH_c, and $[\text{M}^{2+}]$ in Table I, values of k_3 have been calculated and are presented in Table II. As noted in the previous section, $[\text{OH}^-]$ was calculated from pH_c and the literature value for K_ω at the desired temperature and ionic strength. The standard deviations for the k_3 values are approximately 10%. Our values for Cu^{2+} and Ni^{2+} at 25° and 0.10 M ionic strength compare well with those of 1.48×10^7 and 6.7×10^4 M^{-2} sec^{-1} calculated from data of Hay and Walker[6] at 25° and 0.30 M ionic strength.

Table II. Rate Constants, k_3, and Activation Enthalpies for the Metal-Ion-Catalyzed Hydrolysis of Ethyl Oxalate[a]

M^{2+}	Temp, °C	k_3, M^{-2} sec^{-1}	ΔH^*_3
Cu^{2+}	15.4	1.25×10^7	
Cu^{2+}	20.4	1.58×10^7	
Cu^{2+}	25.0	1.63×10^7	6.2 ± 0.5
Cu^{2+}	30.2	2.25×10^7	
Cu^{2+}	35.0	2.59×10^7	
Cu^{2+}	39.8	3.18×10^7	
Cu^{2+}	45.0	3.51×10^7	
Pb^{2+}	15.0	2.01×10^6	
Pb^{2+}	20.8	2.70×10^6	
Pb^{2+}	24.9	3.72×10^6	9.1 ± 0.3
Pb^{2+}	29.7	4.49×10^6	
Pb^{2+}	34.9	5.86×10^6	
Pb^{2+}	40.0	7.72×10^6	
Zn^{2+}	14.7	5.19×10^4	
Zn^{2+}	20.3	7.73×10^4	
Zn^{2+}	24.9	11.4×10^4	12.8 ± 0.5
Zn^{2+}	30.1	15.7×10^4	
Zn^{2+}	35.1	23.8×10^4	
Ni^{2+}	15.3	4.86×10^4	
Ni^{2+}	20.3	6.56×10^4	
Ni^{2+}	25.0	6.81×10^4	8.3 ± 0.6
Ni^{2+}	30.3	10.3×10^4	
Ni^{2+}	35.0	13.5×10^4	
Co^{2+}	15.0	2.30×10^4	
Co^{2+}	20.2	3.29×10^4	
Co^{2+}	25.0	4.15×10^4	9.3 ± 0.8
Co^{2+}	29.8	4.96×10^4	
Co^{2+}	34.8	7.98×10^4	
Mg^{2+}	15.4	5.94×10^2	
Mg^{2+}	20.4	7.64×10^2	
Mg^{2+}	25.1	10.2×10^2	10.3 ± 0.4
Mg^{2+}	29.6	12.0×10^2	
Mg^{2+}	35.1	19.0×10^2	
Mg^{2+}	39.5	23.8×10^2	

[a] $\mu = 0.10$ M (KNO_3).

The rate of the Cu^{2+}-catalyzed hydrolysis of $EtOx^-$ was determined as a function of the ionic strength of the solution. These values of k_{obsd} are tabulated in Table III. If the data at pH_c 5.34 are plotted as log k_{obsd} *vs.* $\mu^{1/2}/(1 + \mu^{1/2})$, according to the Debye–Hückel equation, a slope of −1.7 ± 0.4 is obtained. At pH_c 5.54, the slope is essentially the same (−1.6 ± 0.6), although the scatter in the data is greater.

Table III. Ionic Strength Dependence of the Rate of Cu^{2+}-Catalyzed Hydrolysis of Ethyl Oxalate at pH_c 5.34 and 5.54 (25.0°)

pH_c 5.34[a]		pH_c 5.54[b]	
$10^2\mu$, M (KNO_3)	10^4k_{obsd}, sec^{-1}	$10^2\mu$, M (KNO_3)	10^4k_{obsd}
1.33	2.92	0.42	1.50
1.83	2.73	0.66	1.24
2.34	2.67	0.92	1.34
2.84	2.43	1.42	1.09
3.34	2.40	2.42	1.05
3.84	2.18	2.92	1.05
5.34	2.17		

[a] $[\text{EtOx}^-] = 8.0 \times 10^{-4}$ M; $[\text{Cu}^{2+}] = 4.2 \times 10^{-3}$ M. [b] $[\text{EtOx}^-] = 4.0 \times 10^{-4}$ M; $[\text{Cu}^{2+}] = 1.3 \times 10^{-3}$ M.

On the basis of all of the above rate data, we propose that the metal-catalyzed hydrolysis of ethyl oxalate occurs *via* the following general mechanism.

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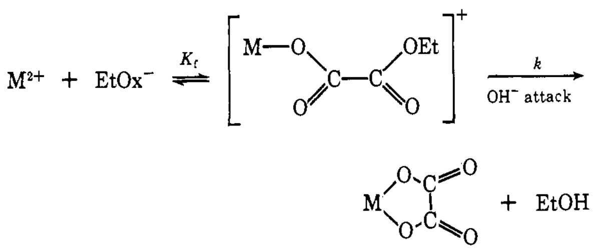
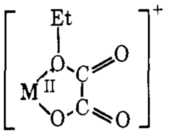


(6)

The initial step is the coordination of $EtOx^-$ by the metal ion. Using the estimated value of log K_f (2.06) for $M^{2+} = Cu^{2+}$, one can calculate that approximately 50% of the $EtOx^-$ is coordinated to Cu^{2+} for typical reaction solutions containing 10^{-2} M Cu^{2+} and 10^{-3} M $EtOx^-$. As compared to K_f values found for other ligands (see below) this value seems unusually high. Because of the experimental difficulties associated with determining K_f, it is possible that this value is in fact too high and the extent of $EtOx^-$ coordination is significantly lower than 50%. For other metal ions which probably give lower K_f values, the amount of coordinated $EtOx^-$ would be even less. In general, the equilibrium associated with K_f probably lies toward the left under the conditions of the kinetic studies, and most of the $EtOx^-$ is uncoordinated.

The form of the coordinated ester may be that shown in (6) where there is no direct coordination of the ester group to the metal ion or there may be direct coordination either through the ether oxygen or carbonyl oxygen of the ester group, *e.g.*



The experimentally estimated log K_f value (2.06) for Cu^{2+} is somewhat higher than would be expected from the pK_a of HEtOx. As has been pointed out for substituted acetates ($XCH_2CO_2^-$), more basic acetates coordinate with Cu^{2+} more strongly than do those of lower basicity.[14] In the present situation, however, $EtOx^-$ apparently coordinates to Cu^{2+} more strongly than does $CH_3CO_2^-$ (log K_f = 1.8) despite the fact that the latter is more basic (pK_a = 4.54) as compared to $EtOx^-$ (pK_a = 1.72). The unusually high stability of Cu(EtOx)$^+$ may indicate that the ligand is bidentate, coordinating through both a carboxylate oxygen and an ester oxygen. Bidentate coordination has been postulated previously for substituted acetates on the basis of their stability constants.[15] Because of the experimental uncertainty in K_f in this case, however, it is not possible to reach specific conclusions regarding the nature of the $EtOx^-$ coordination.

The rate-determining step of the hydrolysis in mechanism 6 is the attack of OH^- upon the carbon of the ester group. This ester may or may not be directly coordinated to the metal ion. The high rate of catalysis by the metal ion suggests that the ester group does coordinate in some manner to the metal ion.

That the product of the reaction, M(Ox), does not catalyze the hydrolysis of EtOx was shown by adding to a reaction solution an amount of oxalate, Ox^{2-}, equivalent to the Cu^{2+} concentration. Precipitation of Cu(Ox) occurred, but the remaining solution of Cu(Ox) did not catalyze the hydrolysis of $EtOx^-$ at pH 5.10.

Since mechanism 6 requires the coordination of $EtOx^-$ to the metal ion, removal of the coordinating $-COO^-$ group in $EtOx^-$ should diminish the catalytic effect of the metal ion. Hence the hydrolysis of diethyl oxalate in the presence of 8.3×10^{-3} M Cu^{2+} and at pH$_c$ 5.03 and 25° proceeded with a half-time for both ester groups of 252 min as compared to 52 min for $EtOx^-$. In the absence of the Cu^{2+}, no measurable hydrolysis occurred at this pH. Although Cu^{2+} does catalyze the hydrolysis of diethyl oxalate, it is considerably less than that for $EtOx^-$. It is known that the non-metal-ion-catalyzed base hydrolysis of diethyl oxalate[16] proceeds much faster than that of $EtOx^-$.

The effect of ionic strength on the rate (k_{obsd}) of the Cu^{2+}-catalyzed hydrolysis of $EtOx^-$ has also been examined. According to mechanism 6, changes in ionic strength would effect three constants: K_ω (used to calculate $[OH^-]$ from pH$_c$), K_f, and k. Using the Debye–Hückel equation for calculating activity coefficients, $\log \gamma_\pm = -0.5Z_1Z_2\mu^{1/2}/(1 + \mu^{1/2})$, a plot of log K_ω *vs.* $\mu^{1/2}/(1 + \mu^{1/2})$ should give a slope of +1; a similar plot of K_f should give a slope of −2, and a plot of log k a slope of −1. The slope of a plot of k_{obsd} *vs.* $\mu^{1/2}/(1 + \mu^{1/2})$ should be the sum of the slopes predicted for K_ω, K_f, and k. This overall slope of −2 is in reasonably good agreement with the experimentally observed value of −1.7 ± 0.4. The ionic strength results are therefore consistent with mechanism 6.

It should be emphasized that mechanism 6 is not the only one which fits the kinetic data. It is possible, but we feel unlikely, that the OH^- dependence derives from the formation of Cu(OH)$^+$ which might act as a nucleophile toward $EtOx^-$. A related mechanism has been postulated[17] for the hydrolysis of *p*-nitrophenyl acetate as catalyzed by the hydroxo glycylglycine complex of copper(II), Cu(glygly)(OH). Another possible mechanism is one involving the formation of Cu(EtOx)(OH) in which hydrolysis occurs by internal attack on the coordinated ester by the coordinated OH^- group. Good evidence for this mechanism has been found[18] in the ester hydrolysis of $NH_2CH_2CO_2R$ in $Co(en)_2(Br)(NH_2CH_2CO_2R)^{2+}$. This mechanism cannot be discounted in the present study, but previous studies[19] of the hydrolysis of amino acid ester derivatives as catalyzed by metal ions and using several nucleophiles supported a mechanism of type 6. For this reason we, at the moment, prefer mechanism 6, and for subsequent discussion will assume that this is the correct one.

The predicted rate for the hydrolysis according to mechanism 6 is

$$\text{rate} = k[MEtOx^+][OH^-] = kK_f[EtOx^-][M^{2+}][OH^-] \quad (7)$$

Comparing this equation with the experimental rate law 5 gives the equation

$$k_3 = kK_f \quad (8)$$

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If the stability constant K_f were known, it would be possible to obtain the rate constant k for OH^- attack on the ester in $M(EtOx)^+$. These rate constants could then be compared with the constant for OH^- attack on the free $EtOx^-$.

Toward this end log K_f for the interaction of Cu^{2+} with $EtOx^-$ was estimated (see above) by pH titration to be 2.06 at the ionic strength of the kinetic studies. Since most of the other metal ions with $EtOx^-$ were likely to give even lower values of K_f, they would be very difficult to measure experimentally. Hence they were estimated from known values[20] of K_f^{MOAc} for acetate coordination, $M^{2+} + OAc^- \rightleftharpoons M(OAc)^+$. It was assumed that stability constants for $EtOx^-$, K_f^{MEtOx}, were proportional to those for acetate, K_f^{MOAc}. Thus K_f^{MEtOx} values were calculated from ratios of the type $K_f^{MEtOx}/K_f^{CuEtOx} = K_f^{MOAc}/K_f^{CuOAc}$. The values of log K_f^{MOAc} used in the calculations were taken from the literature[20] and are given in Table IV. The estimated values of log K_f^{MEtOx} are also presented in the table. Rate constants, k (Table IV), for the OH^- attack step in mechanism 6 were calculated from the estimated values of K_f^{MEtOx} using eq 8.

Table IV. Estimated Kinetic Parameters Associated with k in Mechanism 6[a]

M^{2+}	Log K_f^{MOAc} [b]	Log K_f^{MEtOx}	$10^{-2}k$, M^{-1} sec^{-1}	ΔH^*	ΔS^*, eu
Cu^{2+}	1.8	2.1	1410	6.2	−14
Pb^{2+}	2.1	2.4	162	9.1	−8.7
Zn^{2+}	1.0	1.3	63	12.8	−1.9
Ni^{2+}	1.0	1.3	37	8.3	−14
Co^{2+}	0.9	1.2	29	9.3	−11
Mg^{2+}	0.37	0.63	0.30	10.3	−13
None			0.0069	7.1	−35

[a] At 25° and $\mu = 0.1$ (KNO_3). [b] Reference 20.

It can be seen that the rates of hydrolysis decrease with the metal ion in the order $Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} \gtrsim Co^{2+} > Mg^{2+}$. A similar order was observed[21] for the base-catalyzed hydrolysis of ethyl glycinate in the metal-ion complexes $M(NH_2CH_2CO_2Et)^{2+}$. Values of $10^{-4}k$ (M^{-1} sec^{-1}) decreased as follows: Cu^{2+} (7.64) > Zn^{2+} (2.33) > Co^{2+} (0.99) > Ni^{2+} (0.398). For ethyl glycinate, coordination of the ester to Cu^{2+} enhances the rate of base hydrolysis by a factor of 1.2×10^5 as compared to the non-metal-ion-catalyzed rate (0.635 M^{-1} sec^{-1}).[22] For $EtOx^-$, base hydrolysis of $EtOx^-$ occurs 2×10^5 faster when the ester is coordinated to Cu^{2+}. Thus for both esters, coordination to Cu^{2+} brings about essentially the same increase in rate of hydrolysis.

The rate constants, $10^{-2}k$ (M^{-1} sec^{-1}), for the hydrolysis of ethyl glycinate-*N,N*-diacetic acid in its complexes $M(O_2CCH_2)_2NCH_2CO_2Et$ follow a similar trend with the different metal ions: Pb^{2+} (283) > Cu^{2+} (218) > Zn^{2+} (66.2) > Co^{2+} (10.1) > Ni^{2+} (3.89) > Mg^{2+} (very slow).[23] While the effect of the metal ions is similar with all three esters, there are some differences. For example, for $NH_2CH_2CO_2Et$ and $M(O_2CCH_2)_2NCH_2CO_2Et$, $Co^{2+} > Ni^{2+}$, but for $EtOx^-$ the order is reversed, $Ni^{2+} > Co^{2+}$. The difference in rates between Ni^{2+} and Co^{2+}, however, is not large. A somewhat greater difference is observed in the relative catalytic activities of Pb^{2+} and Cu^{2+}. For $M(O_2CCH_2)_2NCH_2CO_2Et$, Pb^{2+} is better than Cu^{2+}, but the reverse is observed for $EtOx^-$. These differences, as well as the agreements, are very difficult to explain. In general, the better catalysts are those metal ions, such as Cu^{2+} and Pb^{2+}, which form the most stable complexes. A more quantitative correlation does not seem possible at this time. It should be noted, however, that the catalysis by the metal ions reported in this paper is several orders of magnitude larger than for Tl^+, Ba^{2+}, and $Co(NH_3)_6{}^{3+}$ which were studied previously.[24]

In an attempt to determine what factors influence the value of k, ΔH^* and ΔS^* have been estimated from the experimental enthalpies of activation, ΔH^*_3 (Table II). In terms of mechanism 6, ΔH^*_3 is the sum of ΔH for K_f and ΔH^* for k. Since it has been established that the enthalpy associated with coordination of a carboxylate donor ligand to Co^{2+}, Ni^{2+}, Zn^{2+}, and Cu^{2+} is near zero ($\pm \approx 1$ kcal/mol),[25] we have assumed that ΔH associated with K_f is zero. Therefore ΔH^* for the rate-determining step is equal to ΔH^*_3. These values are given in Table IV. Using these values of ΔH^* and the estimated k values (Table IV) at 25°, ΔS^* has been calculated from the transition state theory equation: $\Delta S^* = 2.3R \log k - 2.3R \log kT/h + \Delta H^*/T$. These estimated values of ΔS^* are also given in the table. It should be emphasized that the values of ΔH^* and ΔS^* are only estimates and may deviate from the correct values by perhaps ± 1.5 kcal/mol and ± 5 eu, respectively.

For comparison with the estimated rate parameters for OH^- attack on $MEtOx^+$, Table IV also records the directly measured results for OH^- attack on the free $EtOx^-$. As noted previously, the coordination of $EtOx^-$ to a metal ion greatly accelerates the rate of base hydrolysis of the ester. The effect of the metal ion is to make ΔS^* about 20 eu more positive, while leaving the ΔH^* unchanged or perhaps becoming slightly higher. Thus the catalytic effect of the metal ion results from an increased entropy of activation. This is not unexpected because the $MEtOx^+$ and OH^- ions are coming together in the rate-determining step to give a neutral and considerably less solvated activated complex. It had been noted previously[23] that the catalytic effect of the metal ion (Sm^{3+} or Lu^{3+}) in the base hydrolysis of $M(O_2CCH_2)_2NCH_2CO_2Et^+$ was caused by an increase in ΔS^* of approximately 20 eu; the ΔH^* was essentially unchanged by the metal ion. However, for 2+ metal ions (Cu^{2+}, Ni^{2+}, and Pb^{2+}) which gave neutral ester complexes, $M(O_2CCH_2)_2NCH_2CO_2Et$, the ΔS^* was unchanged and a decrease in ΔH^* was responsible for the catalytic effect of the metal ion.

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