$$k_{\text{obsd}} = \frac{k_{\text{in}}K(\text{Y}) + k'_{\text{in}}K'(\text{Y})K_{\text{h}}/(\text{H}^+)}{1 + K(\text{Y})} \qquad \text{(A31)}$$

It is obvious that the ratio of the slope to the intercept of $1/k_{\text{obsd}}$ *vs.* 1/(Y) plots for the ion-pair-interchange mechanism (inverse of eq A31) is constant and independent of the acidity. However, such a simplified plot is not possible for the five-coordinate-intermediate mechanism except under the unlikely circumstance that $k_3/k_2 = K$ and $k'_3/k'_2 = K'$, when eq A30 and A31 become mathematically identical.

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Metal Ion Catalysis of *S*-Ethyl Thiooxalate Hydrolysis

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Kinetic studies of the base hydrolysis of ethyl thiooxalate, $^-O_2CCOSEt$ ($EtSOx^-$), to give $C_2O_4^{2-}$ and EtSH have been carried out in the absence and presence of metal ions, M^{2+}. With Pb^{2+}, Ni^{2+}, and Mg^{2+}, the rate of ester hydrolysis follows the expression: rate = $k_3[EtSOx^-][M^{2+}][OH^-]$. As previously suggested for the metal ion catalyzed hydrolysis of the analogous ethyl oxalate ($EtOx^-$), the mechanism of the reaction is believed to involve rapid coordination of the ester by the metal ion followed by rate-determining OH^- attack on the ester. At 25° the values of k_3 (M^{-2} sec^{-1}) decrease with the metal ion as follows: Pb^{2+} (1.69×10^6) > Ni^{2+} (1.80×10^4) > Mg^{2+} (1.78×10^2). It was observed that each of these metal ions accelerated the rate of hydrolysis of both $EtOx^-$ and $EtSOx^-$ by essentially the same factor suggesting that the sulfur (or ether oxygen) is not coordinated to the metal ion in the M(ester)$^+$ species undergoing OH^- attack.

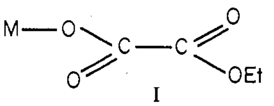
Introduction

In an earlier paper,[2] we discussed the metal ion catalyzed hydrolysis of ethyl oxalate, $^-O_2CCO_2Et$ ($EtOx^-$). The kinetic and equilibrium data for that reaction were interpreted in terms of the mechanism

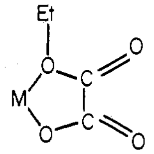
$$M^{2+} + EtOx^- \overset{K_f}{\rightleftarrows} MEtOx^+ \qquad (1)$$

$$MEtOx^+ + OH^- \xrightarrow{k} M(C_2O_4) + EtOH \qquad (2)$$

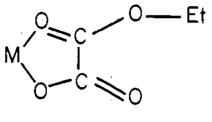
Initial coordination of the ester (eq 1) was rapid; this was followed by OH^- attack on the coordinated ester in the rate-determining step. An unresolved aspect of the reaction was the nature of $EtOx^-$ coordination to the metal in the $MEtOx^+$ intermediate. There were three possibilities



I



II



III

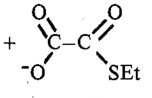
In all cases, electron withdrawal by the positive metal ion would be expected to facilitate OH^- attack at the ester carbonyl carbon atom, thereby enhancing the rate of hydrolysis.

Support for structure I derives from the known increase in rate on neutralizing the negative charge of the anionic carboxylate group. That is, base hydrolysis at 25° of one ester group in EtO_2CCO_2Et occurs at a rate (3960 M^{-1} sec^{-1} [3]) which is 5.8×10^3 times faster than that of $^-O_2CCO_2Et$ (0.687 M^{-1} sec^{-1} [2]). By comparison, when bound to Cu^{2+} as $Cu(EtOx)^+$, the ester hydrolyzed at a rate (1.4×10^5 M^{-1} sec^{-1} [2]) which was 2×10^5 times greater than that for free $EtOx^-$. This increased rate is not so large that it could not be accounted for by a charge effect in a structure such as I. The rates with other metal ions were even less than observed for Cu^{2+} and could even more readily be explained in terms of structure I.

Support of structure II comes from an X-ray investigation[4] of the ester complex $Cu[N(CH_2CO_2)_2CH(i\text{-}Pr)CO_2Et](H_2O)_2$, which shows weak coordination of the C–O–Et oxygen atom to the Cu(II). This suggests that complex II may be the active form of the ester during hydrolysis.

Acid-catalyzed hydrolyses of esters have long been believed[5] to proceed *via* an intermediate in which the carbonyl oxygen of the ester was protonated. In the same manner metal ions acting as Lewis acids might also be expected to coordinate at that oxygen as shown in structure III.

It should be emphasized that while structures II or III may be the active form for OH^- attack, the known weak coordinating ability of ester groups[6] suggests that the predominant form of $MEtOx^+$ in solution is structure I. The purpose of the present research was to establish the importance (or lack thereof) of structure II to $EtOx^-$ hydrolysis. We have therefore examined the metal ion catalyzed hydrolysis of the analogous thio ester *S*-ethyl thiooxalate ($EtSOx^-$)



$$M^{2+} + {}^-O(O)C\text{–}C(O)SEt + H_2O \rightarrow M(C_2O_4) + EtSH + H^+ \qquad (3)$$

If structure II is the form of the ester undergoing OH^- attack, its concentration should change markedly as the ether oxygen is replaced by sulfur; this would in turn affect the rate of hydrolysis correspondingly. On the other hand,

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[1] Fellow of the Alfred P. Sloan Foundation, 1970–1972.

[2] G. L. Johnson and R. J. Angelici, *J. Amer. Chem. Soc.*, 93, 1106 (1971).

[3] E. Tommila and H. Sternberg, *Suom. Kemistilehti B*, 19, 19 (1946); *Chem. Abstr.*, 41, 5369*i* (1947).

[4] R. A. Jacobson and J. Rodgers, cited by B. E. Leach and R. J. Angelici, *Inorg. Chem.*, 8, 907 (1969).

[5] M. L. Bender, *Chem. Rev.*, 60, 53 (1960).

[6] R. J. Angelici and B. E. Leach, *J. Amer. Chem. Soc.*, 90, 2499 (1968).

if structure II is not involved in the hydrolysis of these esters, one would expect to find that metal ions catalyze the hydrolysis of both $EtOx^-$ and $EtSOx^-$ to the same extent.

Experimental Section

Materials. Oxalyl chloride and ethanethiol were obtained from Aldrich Chemical Co. Potassium ethyl oxalate was that previously prepared and purified.[2] Reagent grade metal ion salts were used in the following forms: $Cu(NO_3)_2 \cdot 3H_2O$, $Pb(NO_3)_2$, $Zn(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $Hg(NO_3)_2 \cdot H_2O$. Except for $AgNO_3$ and KNO_3 which were weighed out directly, aqueous solutions of the metal ions were standardized by titration with EDTA, according to Schwarzenbach.[7] Carbonate-free NaOH was standardized against dried potassium acid phthalate to the phenolphthalein end point. Doubly distilled water was used in all solutions.

Preparation of Potassium *S*-Ethyl Thiooxalate (KEtSOx). Dithioethyl oxalate, $H_5C_2SCOCOSC_2H_5$, prepared[8] from oxalyl chloride and ethanethiol, was half-hydrolyzed as follows. Approximately 5.0 g (0.028 mol) of the dithio compound was dissolved in 50 ml of 50% by volume aqueous *tert*-butyl alcohol. An equal volume of the mixed solvent, containing 1.81 g (0.028 mol) of KOH, was added drop by drop, with constant stirring, to the dithio solution within approximately 15 min. The solvent was immediately evaporated by means of a rotary evaporator, and the remaining white solid was dried under vacuum and kept in a desiccator. *Anal.* Calcd for $KO_2CCOSC_2H_5$: C, 27.89; H, 2.92; S, 18.61. Found: C, 27.58; H, 2.80; S, 18.36. A weighed amount of the product was also hydrolyzed with concentrated NaOH, and the excess base was titrated with standard HNO_3, using phenolphthalein indicator. This method indicated a purity of better than 99% for the ester. A test of KEtSOx for oxalate ion ($CaCl_2$ in acetic acid–acetate solution[9]) was negative. The proton nmr spectrum of the compound in D_2O, using $(CH_3)_3SiCH_2CH_2CH_2SO_3Na$ as reference, showed a single ethyl group, a quartet at τ 7.10 ($J = 7.5$ Hz), and a triplet at τ 8.80 ($J = 7.5$ Hz), integrating in a 2:3 ratio. The corresponding resonances for the oxygen analog, KEtOx, occurred at τ 5.75 ($J = 4.5$ Hz) and τ 8.70. The pK_a of HEtSOx at 25° and ionic strength of 0.40 (KNO_3) was 1.73, as determined by a previously reported method.[2]

Kinetic Measurements. Rates of ester hydrolysis were determined with a Radiometer TTT1c|SBR2|SBU1|TTTA31 pH meter, recorder, syringe buret, and microtitration assembly, respectively. The titrator was set for pH-Stat work, and the pH was maintained at a preset value by addition of 0.020 *M* NaOH. The recorder plotted the amount of NaOH added as a percentage of the total buret capacity *vs.* time. The buret was calibrated by weighing the water delivered when the buret was manually operated. The pH meter was calibrated in terms of hydrogen ion concentration, pH_c, by titrating a solution of 0.0100 *M* HCl and 0.100 *M* KNO_3.[10] The hydrogen ion concentration was calculated assuming complete dissociation of HCl. Calibration at high pH readings was made using the added hydroxide ion concentration and $K_w = 1.615 \times 10^{-14}$ calculated from data for 0.10 *M* KBr.[11]

All reactions were carried out in a double-walled vessel of 15-ml capacity using Radiometer glass (G2222C) and fiber junction calomel (K4112) extension electrodes. The solutions were maintained at the desired temperature (±0.05°) by circulation of thermostated water through the outer jacket of the reaction vessel. In each kinetic experiment, the appropriate amounts of metal ion, KNO_3, and water were pipetted into the reaction vessel, prepurified nitrogen which had been passed through concentrated aqueous NaOH was bubbled into the solution, and the solution was allowed to reach temperature equilibrium (15–20 min). By manual operation of the buret, NaOH was added to bring the solution to the desired pH. An appropriate amount of KEtSOx solution, prepared immediately before each reaction, was then pipetted into the vessel to begin the reaction. The initial concentration of KEtSOx was 9×10^{-4} *M* in most reactions. Metal ion concentrations varied from 1.6×10^{-2} to 4.1×10^{-3} *M*. Ionic strength was maintained at 0.100 *M* with KNO_3.

If the reaction was allowed to proceed for many half-lives, the amount of NaOH consumed was almost always greater than that calculated from eq 3, presumably due to the formation of metal–hydroxide complexes. Therefore, the method of Guggenheim[12] was used to determine pseudo-first-order rate constants, k_{obsd}. Plots of log $(\%_t - \%_{t+\Delta t})$ *vs.* time, where Δt is a constant increment of time which was estimated to be greater than 2 half-lives for each reaction, were linear. Slopes of the resulting lines gave k_{obsd}.

Only in one instance, Pb^{2+}-catalyzed hydrolysis, did the reaction give an actual end point which agreed with the theoretical end point. For this reaction, plots made with either log $(\%_{end} - \%_t)$ *vs.* time or the Guggenheim method gave the same value of k_{obsd}.

Kinetic Measurements in Carbonate-Bicarbonate Buffer Solutions. Since the hydrolysis of $EtSOx^-$ was carried out at pH values above 9.5 where the product EtSH is partially ionized to EtS^- and N_2 bubbling through the solution removed some EtSH, the rate of this reaction could not be measured readily by the pH-Stat method. Instead it was carried out in buffered solutions made up of varying amounts of 0.10 *M* Na_2CO_3 and 0.10 *M* $NaHCO_3$. Delory and King[13] have tabulated pH values for these carbonate–bicarbonate mixtures at 20 and 37°.

The same thermostated Radiometer vessel as described above (without electrodes) was used to contain the reaction. It was begun by pipetting a freshly prepared KEtSOx solution into the thermostated buffer solution (giving a 9×10^{-4} *M* $EtSOx^-$ solution) maintained at an ionic strength of 0.28 *M* with KCl (KCl was used because of ultraviolet absorption of KNO_3 at 270 nm; the value 0.28 *M* was the lowest ionic strength obtainable from the Na_2CO_3 and $NaHCO_3$ concentrations in the reaction solutions).

At various time intervals, 0.5-ml samples were syringed from the reaction solution and transferred to a 5-ml volumetric flask containing a few drops of 0.002 *M* HNO_3, and the solution was diluted with water to the mark. The acid lowered the pH of the solution to approximately 7, which effectively stopped the hydrolysis. The diluted solution was mixed well, and its absorptions at 270 and 280 nm were read on a Beckman DB-G spectrophotometer. Eight to ten samples were taken during each run. At the wavelength used, $EtSOx^-$ was the only absorbing species, and its absorption obeyed Beer's law.

Plots of log $(A - A_\infty)$ *vs.* time (where *A* is absorption at any time *t* and A_∞ is the absorption at infinite time) were linear, and pseudo-first-order rate constants were calculated from the slopes of these lines. A_∞ was 0.0 absorption unit at 270 nm and 0.01 absorption unit at 280 nm. To test for possible buffer catalysis, the reactions were also run at half the buffer concentration. The rates were unchanged, indicating that the buffer was not involved in the hydrolysis.

Two metal ion catalyzed hydrolyses were also followed by ultraviolet spectroscopy. The reaction solutions were made up in the same concentrations as those used in the pH-Stat method, and the pH-Stat unit was used to keep the pH of the reaction constant. The sampling technique was the same as described for the uncatalyzed hydrolysis. The metal ions studied, Pb^{2+} and Mg^{2+}, did not absorb in the 270–280-nm range. Slopes of log $(A - A_\infty)$ *vs.* time plots gave k_{obsd} values which were within experimental error of those obtained using the pH-Stat method.

Results

Non Metal Ion Catalyzed Hydrolysis of $EtSOx^-$. The values of k_{obsd} recorded in Table I indicate that the hydrolysis of $EtSOx^-$ in the absence of metal ions proceeds according to the rate law

$$\text{rate} = k_2[EtSOx^-][OH^-] \tag{4}$$

where $k_{obsd} = k_2[OH^-]$. To evaluate k_2, it was necessary to calculate $[OH^-]$ from pH_c and the expression $K_w = [H^+][OH^-]$. Standard tabulated values of pK_w at 0.28 *M* ionic strength were used:[11] 14.10 (20°), 13.94 (25°), 13.63 (37°). The values of k_2 at 0.28 *M* ionic strength are 0.365 (20°) and 1.10 M^{-1} sec^{-1} (37°).

For comparison with rate constants of the metal ion catalyzed hydrolyses, the k_2 value at 0.28 *M* ionic strength was converted to that at 0.10 *M* by adjusting the activity coefficients with the equation[14]

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(7) G. Schwarzenbach, "Complexometric Titrations," translated and revised by H. Irving, Interscience, New York, N. Y., 1957.

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(11) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd ed, Reinhold, New York, N. Y., 1958, pp 635, 752.

(12) E. A. Guggenheim, *Phil. Mag.*, 2 [7], 538 (1926).

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$$\ln k = \ln k_0 + 2Z_AZ_B\alpha\sqrt{\mu}$$

where μ is the ionic strength, α is the constant 1.17, Z_A and Z_B are the charges on the $EtSOx^-$ and OH^- ions, and k_0 is the rate constant at infinite dilution. The average values of k_2 at 0.10 M ionic strength were calculated to be 0.22 M^{-1} sec^{-1} at 20° and 0.65 M^{-1} sec^{-1} at 37°. From these constants the enthalpy, ΔH^*, and entropy, ΔS^*, of activation at 25° were evaluated as 9.9 ± 1.1 kcal/mol and −9.8 ± 3.6 eu, respectively, where the error limits are average deviations.

Metal Ion Catalyzed Hydrolysis of $EtSOx^-$. Catalysis by Pb^{2+}, Ni^{2+}, Mg^{2+}. The rate of $EtSOx^-$ hydrolysis in the presence of Pb^{2+}, Ni^{2+}, and Mg^{2+} follows the rate law

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

where $k_{obsd} = k_3[M^{2+}][OH^-]$. Values of k_{obsd} for these hydrolyses are presented in Table I; from k_{obsd}, pH_c, and $[M^{2+}]$, values of k_3 have been calculated and are included in Table II. The $[OH^-]$ was calculated from pH_c and literature values[11,15] of pK_w at the desired temperatures and 0.10 M ionic strength. Attempts to measure the rates at higher concentrations of metal ion (Pb^{2+} or Ni^{2+}) or $[OH^-]$ were thwarted by precipitation of the metal hydroxides. Enthalpies and entropies of activation at 25° were calculated for the reactions involving Pb^{2+} and Mg^{2+}; these values are given also in Table II.

Catalysis by Co^{2+}. Kinetic data for $EtSOx^-$ hydrolysis in the presence of Co^{2+} are shown in Table III. In contrast to the rate law found for Pb^{2+}, Ni^{2+}, and Mg^{2+}, this reaction follows the expression: rate = $k_{Co}[EtSOx^-][Co^{2+}]$, where $k_{Co} = 9.05 \times 10^{-3}$ M^{-1} sec^{-1}. The lack of dependence on $[OH^-]$ is unexpected in view of the behavior of the other metal ions in the $EtSOx^-$ hydrolysis and also the Co^{2+}-catalyzed hydrolysis of the oxygen analog $EtOx^-$ for which a first-order OH^- dependence was noted.[2]

Catalysis by Cu^{2+}, Ag^+, and Cd^{2+}. Additional complications were encountered with these metal ions. The reaction with Cu^{2+} was studied at an ionic strength of 0.10 M over a pH_c range of 4.91-5.56, a $[Cu^{2+}]$ range of 4.2×10^{-3} to 16.7×10^{-3} M, and $[EtSOx^-] = 9.00 \times 10^{-4}$ M at 25°. The rate data fit the equation: rate = $k_{Cu}[Cu^{2+}]^{0.57} \cdot [OH^-]^{0.43}[EtSOx^-]$, where $k_{Cu} = 49$ M^{-1} sec^{-1}. This reaction was complicated by precipitate formation presumably due to Cu^{2+} oxidation of the product EtSH, which is known to occur under these conditions.[16]

Similar difficulties were encountered in the reaction with Ag^+. In this case the rate was found to follow the expression: rate = $k_{Ag}[Ag^+]^{2.56}[OH^-][EtSOx^-]$ where $k_{Ag} = 2.4 \times 10^8$ $M^{-3.56}$ sec^{-1}. This was determined from data obtained over the pH_c range of 7.24-7.65 and Ag^+ concentrations of 4.0×10^{-3} to 8.0×10^{-3} M; other conditions were the same as for Cu^{2+}. Precipitation also occurred during this reaction presumably due to the formation of AgSEt.

The rate of $EtSOx^-$ hydrolysis in the presence of Cd^{2+} was studied over the 7.26-7.64 pH_c range with $[EtSOx^-] = 9.0 \times 10^{-4}$ M and $[Cd^{2+}] = 4.6 \times 10^{-3}$ to 18×10^{-3} M. Under these conditions the reaction was first order in $EtSOx^-$ and $[OH^-]$ but was independent of $[Cd^{2+}]$, suggesting that the $EtSOx^-$ was completely coordinated to the Cd^{2+} in the range of Cd^{2+} concentrations used. Unfortunately when both $[EtSOx^-]$ and $[Cd^{2+}]$ were reduced 10-fold, the k_{obsd} values were also reduced 10-fold but were still independent of $[Cd^{2+}]$. Because of the inconsistency of these results at the two different concentration levels, the reaction was not pursued further.

Table I. Rates of Hydrolyses of *S*-Ethyl Thiooxalate[a]

pH_c	$10^3[M^{2+}]$, M	Temp, °C	10^4k_{obsd},[b] sec^{-1}
	No Metal Ion		
10.28		20.0	0.691
10.53		20.0	1.41
9.50		37.0	1.29
9.90		37.0	4.32
10.28		37.0	7.55
10.57		37.0	13.9
	Pb^{2+}		
5.40	8.21	25.0	0.607
5.73	8.21	25.0	1.21
5.92	8.21	25.0	1.77
5.73	16.42	25.0	2.55
5.73	4.10	25.0	0.577
5.73	8.21	30.0	2.04
5.73	8.21	35.0	4.43
5.73	8.21	40.0	8.77
	Mg^{2+}		
9.02	8.22	25.0	0.248
9.53	8.22	25.0	0.706
10.04	8.22	25.0	2.65
9.02	16.44	25.0	0.520
9.53	4.11	25.0	0.346
9.02	8.22	30.0	0.431
9.02	8.22	35.0	0.718
9.02	8.22	40.0	1.26
	Ni^{2+}		
7.47	8.24	25.0	0.658
7.68	8.24	25.0	1.11
7.89	8.24	25.0	2.15
7.68	16.48	25.0	2.54
7.89	4.12	25.0	0.815

[a] $[EtSOx^-] = 9.00 \times 10^{-4}$ M; $\mu = 0.10$ M (KNO_3). Ionic strength was 0.28 (KCl) in reactions containing no metal ion. [b] Average deviations for the k_{obsd} values were ±10% or less.

Table II. Rate Constants, k_3, and Activation Parameters for Metal Ion Catalyzed Hydrolyses of $EtSOx^-$ by Pb^{2+}, Mg^{2+}, and Ni^{2+}

M^{2+}	Temp, °C	k_3, M^{-2} sec^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
Pb^{2+}	25.0	1.69×10^6	10.7 ± 0.1[a]	−5.6 ± 0.4[a]
	30.0	1.97×10^6		
	35.0	2.98×10^6		
	40.0	4.25×10^6		
Ni^{2+}	25.0	1.80×10^4		
Mg^{2+}	25.0	1.78×10^2	6.3 ± 0.1[a]	−23.7 ± 0.4[a]
	30.0	2.13×10^2		
	35.0	2.45×10^2		
	40.0	3.12×10^2		

[a] Error limits are average deviations.

Table III. Co^{2+}-Catalyzed Hydrolysis of $EtSOx^-$ at 25°

pH_c	$10^3[Co^{2+}]$,[a] M	10^4k_{obsd}, sec^{-1}	pH_c	$10^3[Co^{2+}]$,[a] M	10^4k_{obsd}, sec^{-1}
7.57	8.24	0.729	7.79	16.5	1.41
7.79	4.12	0.420	7.98	8.24	0.737
7.79	8.24	0.736			

[a] $[EtSOx^-] = 9.00 \times 10^{-4}$ M; $\mu = 0.10$ (KNO_3).

Discussion

Non Metal Ion Catalyzed Hydrolysis. Like the base-catalyzed hydrolysis of its oxygen analog $(EtOx^-)^2$, the hydrolysis of $EtSOx^-$ followed a rate law (eq 4) which showed first-

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(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N. Y., 1961, p 150.

(15) R. A. Robinson and R. H. Stokes, "Electrolytic Solutions," Academic Press, New York, N. Y., 1955, p 506.

(16) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. 1, Chemical Publishing Co., New York, N. Y., 1958, p 145.

order dependence on both ester and OH^- concentrations. Such a rate law is generally interpreted in terms of rate-determining OH^- attack at the carbonyl carbon atom followed by rapid removal of EtOH. As commonly found[17] for analogous oxygen and thiol esters, the rate constants (k_2) for base hydrolysis of $EtOx^-$ (0.687 M^{-1} sec^{-1}) and $EtSOx^-$ (0.299 M^{-1} sec^{-1}, interpolated from data in the Results) at 25° are very similar. Despite the similarity of their rates at 25°, the activation parameters (25°) for $EtOx^-$ ($\Delta H^* = 7.1$ kcal/mol, $\Delta S^* = -35$ eu) and $EtSOx^-$ ($\Delta H^* = 9.9$ kcal/mol, $\Delta S^* = -9.8$ eu) do differ substantially.

Metal Ion Catalyzed Hydrolysis. For the three metal ions Pb^{2+}, Ni^{2+}, and Mg^{2+}, the rates of $EtSOx^-$ hydrolysis (eq 3) followed a rate law (eq 5) which showed first-order dependences on the concentrations of $EtSOx^-$, metal ion, and OH^-. This was the same expression found[2] for the metal ion catalyzed hydrolyses of $EtOx^-$. Like the $EtOx^-$ hydrolysis, the logical mechanism for the catalyzed hydrolysis of $EtSOx^-$ is initial coordination of the ester substrate to the metal ion followed by rate-determining OH^- attack at the ester carbon, as given in eq 1 and 2. In terms of this mechanism, the experimental $k_3 = K_f k$.

As noted in the Introduction, the predominant coordinated form of the ester is most probably that shown in structure I but structure II or III could be the reactive form undergoing OH^- attack. If II is the reactive form, replacement of the ether oxygen by sulfur should markedly change the amount of reactive form in solution and therefore alter the overall rate of hydrolysis of the ester. As has been pointed out[18] in discussions of the "hard" and "soft" nature of metal ions and donor atoms, equilibrium constants for the coordination of O and S donors may differ by several orders of magnitude depending on the metal ion. Thus if structure II is of major importance in the catalysis by metal ions, it would be anticipated that the rates of metal ion catalyzed hydrolyses of $EtOx^-$ and $EtSOx^-$ would also differ by similar large factors. Moreover, relatively soft metal ions (*e.g.*, Pb^{2+} [19]) should promote the hydrolysis of the sulfur ester over that of $EtOx^-$, whereas hard metal ions (*e.g.*, Mg^{2+}) should promote the oxygen analog.

In comparing relative rates of the metal ion catalyzed hydrolyses, of $EtOx^-$ and $EtSOx^-$, we have determined the catalytic effect of each metal ion on the esters by dividing the metal ion catalyzed rate constants by the non metal ion catalyzed constants (*i.e.*, k_3/k_2 from eq 4 and 5). These ratios are given in Table IV.

Table IV. Relative Catalytic Effects of Metal Ions on the Hydrolysis of $EtOx^-$ and $EtSOx^-$ at 25°

$EtOx^-$		$EtSOx^-$	
M^{2+}	$k_3/k_2, M^{-1}$	M^{2+}	$k_3/k_2, M^{-1}$
Pb^{2+}	5.8×10^6	Pb^{2+}	5.4×10^6
Ni^{2+}	6.3×10^4	Ni^{2+}	9.9×10^4
Mg^{2+}	5.9×10^2	Mg^{2+}	14.8×10^2

If it is assumed that K_f (eq 1) is the same for $EtOx^-$ and $EtSOx^-$ with any given metal ion, then variations in the ratio k_3/k_2 must be due to either a chelation equilibrium such as structure I going to II or III or it may be due to a different rate of OH^- attack on the esters in the metal complex. The assumed constancy of K_f for $EtOx^-$ and $EtSOx^-$ is reasonable in that both ligands have the same pK_a values (1.73) and would presumably also bind metal ions with very similar K_f values.[20]

The k_3/k_2 ratios for any given metal ion are remarkably similar for $EtOx^-$ and $EtSOx^-$ and do not differ by more than a factor of 3 for any of the metal ions. That is, the replacement of the ether oxygen in $EtOx^-$ by sulfur hardly changes the catalytic effect of the metal ion. This strongly suggests that structure II is *not* the active form undergoing OH^- attack. This leaves structures I or III as possible reactive intermediates. Although the present study does not aid in distinguishing these possibilities, arguments in the Introduction suggest that structure I may be slightly more probable.

Registry No. *S*-Ethyl thiooxalate, 37549-02-3; lead, 7439-92-1; magnesium, 7439-95-4; nickel, 7440-02-0; cobalt, 7440-48-4; copper, 7440-50-8; silver, 7440-22-4; cadmium, 7440-43-9.

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