

quantum yield at about 4.2 eV.²⁹ Case A predicts two such transitions to the 5b₂ orbital, one at 3.5 eV and the other at 4.3 eV. Thus it is quite possible that it is these transitions to the 5b₂ orbital which weaken the Pt-ethylene bond and allow the aquation to take place. For case B, only one transition in this region is predicted, at 4.2 eV.

In summary, we believe that these results have provided not only new insight regarding the bonding in Zeise's anion but also a reasonable description of the optical spectrum and certain features of the photochemistry. Thus we are encouraged that the SCF-X α -SW method will provide useful information about other complex systems in the future.

Zinc(II) Catalysis of Oxalacetate Enolization and Decarboxylation

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Abstract: Detailed studies are reported for the Zn(II) catalyzed decarboxylation of oxalacetate. Two relaxations were observed, an initial absorbance increase being complete in about 30 sec and a subsequent absorbance decrease being complete after 15–30 min. Observation of these absorbance changes as functions of total metal ion, total acetate buffer, and hydrogen ion concentrations led to identification and characterization of the processes and of participant species. Use of high speed computational techniques allowed resolution of observed relaxation times into microscopic rate constants and definition of a number of formation constants for participant Zn(II)-oxalacetate complexes. The first relaxation arises from metal ion promoted keto-enol tautomerization and the second from catalyzed decarboxylation. The subsequent protonation of zinc pyruvate enolate product is rapid and unobservable.

Decarboxylation of β -keto acids is an important metabolic process in many biological systems. It is catalyzed by certain classes of enzymes that have a metal ion requirement and by metal ions alone, albeit at slower rates. Similarities in the enzymatic and chemical processes have stimulated interest in the single metal ion catalyzed reactions as models for the enzymatic systems.^{2–8} This interest has been focused mainly on the decarboxylation of oxalacetic acid (H₂oxac) and its derivatives.^{9–28}

When metal ion and oxalacetate solutions are mixed, an absorbance increase occurs which achieves a maximum value in a few seconds. It is followed by a slower absorbance decrease over a period of minutes. Steinberger and Westheimer⁹ observed similar behavior in the Cu(II) and Fe(III) catalyzed reactions of α,α -dimethyl oxalacetate, which can exist only in the keto form. These workers proposed the highly absorbing complexed pyruvate enolate, whose formation would give rise to the absorbance increase, as an intermediate.

(1) Support of this research by a grant from the National Science Foundation is gratefully acknowledged.

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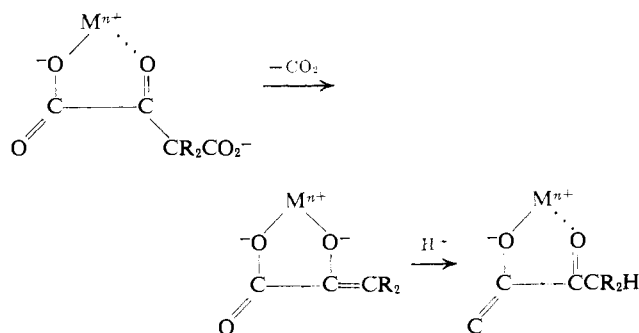
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Interpretation of the similar absorbance changes in the oxac systems is not as straightforward because oxac itself can exist in either keto or enol forms.

Gelles and Hay¹⁷ showed that the zero time ab-

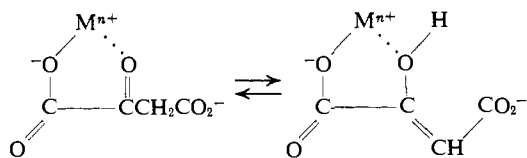
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sorbance of Cu(II) and Zn(II) oxac²⁻ solutions, as obtained from the extrapolation of the response of a conventional spectrophotometer, indicates formation of oxac enol complexes in proportions greater than that of uncomplexed oxac. They concluded that these reactions are fast and that the absorbance increase arises from the formation of intermediate pyruvate enolate. Bamann and Sethi,²⁴ on the other hand, report that the intensity of the absorption maximum varies with the nature of the metal ion and conclude that this first change arises from metal ion promoted enolization of oxac. This evidence does not rule out pyruvate enolate formation, however, because the maximum concentration of an intermediate formed in a two-step process depends on the relative rates of the two steps. In this case, these rates are most likely to be metal ion dependent. Leong and Leussing²⁹ found evidence that appreciable amounts of a pyruvate enolate complex are formed in the Cu(II) catalyzed decarboxylation of oxac. A tentative rate law for the ketonization of this intermediate was proposed. Evidence that the intermediate reacts with free pyruvate to form pyruvate dimer was also presented.

Another aspect of metal ion catalyzed decarboxylation reactions requires clarification. In a series of reactions studied at varying pH, it is typically observed that the pH-rate profile exhibits a maximum. The decrease in rate at higher pH values has been attributed to the formation of a seven-membered chelate ring,³⁰ a dinuclear complex, M₂oxac²⁺,^{17,18} a 1:1 enolate complex, MH₋₁oxac⁻,³¹ and metal hydroxide.^{24,25}

With the hope of elucidating these points, we have undertaken studies of these reactions using stopped flow techniques and modern computational methods in data analysis.^{29,32}

Experimental Section

Sample Preparation. Stock solutions were prepared from chemicals and solvent obtained from commercial sources. Oxalacetic acid, purchased from Nutritional Biochemicals Corp., Cleveland, Ohio, was determined by titration to be 97.7% pure. It was stored under refrigeration and used without further purification. Zinc chloride solutions were made by dissolving Zn metal granules in a minimal amount of concentrated hydrochloric acid. The Zn(II) content was determined by the method of Schwarzenbach and Flashka.³³ Dilute acetic acid, sodium hydroxide, and potassium chloride solutions were prepared in the usual manner. All stock solutions were stored in polyethylene bottles. Doubly distilled, deionized water served as solvent after deaeration by boiling. Solid materials were usually weighed out by difference on a Satorius analytical balance, Type 2433.

Two sample solutions were freshly prepared for each experimental run by buret delivery of appropriate amounts of stock solutions into two 100-ml volumetric flasks. The one contained zinc ion and

the other oxalacetic acid. Both were similarly buffered by addition of acetic acid and sodium hydroxide solutions. The ionic strength was held at 0.1 M, where possible, by addition of suitable amounts of aqueous KCl. Total concentrations of reactants in the final reaction mixtures were in the ranges 1–20 × 10⁻³ M for Zn(II), 1–20 × 10⁻² M for acetate, and 1–10 × 10⁻⁴ M for oxalacetate. pH determinations of representative reaction mixtures were made with a Radiometer (Copenhagen) pH Meter 25. Experiments were performed in the range pH 3–5 at 25.0°.

Instrumentation. The first relaxation (keto ⇌ enol, see below) was studied with a Durrum-Gibson stopped-flow apparatus interfaced with a Nova minicomputer for data acquisition, storage, and evaluation. The relaxation was complete in about 30 sec.

The second relaxation (decarboxylation) was studied with a Cary-14 recording spectrophotometer. The relaxation was complete in about 30 min. Equal volumes (usually 7 ml) of each reactant solution were bureted into a small beaker, mixed by swirling, and transferred into a cylindrical, 1-cm Teflon-stoppered quartz cuvette. Sample temperature was maintained at 25° by a constant flow of thermostated water through a close-fitting brass cuvette holder block mounted in the Cary-14 sample cell compartment.

Carbon dioxide evolution was followed in a sealed system connected to a Texas Instrument Precision Pressure Gage, Model 145-01, the output of which was continuously monitored with a Hewlett-Packard 7101BM strip recorder. These experiments were run at ambient temperature (~23°).

The spectrophotometric reactions were quantitatively followed by the observation of absorbance changes in the 280–315-nm region of the visible spectrum. In these reaction systems this wavelength region corresponds to the region of enol absorbance. The absorbance was monitored until its rate of change became zero, *i.e.*, until $t \rightarrow t_{\infty}$ for each reaction, where $t =$ time.

Apparent relaxation times, τ , were extracted from the experimental data with a program FITFC that obtains the optimum values of τ , A_{∞} , and A_1 that give the best least-squares fit to the equation

$$A_t = A_1 e^{-t/\tau} + A_{\infty}$$

where A_t is the measured absorbance at time, t , and A_{∞} is the absorbance at long times, t_{∞} . In the stopped flow experiments about 200 absorbance points were logged in each run, and six-ten replicate runs were made. The calculated values of χ^2 were consistent with the estimated errors in the absorbance measurement. This "goodness of fit" was taken to signify that no other resolvable relaxation exists in the time range covered. On the Cary experiments, the absorbance was known with greater precision, and a fewer number of absorbance points, 100–200, were employed.

The relaxation time concentration data were analyzed with an improved version of the computer routine CORNEK.³⁴ This new version included the subroutine GENDIS for calculation of the general distribution of species concentrations and the Marquardt CURFIT subroutine³⁵ to obtain optimum values of rate constants and complex formation constants pertaining to trial reaction models. Provision was also made for fitting the rate constants at constant or at variable ionic strength because in some of the reactions high Zn(II) concentrations caused the ionic strength to be greater than 0.1. This correction was made using the Davies equation

$$-\log f = 0.5z^2 [I^{1/2} / (1 + I^{1/2}) - 0.2I]$$

Results

The two relaxation times which are observed when Zn(II) and oxac²⁻ solutions are mixed are illustrated in Figure 1. The faster process, for which the relaxation time is designated as τ_1 , is shown in the inset, and the slower process, which gives τ_2 , is shown in the main body of the diagram. As is evident from this figure the values of τ_1 and τ_2 are sufficiently far apart so that the processes giving rise to these changes can be treated separately; *i.e.*, in analyzing the τ_1 data, the slower reactions can be ignored, while in analyzing the τ_2 data the faster reactions can be safely assumed to have come to equilibrium.

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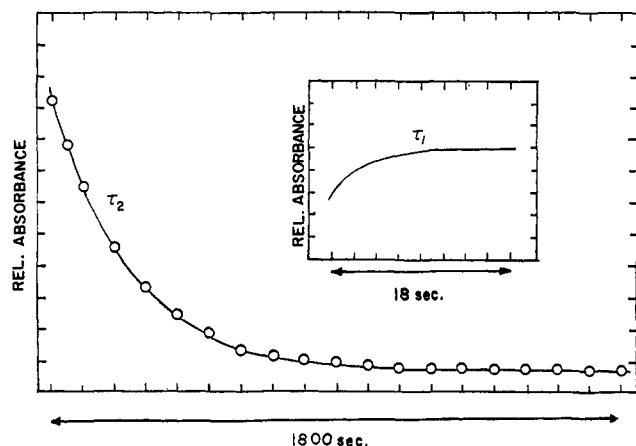


Figure 1. Relative absorbance vs. time: $1.5 \times 10^{-2} M [Zn^{2+}]_{TOT}$, $3.0 \times 10^{-4} M [oxac^{2-}]_{TOT}$, $9.4 \times 10^{-2} M [OAc^-]_{TOT}$, pH 4.95, 25° , $I = 0.1$, λ 280 nm; inset, stopped flow trace, 1 unit of ordinate = 0.13 absorbance; main, spectrophotometer trace, 1 unit of ordinate = 0.10 absorbance.

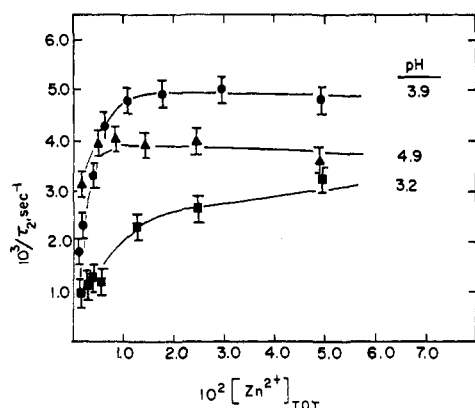


Figure 2. Reciprocal of observed decarboxylation relaxation time vs. total zinc(II) concentration. At various pH, 25° , $I \sim 0.1$. Solid line is theoretical line.

While only two relaxations were observed in these experiments, several processes which must be considered are present. Protonation reactions of the $oxac^{2-}$ carboxylate groups are fast and can be considered to be in rapid preequilibrium with the rate determining step, as can also be the Zn(II) complexation reactions of $oxac^{2-}$. Another process involves hydration–dehydration of oxalacetate which has been shown to be partially hydrated in solution.³⁶ Relaxation times computed from reported hydration–dehydration rate constants are of the order of 0.1 sec in the absence of complexing metal ions. Attempts to observe relaxation arising from these processes under our experimental conditions failed either because of a low amplitude and/or because these rates were appreciably accelerated by Zn(II). This latter possibility is highly likely owing to the reported catalytic effect of Zn(II) on pyruvate hydration–dehydration rates.³⁷

Other reactions which are present and must be considered are keto–enol transformation and decarboxylation and ketonization of the pyruvate enolate. Two series of experiments indicated that this last reaction is fast and need not be considered in the rate limiting pro-

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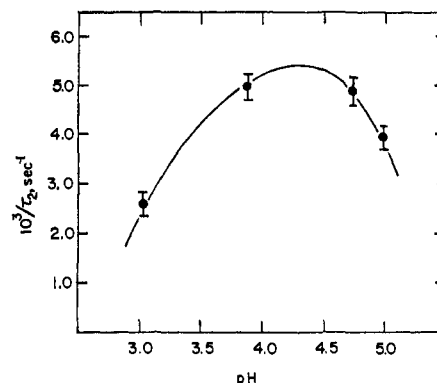
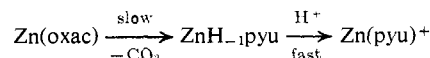


Figure 3. Reciprocal of observed decarboxylation relaxation time vs. pH: $3 \times 10^{-2} M [Zn^{2+}]_{TOT}$, $0.1 M [OAc^-]_{TOT}$, 25° . Solid line is theoretical line.

cess. The rate constant for CO_2 evolution from Zn(II)– $oxac^{2-}$ solutions was found to be identical within the experimental uncertainties to $1/\tau_2$ as measured from the slower absorbance changes, and it was not found possible to trap intermediate $ZnH_{-1}pyu$ with added pyruvate to form pyruvate dimer. Indeed, the rate of Zn(II) catalyzed pyruvate dimerization was found to be unaffected by the presence of oxac. Further, support that ketonization of the zinc(II) pyruvate enolate is fast comes from the fact that τ_2 did not show the pH dependence found by Leong and Leussing for the ketonization of $CuH_{-1}pyu$.²⁹ These results show that the rate of protonation of $ZnH_{-1}pyu$ is fast compared to the rate of breaking of the $oxac^{2-}$ carbon–carbon bond.



Since the slower of the absorbance changes was found to be associated with CO_2 loss, the faster was assigned to ketonization–enolization processes. As described below, it was found possible to provide an interpretation of the data which is consistent with both this assignment and earlier results reported by Banks from studies of the rates of oxac ketonization in the absence of metal ions at 1.5° .³⁸

In fitting a reaction model to the decarboxylation rates, it is convenient to follow the precedent set by earlier workers and to consider only the macroscopic reactions by ignoring the keto–enol reactions. In the case of Zn(II) this is acceptable owing to the large difference that exists between decarboxylation and tautomerization rates.

Those results that can conveniently be represented on a two-dimensional plot are shown in Figure 2 where $1/\tau_2$, the reciprocal of the observed decarboxylation relaxation time, is plotted vs. the total Zn(II) concentration for various values of pH. The pH–rate profile is shown in Figure 3. It is seen in Figure 2 that at low Zn(II) concentration levels in all buffers the decarboxylation rate increases with an increasing concentration of Zn(II), and at pH 3.9 and 4.9 a limiting rate is attained at higher levels of Zn(II). Qualitatively, this behavior is consistent with a model in which an easily dissociated kinetically active $Zn(oxac)$ complex is formed. Competition between protons and Zn(II) accounts for the shape of the curve in the low pH region

(38) B. E. C. Banks, *J. Chem. Soc.*, 63 (1962).

Table II. Microscopic Rate and Equilibrium Constants for the Keto and Enol Forms of Oxac, 25°, *I* = 0.1

Reaction path	$(k_f + k_b),$ $M^{-1} \text{ sec}^{-1}$	K_{eq}	$k_f, M^{-1} \text{ sec}^{-1}$	$k_b, M^{-1} \text{ sec}^{-1}$	$K_{eq} = [\text{enol}]/$ $[\text{keto}]$	Ref
$\text{oxac}_k^{2-} + \text{H}^+$	1.16×10^3	0.18	1.8×10^2	9.8×10^2	38 (1.5°)	
$\text{oxac}_k^{2-} + \text{HOAc}$	1.12×10^4	0.164 ^a	$(1.59 \pm 0.03)10^3$	$(9.70 \pm 0.18)10^3$	This work (25°)	
	1.44	0.18	0.22	1.22	38 (1.5°)	
	8.39	0.164 ^a	(1.18 ± 0.05)	(7.20 ± 0.30)	This work (25°)	
$\text{oxac}_k^{2-} + \text{OAc}^-$	0.043	0.18	0.0066	0.036	38 (1.5°)	
$\text{Zn}(\text{oxac})_k + \text{H}^+$ ^b	$(7.60 \pm 0.52)10^2$	≥ 9	6.84×10^2	$\leq 7.6 \times 10$	This work (25°)	
$\text{Zn}(\text{oxac})_k + \text{HOAc}^b$	(3.97 ± 0.49)	≥ 9	3.54	≤ 0.40	This work (25°)	
$\text{Zn}(\text{oxac})_k + \text{OAc}^-$ ^b	(6.25 ± 0.61)	≥ 9	5.62	≤ 0.63	This work (25°)	
$\text{Zn}(\text{oxac})_k \xrightarrow{k_{-\text{CO}_2}} \text{ZnH}_{-1}\text{pyu} + \text{CO}_2, k_{-\text{CO}_2} = 0.07 \text{ sec}^{-1}$						

^a Reference 39. ^b $\log \beta_{\text{Zn}(\text{oxac})} = 2.41$.

limiting rates attained at high Zn(II) concentrations directly give the tautomerization rates of these complexes. Qualitatively, the pH dependence of the reaction rate of uncomplexed oxac is observed in the extrapolated intercepts. It is apparent that Zn(II) complexation inhibits the keto-enol relaxation process, in contrast to the results observed for decarboxylation. The pronounced pH dependence shown by the reactions of complexed and uncomplexed oxac in Figure 4 indicates the presence of acid catalyzed paths in the tautomerization of both these species.

In the numerical analysis of 79 data points, the best model which was found to fit the results incorporated proton and acetic acid catalysis of uncomplexed oxac²⁻ and proton, acetic acid, and acetate catalysis of Zn(oxac). There was no indication from the results that the assumption of rapid Zn₂H₋₁oxac⁺ formation is not valid.

The equilibrium constant for the tautomerization of any given form of oxac, e.g., Zn(oxac)_k ⇌ Zn(oxac)_e, is a unitless number. Because of this, relaxation experiments are only able to yield the sum of the forward and backward rate constants for any given reaction path. The values found for these sums are given in Table II. The absolute forward rate constants relate to the sums in the following manner

$$k_f + k_b = k_f(1 + 1/K_{eq})$$

Tate, *et al.*, have spectrophotometrically determined the enol/keto ratios for unprotonated and protonated oxac²⁻.³⁹ On the basis of the assumption that the extinction coefficients of the keto and enol forms are invariant on complexing, they have also calculated the enol content of Mg(oxac).³¹ From the maximum value of the absorption which is observed at 280 nm in Zn(oxac) solutions, we estimate an enol/keto ratio of 9, or greater, for Zn(oxac) using this same assumption. This value and those reported earlier for uncomplexed oxac²⁻ were used to calculate the absolute values of the forward and backward tautomerization constants which are also given in Table II.

Discussion

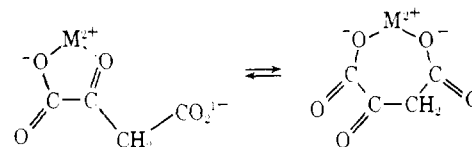
Tate, Grzybowski, and Datta have determined that 14% of oxac²⁻ is present as the enol at 25°, *I* = 0.1, and the enol content decreases to 11% in H(oxac)⁻ and to 5% in H₂oxac.³⁹ Complexing with Mg(II), on the

(39) S. S. Tate, A. K. Grzybowski, and S. P. Datta, *J. Chem. Soc.*, 1372 (1964).

other hand, increases the enol content of oxac²⁻ to 24%. Our results indicate that complexation with the softer Lewis acid, Zn(II), further increases the proportion of enol to around 90%. Metal ion stabilization of the enol, no doubt, arises from the greater affinity, in the chelate ring, of a metal ion for an oxygen atom of an OH group compared to an oxygen atom of a carbonyl group.

Gelles and Salama have performed time-dependent potentiometric studies on Zn(II)-oxac solutions.¹⁸ From the results which had been back-extrapolated to the time of mixing, they concluded that Zn(II) reacts rapidly with oxac²⁻ to form the complexes Zn(oxac) and Zn₂oxac²⁺. Their value for the formation constant of the 1:1 complex, 10^{2.4} M⁻¹ after correction to an ionic strength of 0.1, is in remarkably good agreement with our kinetically determined value of 10^{2.41}.

Nmr measurements have shown that metal ion-oxac²⁻ complexes form five-membered chelate ring structures.²⁶ The formation constant found for Zn(oxac) is consistent with these findings. The complex is somewhat more stable than that formed between Zn(II) and pyruvate ($K_1 = 10^{1.16}$),⁴⁰ showing the favorable influence of a second carboxylate group, and is also more stable than the analogous Zn-succinate complex (10^{1.76}),⁴¹ in which a seven-membered chelate ring is formed through coordination of the two carboxylate groups. This last value is sufficiently large, however, to suggest that an appreciable fraction, perhaps 10–20%, may exist in solution in the seven-member ring form. The reaction five ⇌ seven-membered ring is fast, metal and H⁺ independent, and cannot account for the inhibition of decarboxylation at high pH.

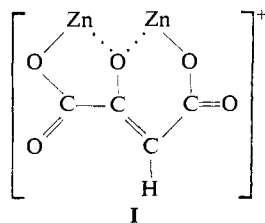


Gelles and Salama¹⁸ report the existence of a 2:1 complex, Zn₂oxac²⁺, from their potentiometric studies; while in their studies of Mg²⁺ catalysis, Kosicki and Lipovac¹⁹ invoked the formation of a 1:1 deprotonated enolate, MgH₋₁oxac⁻, to account for inhibition in the higher pH regions. Our kinetic data require only the

(40) D. E. Tallman and D. L. Leussing, *J. Amer. Chem. Soc.*, **91**, 6253 (1969).

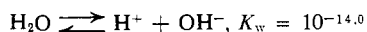
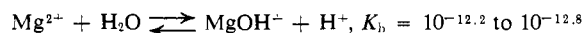
(41) L. G. Sillen and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964); **No. 25** (1971).

presence of a deprotonated dinuclear species, $Zn_2H_{-1}oxac^+$, in addition to $Zn(oxac)$ to account for the results. High absorbance in the spectral region in the uv region suggests that the dinuclear complex is an enolate. A possible structure is

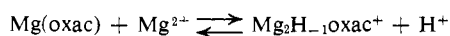


It is known that the enolate form of oxac does not undergo decarboxylation; so it is reasonable that this complex was also found to be inactive.

The magnesium data^{19,39} are open to an alternate interpretation which supports our proposal that a dinuclear enolate complex is formed and resolves some apparent discrepancies. In dilute Mg^{2+} solutions containing a slight excess of $oxac^{2-}$, the presence of a buffer region in the vicinity of pH 9–10 has been reported by Tate, *et al.*³¹ This has been attributed to the ionization, $Mg(oxac)_e \rightleftharpoons MgH_{-1}oxac^- + H^+$, corresponding to a pK_a of 9.5. The pK_a of uncomplexed $oxac_e^{2-}$ is 12.18. The enhancement of the $oxac^{2-}$ acidity by 2.6 pK_a units on coordination to the Mg^{11} is reasonable considering the observed effect of Mg^{2+} on the ionization of water



In contrast, the kinetic studies of Kosicki and Lipovac¹⁹ at high concentration levels of Mg^{2+} (0.03 *M* and greater) in excess over oxac show that the pH-dependent inhibition of decarboxylation sets in at the relatively low pH of 5.5 and becomes more pronounced as the Mg^{2+} concentration is further increased.¹⁹ Quite obviously, the tendency for coordinated $oxac^{2-}$ to lose a proton increases at higher Mg^{2+} concentrations. This behavior cannot be interpreted on the basis of the formation and ionization of only $Mg(oxac)$ but is very easily explained by the additional reaction



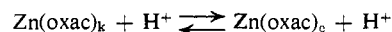
The large decrease in the enol pK_a suggests that both metal ions are coordinated to the enolate oxygen atom as shown in structure I.

Gelles and Salama¹⁸ describe in detail the results of potentiometric determinations on $Zn(II)-oxac^{2-}$ solutions. Using the formation constants given in Table I for the present study, it is possible to calculate theoretical pH values for the Gelles and Salama experiments which agree within a few hundredths of a pH unit with those reported. The concentration levels of $Zn_2H_{-1}oxac^-$ under their experimental conditions are calculated to be negligible and cannot account for the very small pH trends from which the formation of Zn_2oxac^{2+} was deduced. Since our results show no evidence for the presence of this complex, we consider its formation to be doubtful. Perhaps, the extrapolation made by Gelles and Salama to zero time is in slight error owing to the presence of two rate processes instead of one as they assumed.

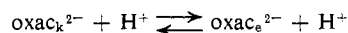
Pedersen¹⁰ and Gelles and Salama¹⁸ present evidence that at pH levels of about 2 a protonated complex, $ZnH(oxac)$, is kinetically active. Our data did not show the influence of such a species, probably because the lower pH range which had been investigated in this work was about 3.0.

The rates of the prototropic shift of oxac in the absence of complexing metal ions at 1.5° has previously been investigated by Banks.³⁸ In acetate buffers, proton, acetic acid, and acetate catalyzed paths were observed. Compared to the active acid catalysts, acetate was found to be a weak base catalyst and showed a relatively low rate constant. In the present investigation at 25° uncomplexed $oxac^{2-}$ was found to tautomerize *via* only proton and acetic acid catalyzed paths. Acetate catalysis involving uncomplexed oxac was not observed under the conditions employed in the present work, probably because an effort was made to maintain acetate at low concentration levels and to avoid complications which would arise from the extensive formation of acetatozinc(II) complexes. Differences in experimental technique and analysis of the data between Bank's and our investigation preclude the evaluation of accurate activation energies from the two sets of rate constants given in Table II, but, qualitatively, these energies seem to be of the order of 15 kcal mol⁻¹.

The present results show that $Zn(II)$ complexed $oxac^{2-}$ undergoes tautomerization *via* proton, acetic acid, and acetate catalyzed paths. The forward rate constant for the reaction



is about 43% of that found for the corresponding reaction of uncomplexed $oxac^{2-}$

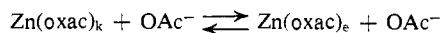


while the comparable rate constants for acetic acid catalysis show that the rate constant for $Zn(oxac)$ is higher by a factor slightly greater than 2. It would appear from this that coordination of $oxac^{2-}$ to $Zn(II)$ tends to activate the ligand and increase the rate of acid catalysis to a slight extent, but electrostatic repulsion arising from the presence of a positive $Zn(II)$ ion near the carbonyl group is apparently sufficient to inhibit proton catalysis. Because the basicity of a ligand donor atom is generally reduced when it forms a σ bond to a metal ion, the metal ion cannot facilitate the ease with which a carbonyl group can acquire a proton. Metal ion activation must then be associated with the tendency of the metal ion to stabilize the enol form of the ligand. This implies that the activated complex contains the ligand in the enol form to some extent. The two effects tend to cancel so that the net change in activation relative to uncomplexed $oxac^{2-}$ is small.

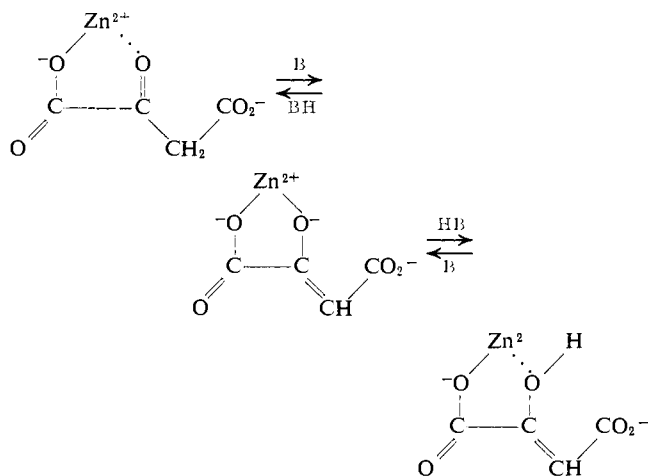
While the forward rate constants for the keto \rightarrow enol conversion show a relatively small dependence on the presence of $Zn(II)$, the backward rate constants are markedly decreased on complexation. Thus, the change in the enol/keto equilibrium constant on complexation arises largely from the effect of metal ion on the back-reaction. Because the relaxation time is determined by the sum $k_f + k_b$, it is this large decrease in k_b that mainly accounts for the $Zn(II)$ inhibition which is evident in the relaxation rates in Figure 4.

Although uncomplexed $oxac^{2-}$ was found to undergo

no appreciable base catalysis under the experimental conditions employed in this work, Zn(oxac) was found to be susceptible to acetate catalysis. The forward rate constant given in Table II for the reaction



at 25° is about a factor of 10 again as large as the value estimated for uncomplexed oxac²⁻ from Bank's value at 1.5° with an assumed activation energy of 15 kcal mol⁻¹. Thus, it appears that the presence of a complexing metal ion very significantly promotes base catalyzed tautomerization. The most plausible explanation for this effect is that the metal ion favors the formation of an intermediate enolate complex



Similar intermediates have been shown to be formed in the metal ion catalyzed tautomerization of ace-

tylacetone⁴² and thenoyltrifluoroacetone.⁴³ Unlike oxac, these β -diketones do not show acid catalyzed metal ion promoted paths. This probably is associated with the fact that these ligands are more acidic than oxac²⁻ and have more active methylene protons.

To summarize, the shape of the absorption-time curve which is observed when metal ion and oxac²⁻ solutions are mixed arises from a sequence involving the reactions ketonization \rightarrow enolization, decarboxylation, and ketonization of intermediate pyruvate enolate. These reactions have different rate laws, and it is possible to determine which are being observed from a variation of pH and reactant concentrations. Very likely with most labile divalent metal ions, except Cu(II), the last step in the reaction sequence is fast compared to the first two steps and is not involved in the rate limiting steps. With Cu(II) and many trivalent metal ions, on the other hand, the last step is probably sufficiently slow that it cannot be ignored in an analysis of the rate data.

Gelles and Hay¹⁷ have shown that the macroscopic rate constants for the decarboxylation of metal ion oxalacetate chelates parallel the stability constants of the corresponding oxalate complexes. They have concluded from this that metal ion activation arises from the stabilization of the pyruvate enolate product. While this interpretation is likely to be correct, correlations should be made using the microscopic decarboxylation rate constants which pertain to the keto complexes. Unfortunately, the required enol/keto equilibrium constants are unknown in most cases.

(42) R. G. Pearson and O. P. Anderson, *Inorg. Chem.*, **9**, 39 (1970).

(43) N. Sutin, M. R. Jaffe, D. P. Fay, and M. Cefola, *J. Amer. Chem. Soc.*, **93**, 2878 (1971).