with ether, and filtered through alumina bed. The filtrate was washed with saturated sodium chloride, and dried over anhydrous sodium sulfate, and concentrated in vacuo to give 13-acetoxytridecan-1-al (3) (0.38g, 87%). IR cm^{-1}: 2900, 2750, 1730, 1220. NMR δ: 1.30-1.75 (20H, m), 2.05 (3H, s), 2.40 (2H, *t*), 4.10 (2H, *t*), 9.80 (1H, *t*).

(Z)-13-Octadecen-1-yl acetate (1). To sodium hydride (free of oil : 0.03g) was added dimethyl sulfoxide (3 m*l*), and slowly heated for 1 hr under nitrogen atomosphere. After cooling, to the reaction mixture was added pentylidenetriphenylphosphonium bromide (0.51g) in DMSO (2m*l*) at room temperature. To the reaction mixture was added 13-acetoxytridecan-1-al (3, 0.10g) in DMSO (1 m*l*) and diluted with dry benzene (5 m*l*). The reaction mixture was stirred at room temperature for 3hr and added to water (20m*l*) and extracted with ether: n-hexane (1:1). The organic layer was separated and washed with water and dried over anhydrous magnesium sulfate, and concentrated in vacno, and separated by flash column chromatography using ether: petroleum ether (1:1) as eluent to give (Z)-13-octadecen-1-yl acetate (1) (0.08g, 68%). IR cm^{-1}: 2900, 1750, 1460, 1240, 1040. NMR δ: 0.90 (3H, s), 1.30-1.70 (28, *m*), 2.05 (3H, *s*), 4.05 (2H, *t*), 5.35(2H, *t*).

Field Test. Pheromone vials at a concentration of 50 μg of (Z)-13-octadecen-1-yl acetate (1) per polyethylene capsule were tested in the paddy field of Haenam area. The traps used in these tests were circular water pan (30D × 27H) with 2 rectangular windows (4 × 20cm). Polyethylene vials were held 4-6cm above the water surface of the trap. The traps consisted of trap cover to shade the bait. Water in the traps was treated with dilute detergent solution to increase the trap catch. The insects caught in these traps were counted and checked every 5 days. Blank test has been done with traps without pheromone vials.

References

(1) D. S. Arida, 1979, Insect Sex Pheromones, Entomology Department Seminar (International Rice Research Institute, Manila, Philippines): (Z)-13-Octadecenyl-1-ol acetate was the pheromone mimic of the Rice Leaf Folder Moth (Cnaphalocrocis medinalis).

(2) (a) S-K Kang, J-M Park, J-U Lee and H-G Goh, *Sung Kyun Kwan Univ. Journal*, **34**(2), 429(1983); (b) B. F. Nesbitt, P. S. Beevor, D. R. Hall, R. Lester, and J.R. willians, *J.Cehm, Ecol.*, **6**(2), 385 (1980); (c) H. Kanno, S. Tatsuki, K. Uchiumi, M. Kurihara, J. Fukami, Y. fujimoto, and T. Tatsuno, *Appl. Entomol. Zool.*, **13**(4), 321 (1978).

(3) H. J. Bestmann, R. Wax, and O. Vostrowsky, *Chem. Ber.*, **112**, 3840 (1979).

(4) 1,13-Tridecanediol was easily prepared from 1,11-undecanedicarboxylic acid by esterification (EtOH/H^+), followed by LAH reduction in 82% overall yield.

(5) E. J. Corey and J. W. Suggs, *Tetrahedron Letters*, 2647 (1975).

(6) J. H. Babler and M. T. Coghlan, *Tetrahedron Letters*, 1971 (1979).

Kinetics of the Zn(II)-Catalyzed Hydrolysis of 2-Acetylpyridineketoximyl Diphenyl Phosphate

Junghun Suh† and Kyung Il Kim

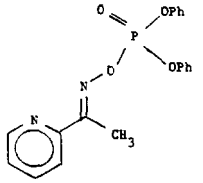
Department of Chemistry, Seoul National University, Seoul 151, Korea

(Received March 22, 1985)

Kinetic data of the Zn(II) ion-catalyzed hydrolysis of 2-acetylpyridineketoximyl acetate (*S*) are measured. The reaction proceeds through the accumulation of an intermediate (*I*). 2-Acetylpyridineketoxime (Ox) is released in the breakdown step of *I*. Phenol is not formed as a part of the products, and, therefore, diphenyl phosphate and *Ox* are produced by the breakdown of *I*. Based on the dependence of the rates for the formation and the breakdown of *I* on [Zn(II)] and pH, and considering the UV spectral properties of *I*, the structure of *I* is tentatively assigned as the penta-covalent intermediate formed by the addition of a water molecule to *S*.

Studies on the metal ion-catalyzed reactions of organic compounds have revealed many important catalytic principles.[1,2] In addition, these systems serve as models for metalloenzymes and have proposed catalytic roles of the active-site metal ions. For example, our studies on the Zn(II) or Cu(II)-catalyzed hydrolysis of esters derived from pyridyl oximes disclosed several new catalytic features.[3-7] Moreover, mechanistic data obtained previously for the action of carboxypeptidase A, a metallo-exopeptidase, have been reinterpreted in terms of the catalytic roles disclosed by the model study with the oxime esters.[4,5].

Hydrolysis of phosphate esters is a biologically important reaction.[8-10] We have extended our study to the metal ion-catalyzed hydrolysis of 2-acetylpyridineketoximyl diphenyl phosphate (*S*) in an attempt to understand the catalytic roles of metal ions in both enzymatic and nonenzymatic phosphate hydrolysis. A typical metallo-phosphatase is alkaline phosphatase.[11]



(*S*)

Results

The reaction of S in the presence of Zn(II) ion proceeds through the accumulation of a stable intermediate. A typical spectral change in the UV region during the Zn(II)-catalyzed reaction is illustrated in Figure 1. In this figure, the spectrum of S changes instantaneously to spectrum MS upon the addition of Zn(II) ion due to the formation of the Zn(II) complex of S. Then, spectrum I is attained as the reaction proceeds, which is subsequently changed to the spectrum of the reaction product (P). The absorbance change observed at a fixed wavelength after mixing S with Zn(II) ion is exemplified in Figure 2. This figure indicates the initial formation of an intermediate (I) and the subsequent breakdown of I to the product (P). The overall reaction, therefore, can be represented by the scheme of eq 1.

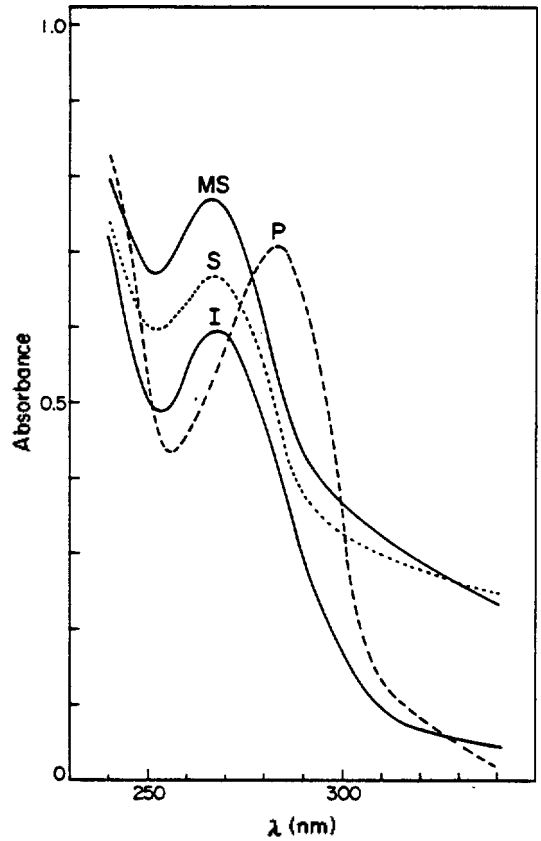


Figure 1. Spectral changes accompanying the hydrolysis of S in the presence of Zn(II). (pH = 6.5, [Zn(II)] = 0.0175 M).

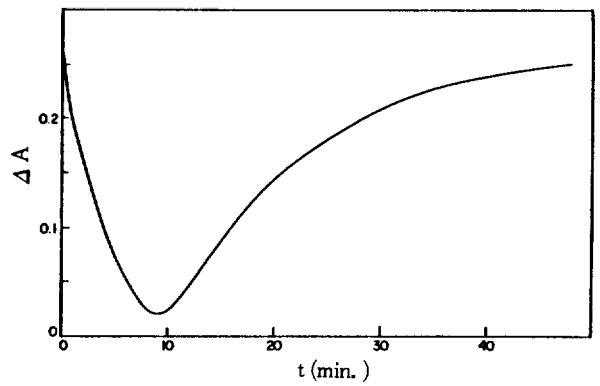


Figure 2. The absorbance change (285.2 nm) in the Zn(II) (0.0125 M)-catalyzed hydrolysis of S at pH 6.5.

$$S \overset{k_{o1}}{\rightarrow} I \overset{k_{o2}}{\rightarrow} P \qquad (1)$$

Parameters k_{o1} and k_{o2} stand for the pseudo-first-order rate constants for the formation and the breakdown, respectively, of intermediate I.

The k_{o1} value was measured at the isosbestic point (270–280 nm) of I and P. The isosbestic point was measured by the repetitive scanning of the reaction mixture after the maximum amount of I accumulated, as illustrated in Figure 3. Measurement of the isosbestic point was performed in each of the buffer solutions used for the kinetic study.

The k_{o2} value was calculated from the absorbance change accompanying the conversion of I to P at wavelengths (285–290 nm) which afforded the largest absorbance difference between I and P. Since the first step of eq. 1 was at least several times faster than the second step, correct estimation of k_{o2} was not difficult.

At a fixed pH, the dependence of k_{o1} and k_{o2} on [Zn(II)] was measured. The k_{o1} value was almost independent of [Zn(II)] when [Zn(II)] was varied over 0.002–0.02 M. This is attributable

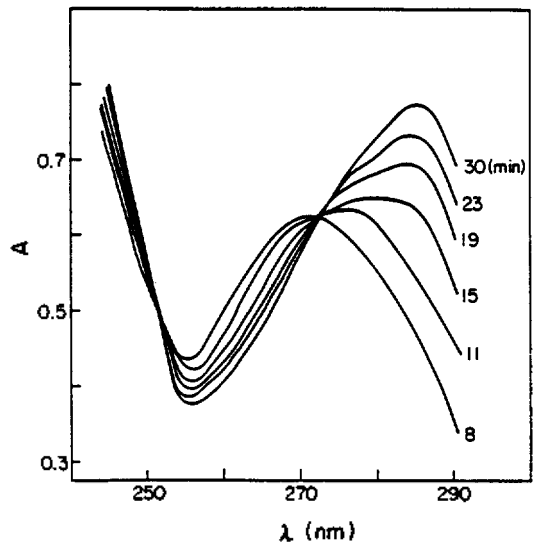


Figure 3. A typical repetitive scanning of a reaction mixture performed in order to determine the isosbestic point of I and P. ([Zn(II)] = 0.02 M, pH 6.5).

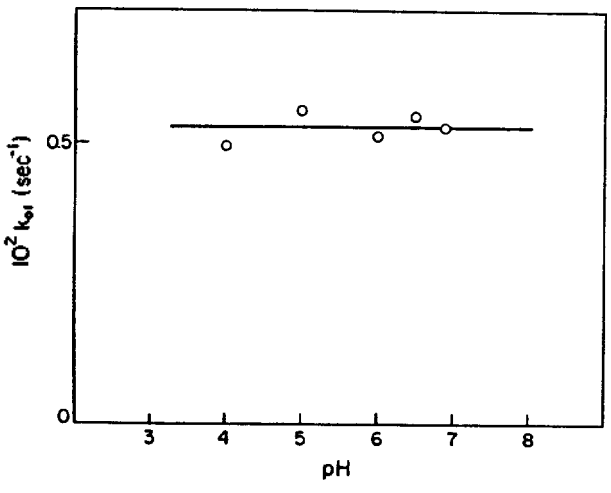


Figure 4. pH dependence of k_{o1} for the Zn(II)-catalyzed hydrolysis of S.

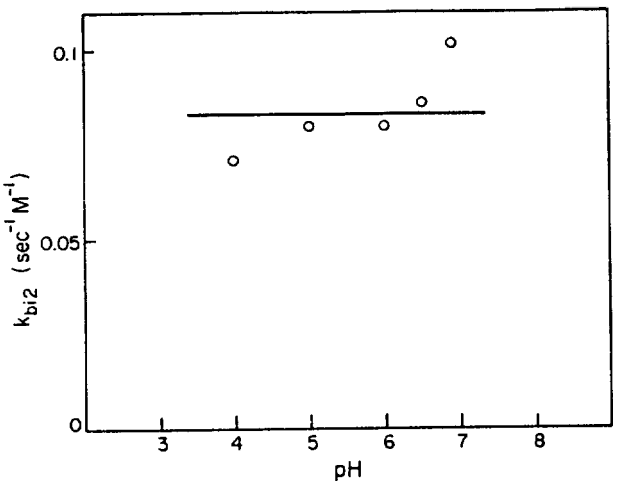


Figure 5. pH dependence of k_{bi2} for the Zn(II)-catalyzed hydrolysis of *S*.

to the almost complete formation of the Zn(II) compelx of *S* at [Zn(II)]≥0.002 M. The k_{o2} value was proportional to [Zn(II)] up to 0.02 *M*, and the slope of the straight line obtained in the plot of k_{o2} against [Zn(II)] is denoted as k_{bi2}. The values of k_{o1} and k_{bi2} obtained at pH 4-7 are illustrated in Figures 4 and 5, respectively.

The spectrum of the reaction product at 270-300 nm illustrated in Figure 1 is characteristic of the Zn(II) complex of 2-acetylpyridineketoxime (Ox). Thus, Ox is not released during the formation of *I*, but is formed as a part of *P*. After the formation of *P* was complete, the reaction mixture was examined for the presence of phenol by the reported colorimetric procedures. However, phenol was not detected as a part of *P*.

Discussion

The results of the dependence of k_{o1} and k_{o2} on [Zn(II)] indicate the strong binding of *S* to Zn(II) but weak formation of the Zn(II) complex of *I*. The simplest scheme that explains the observed kinetic dependence on [Zn(II)] is Scheme 1.

$$\mathrm{Zn(II)}+S \overset{K_f}{\rightleftharpoons} \mathrm{Zn(II)}S \overset{k_1}{\rightarrow} \mathrm{Zn(II)}I \overset{k_2}{\rightarrow} P$$

$$\Big\Downarrow K_f'$$

$$\mathrm{Zn(II)}+I$$

Scheme 1.

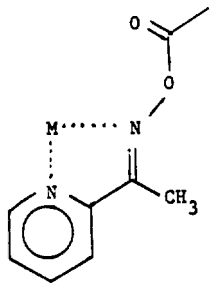
For this scheme, the expressions of k_{o1} and k_{o2} are

$$k_{o1}=k_1K_f[\mathrm{Zn(II)}]/(1+K_f[\mathrm{Zn(II)}]) \quad (2)$$

$$k_{o2}=k_2K_f'[\mathrm{Zn(II)}]/(1+K_f'[\mathrm{Zn(II)}]) \quad (3)$$

When [Zn(II)]>>1/K_f, k_{o1} becomes k_1. When [Zn(II)]<<1/K_f', k_{o2} is proportional to [Zn(II)] with the proportionality constant k_{bi2} being k_2K_f'. The results of the dependence of k_{o1} and k_{o2} on [Zn(II)] (0.002-0.02 *M*) indicate that K_f>500 M^{-1} and K_f'<50 M^{-1}. Thus, *S* is completely bound to Zn(II), while very small portions of *I* are present as Zn(II) *I* under the experimental conditions. The pH dependence of k_{o1} ($=k_1$) and k_{bi2} ($=k_2K_f'$) indicates that hydroxide ion participates neither in the conversion of Zn(II)*S* to Zn(II)*I* nor in the conversion of Zn(II) *I* to *P*.

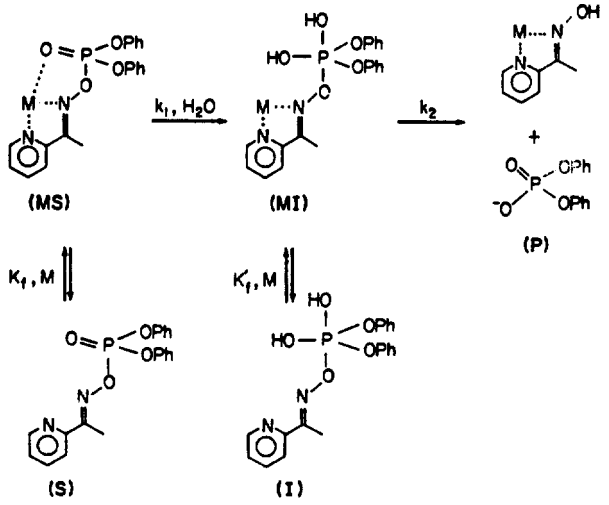
The binding mode in Zn(II)*S* can be assigned as structure *MS* of Scheme 2 on the ground of the large value of K_f. A previous study[5] on the Zn(II) ion-catalyzed hydrolysis of the acetyl ester of *Ox* revealed that the pyridyl nitrogen and the oximyl nitrogen are the coordinating atoms in the Zn(II) complex of the ester as illustrated by *A*. The formation constant for *A* was much smaller than 5 M^{-1}. Thus, an extra binding site in Zn(II)*S* is needed to account for the large K_f value of Zn(II)*S*. This extra binding site in Zn(II)*S* is the P=O oxygen atom, as indicated in *MS*. The different binding modes of *MS* and *A* appear to be resulted in part from the longer lengths of P-O and P=O bonds compared with C-O and C=O bonds. If the carbonyl oxygen of *A* coordinates to the metal ion, examination of molecular models indicates the existence of a significant amount of strain in the structure of the two fused five-membered chelate rings. In structure *MS*, this strain could be relieved by the longer lengths of P-O and P=O bonds.



(*A*)

The Zn(II) complex of Ox is a part of *P*. Colorimetric measurements indicated the absence of phenol in *P*. Thus, *P* should be a mixture of Zn(II)Ox and diphenyl phosphate, as indicated in Scheme 2.

In order to determine the structure of the accumulating intermediate (*I*), attempts were made to isolate *I* in a large quantity. In order to increase [S] above 0.01 *M*, the addition of a large amount of an organic cosolvent was inevitable. This,



Scheme 2.

however, greatly retarded the metal ion-catalyzed conversion of *S* to *I*, and accumulation of *I* in a large scale was not achieved.

The UV spectrum of *I* (Figure 1) at 250-280 nm is similar to that of *S* or *MS* except that the absorbance values are smaller for *I*, indicating that the chromophoric properties of these

species are not much different from each other. Both the formation and the breakdown of *MI* are not affected by pH changes. Therefore, it is very likely that the conversion of Zn(II)*S* to Zn(II)*I* and that of Zn(II)*I* to *P* occur through the participation of water molecules. In addition, the formation constant (K_I') for Zn(II)*I* is much smaller than that (K_I) for Zn(II)*S*, indicating that the third coordinating atom is *S* (*i.e.* the oxygen of the P=O bond) is not available in *I* for metal binding. A likely candidate of Zn(II)*I* which is compatible with these results is structure *MI* of Scheme 2.

The mechanism proposed in Scheme II assumes the formation of *MI* through the addition of a water molecule to the P=O bond and the pH-independent breakdown of *MI*. The expulsion of the oximate ion instead of phenolate from *MI* is attributable to the decreased pK_a of Ox upon metal complexation (pK_a of Zn(II)Ox = 7.0,[5] pK_a of phenol = 10.0).

Whether discrete penta-covalent intermediates such as structure *I* of Scheme 2 exist in the hydrolysis of phosphate triesters has been a controversial issue.[8-10] Little is known about the thermodynamic stability of the penta-covalent species. The structure of the accumulating intermediate is tentatively assigned in the present study on the basis of kinetic and spectral data. Efforts are continuously made in this laboratory to obtain more information on the structure of the intermediate.

Experimental Section

2-Acetylpyridineketoximyl diphenyl phosphate (S). To a mixture of 2-acetylpyridneketoxime and an equimolar amount of diphenyl chlorophosphate in ethyl ether, triethylamine (10% molar excess) was added at room temperature. Five hours later, triethylammonium hydrochloride was removed by filtration, and the resulting mixture was separated on a silica gel column (eluted with ethyl acetate). The isolated product was further purified by recrystallization from ethyl acetate-hexane, mp 91-92°C.

Kinetic measurements. Rate data were obtained on a Beckman model 25 or a Beckman 5260 UV/vis spectrophotometer. Temperature (25°C) was controlled to within ±0.1°C with a Haake E52 circulator. Water was distilled and deionized prior to the preparation of buffer solutions. Zinc chloride was prepared by reacting zinc oxide ('Gold Label', Aldrich) with hydrochloric acid. pH measurements were performed with a Fisher Accumet Model 525 pH meter, and buffers (0.02 *M*) used were acetic acid (pH 4-5) or 4-morpholineethanesulfonate (pH 5.5-7). Stock solutions of *S* were prepared in acetonitrile, and the solutions used for kinetic measurements contained 1×10^{-4} *M* *S* and 0.8% (v/v) acetonitrile (ionic strength 0.3 with NaCl).

Colorimetric determination of phenol. Quantitation of phenol in the product solutions was performed colorimetrically according to the literature,[12] by using either potassium ferricyanide/ferric chloride or *p*-nitrobenzenediazonium fluoroborate.

Acknowledgment. This work was supported by a grant from Korea Science and Engineering Foundation.

References

(1) D. P. N. Satchell and R. S. Satchell, *Annu. Rep. Progr. Chem. Sect. A*, **75**, 25 (1979).
(2) C. J. Hipp and D. H. Busch, "Coordination Chemistry," Ed by A. E. Martell, A. C. S. Monograph 174, Washington (1978), Vol. 2, Chapter 2.
(3) J. Suh, E. Lee, and E. S. Jang, *Inorg. Chem.*, **20**, 1932 (1981).
(4) J. Suh, M. Cheong, and M. P. Suh, *J. Amer. Chem. Soc.*, **104**, 1654 (1982).
(5) J. Suh and H. Han, *Bioorg. Chem.*, **12**, 177 (1984).
(6) J. Suh, M. Cheong, and H. Han, *Bioorg. Chem.*, **12**, 188 (1984).
(7) J. Suh, M. P. Suh, and J. D. Lee, *Inorg. Chem.*, in press (1985).
(8) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968).
(9) C. A. Bunton, *Acc. Chem. Res.*, **3**, 257 (1970).
(10) R. F. Hudson and C. Brown, *Acc. Chem. Res.*, **5**, 204 (1972).
(11) L. B. Spector, "Covalent Catalysis by Enzymes," Springer-Verlag, New York (1982), p. 117-120.
(12) M. Pesez and J. Bartos, "Colorimetric and Fluorimetric Analysis of Organic Compounds and Drugs", Marcel Dekker, New York (1974), Chapter 3.