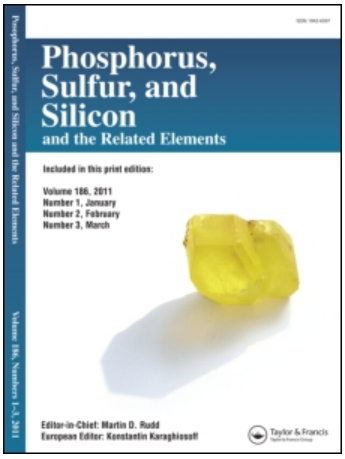

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KINETICS AND MECHANISTIC ASPECTS OF THE HYDROLYSIS REACTION OF CYCLIC PHOSPHONODITHOITES

Sangha Kim[a]; D. Max Roundhill[a]
[a] Contribution from the Department of Chemistry, Tulane University, New Orleans, LA, U.S.A.

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KINETICS AND MECHANISTIC ASPECTS OF THE HYDROLYSIS REACTION OF CYCLIC PHOSPHONODITHIOITES

SANGHA KIM and D. MAX ROUNDHILL*

Contribution from the Department of Chemistry, Tulane University, New Orleans, LA 70118, U.S.A.

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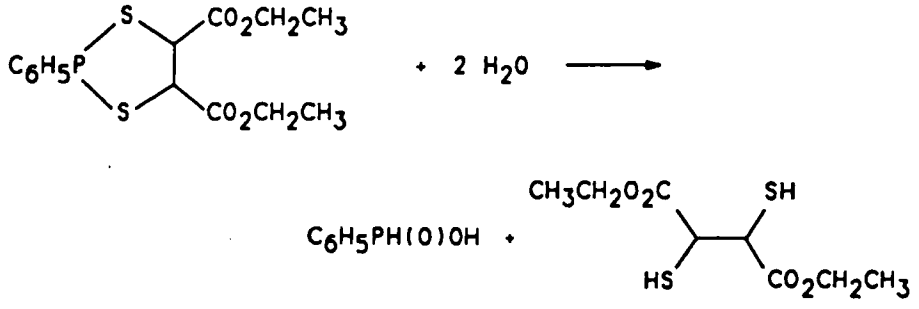
The hydrolysis of the cyclic phosphonodithioite $C_6H_5P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)$ in aqueous acetonitrile follows a rate law that is first order in the concentration of $C_6H_5P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)$, and independent of the water concentration. The values of E_a, ΔH^* and ΔS^* are 10.4 k cal mol^{-1}, 9.6 k cal mol^{-1} and -45 cal mol^{-1} respectively. The isotope effect for D_2O as compared to H_2O is 2.5. A mechanism is proposed whereby a pre-equilibrium is established between the phosphonodithioite and water, with a subsequent proton transfer from water to the tri-coordinate phosphorus occurring in a subsequent step. The slow step involves hydrolytic cleavage of the first phosphorus-sulfur bond. The compound 2-nitro-5-thiocyanatobenzoic acid is used to provide supporting evidence for the formation of an intermediate thiol.

Key words: Phosphonodithioite; hydrolysis; mechanism.

INTRODUCTION

Recently we reported that the cyclic phosphonodithioite $C_6H_5P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)$ could be prepared in good yield by treating phenyldichlorophosphine, $C_6H_5PCl_2$ with diethyl-2,3-dimercaptosuccinate, $(CH(CO_2CH_2CH_3)SH)_2$ in the presence of base.[1] In that previous paper we reported that this cyclic phosphonodithioite undergoes hydrolysis at a faster rate than does its acyclic congener $C_6H_5P(SCH_2CH_2CO_2CH_2CH_3)_2$. Thus, under conditions where the compound $C_6H_5P(SCH_2CH_2CO_2CH_2CH_3)_2$ is hydrolyzed by less than 10%, the cyclic compound $C_6H_5P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)$ undergoes hydrolysis whereby 95% of the compound is converted into the hydrolytic products. The products of the hydrolysis of $C_6H_5P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)$ are phenylphosphinic acid $C_6H_5PH(O)OH$ and diethyl-2,3-dimercaptosuccinic acid (Equation 1). The acyclic compound $C_6H_5P(SCH_2CH_2CO_2CH_2CH_3)_2$ similarly



(1)

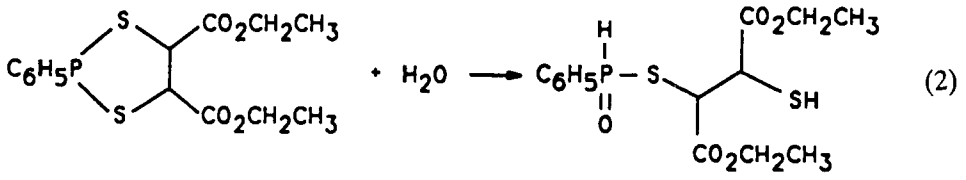
undergoes hydrolysis to phenylphosphinic acid and ethyl-3-mercaptopropanoate. In that previous paper a reaction pathway was proposed whereby the two phosphorus-sulfur bonds underwent sequential hydrolysis to give the final phosphorus and sulfur containing products. Thus a sequential two-step reaction with the intermediate $C_6H_5PH(O)(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)SH)$ was proposed as the first hydrolysis product (Equation 2). However in that earlier paper no evidence was presented to justify the presence of such an intermediate.

In this second paper we now present our experimental results of a kinetic study on the hydrolysis of the cyclic phosphonodithioite $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$. From these data we present a more detailed understanding of the mechanism of this hydrolysis reaction.

RESULT AND DISCUSSION

The cyclic compound $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ dissolves in dry acetonitrile to give a solution which shows an absorption band at 266 nm with an extinction coefficient ($\in$) of $4.5 \times 10^4\ M^{-1}\ cm^{-1}$. Acetonitrile solutions of this compound obey Beers law. The rate data for the hydrolysis reaction were obtained by monitoring changes in the absorbance at 266 nm with time for solutions of the cyclic phosphonodithioite in aqueous acetonitrile, with the mixture thermostated at 50°C. The dependence of the rate on the concentration of $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ was obtained by carrying out a series of hydrolysis reactions using varying concentrations of the cyclic phosphonodithioite dissolved in acetonitrile to which 5% by volume of oxygen-free water had been added. The reaction order in the compound, $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$, as determined by the initial rate method,[2] is first order (Table I). The observed rate constant k calculated from a first order plot is $3.04(8) \times 10^{-4}\ sec^{-1}$.

The dependence of the reaction rate on the water concentration was investigated by following the hydrolysis rate of the reaction with the concentration of $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ fixed at 1.87 mM, and the concentration of water was varied from "dry" to 5% by volume aqueous acetonitrile. This latter 5% aqueous acetonitrile solution has a molar water concentration of 2.92 mM. Analysis of these rate data collected at different water concentrations show that the reaction rate is independent of the water concentration (Table II). Examples of reactions where the rate is independent of the concentration of one of the reactants are rare. We have therefore investigated the possibility that our "dry" acetonitrile contains sufficient water that the apparent independence of the reaction rate on the water concentration is in actuality a case of saturation kinetics in that reagent. We have therefore measured the concentration of water in "dry" aceto-



(2)

TABLE I

Concentration [A] and rate (V) data obtained from the initial rate method for the hydrolysis of $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)-CH(CO_2CH_2CH_3)S)}$ (A) at constant $[H_2O]$

[A] (μM)	ln[A]	$V(M^{-1}sec^{-1}) \times 10^{-4}$	lnV
17.54	-10.95	0.54	-9.83
23.25	-10.67	0.76	-9.49
43.23	-10.05	1.40	-8.88
46.50	- 9.98	1.52	-8.79
61.22	- 9.70	1.54	-8.78
62.02	- 9.69	1.56	-8.77
71.99	- 9.54	1.74	-8.66
77.52	- 9.47	1.85	-8.60
103.08	- 9.18	3.16	-8.06

TABLE II

Concentration and rate (V) data obtained from the initial rate method for the hydrolysis of $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ at constant concentration

$[H_2O]$ (mM)	$ln[H_2O]$	$V(M^{-1}sec^{-1}) \times 10^{-5}$	lnV
0.41	-7.80	3.28	-10.32
1.53	-6.48	4.60	- 9.99
2.90	-5.84	2.75	-10.50
4.80	-5.34	2.40	-10.64

nitrile by NMR. From the integration of the ^1H NMR resonances due to the hydrogens on water and acetonitrile, we determined the approximate concentration of water in the "dry" acetonitrile to be 0.41 mM. Since the concentration of, $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ in the solutions used for the kinetics runs is 10–12 μM, the concentration of water in "dry" acetonitrile is some 40 times that of the concentration of the cyclic phosphonodithioite in solution.

The deuterium isotope effect of the hydrolysis reaction has been measured by performing the reaction of $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ in two separate solutions, one of which contains 5% of H_2O in acetonitrile, and the other contains 5% of D_2O in acetonitrile. Each reaction was carried out under the same

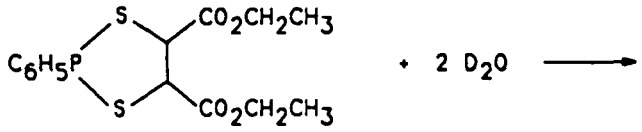
conditions of time and temperature (Equations 1 and 3). The two separate solutions were analyzed for overall conversion using $^{31}P\{^1H\}$ NMR spectroscopy, with the phenylphosphinic acid formed in the hydrolysis reaction showing a resonance centered at δ 21.1. For the protonated form, $C_6H_5PH(O)OH$, this resonance is observed as a singlet, but for the deuterated form, $C_6H_5PD(O)OD$, this resonance is observed as a 1:1:1 "triplet" with a $^1J(PD)$ value of 7.1 Hz. By relative integration of the $^{31}P\{^1H\}$ NMR signals for the reactant and the product after hydrolysis with H_2O, the reaction was approximately 80% complete, and the isotope effect (k_H/K_D) was found to be 2.5. Attempts to measure this isotope effect by using mixed solutions of D_2O and H_2O were unsuccessful because of the facile isotope exchange between $C_6H_5PD(O)OD$ and $C_6H_5PH(O)OH$ (Equation 4).

The vibrational frequency of the O—H bond in water is 3760 cm^{-1}, which 4corresponds to a zero-point energy ($\frac{1}{2}h\nu$) of 22.5 kJ mol^{-1}.[3] For the O—D bond, simple division by 1.414 leads to a value of 2659 cm^{-1} for this frequency. This value for ν(O—D) corresponds to a zero-point energy of 15.9 kJ mol^{-1}. The difference in these zero-point energies is 6.6 kJ mol^{-1}. If we assume that the partition functions for the two isotopic forms are practically the same, the semiclassical ratio k_H/k_D is determined almost entirely by the zero-point energy difference in the initial state.[4] Thus, it is given by

$$k_H/k_D \approx e^{6.6 \text{ kJ mol}^{-1}/RT}$$

$$= 11.6 \text{ at } 323 \text{ K}$$

The rate data can be fitted to the reaction sequence shown in Scheme 1. The failure to detect the intermediate $C_6H_5PH(O)(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)SH)$ by spectroscopic methods (UV-visible and ^{31} P NMR spectroscopy) supports the premise that $k_3 >> k_2$. This conclusion is also supported in our earlier paper where we showed that the hydrolysis of P—S bonds was accelerated by the presence of a [PH(O)] functionality in the compound. Thus, whereas the compound $C_6H_5PH(O)SCH_2CH_2CO_2CH_2CH_3$ underwent complete hydrolysis after 2 hr. at 50°C in aqueous acetone, the compound $C_6H_5P(SCH_2CH_2CO_2CH_2CH_3)_2$ underwent no observable hydrolysis after 15 hr under the same experimental conditions.



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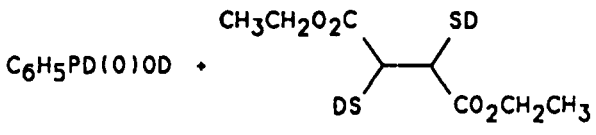


$$C_6H_5PH(O)OH \underset{H_2O}{\overset{D_2O}{\rightleftharpoons}} C_6H_5PD(O)OD \qquad (4)$$

If we designate the compound $C_6H_5P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)$ as A, the first intermediate $C_6H_5P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)\cdot H_2O$ as B, and the second intermediate $C_6H_5PH(O)(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)SH)$ as C (Scheme 1), then we can derive the rate expression as:

$$K = k_1/k_{-1} = \frac{[B]}{[A][H_2O]}$$

Thus, the reaction rate:

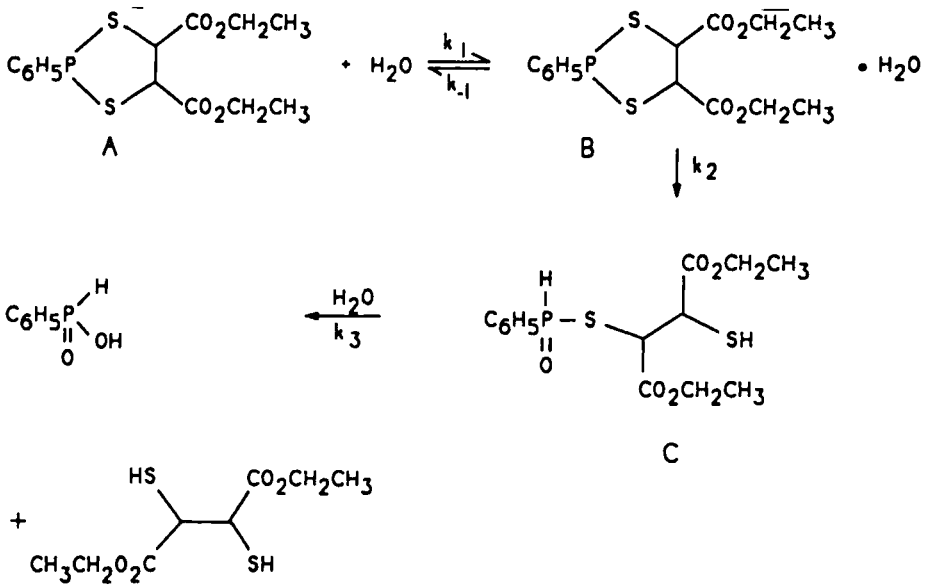
$$V = d[C]/dt = k([A] + [B]) = k_2[B] = k_2K[A][H_2O]$$

Therefore $k([A] + [B]) = k_2K[A][H_2O]$ and $k([A] + K[A][H_2O]) = k_2K[A][H_2O]$. Therefore:

$$k = k_2K[H_2O]/(1 + K[H_2O])$$

when $K[H_2O] >> 1$, then $k = k_2$, and the expression for the rate R becomes independent of $[H_2O]$.

This observation of saturation kinetics with water provides evidence for the first intermediate $C_6H_5P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)\cdot H_2O$. We propose that this intermediate has the water molecule hydrogen bonded to the ester oxygen, thereby favoring intramolecular attack by the water proton at the tricoordinate phosphorus (Figure 1). Such a pathway leads to the formation of the pentacoordinate adduct $C_6H_5(OH)(H)P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)$ (X in Scheme 2), which can transfer a proton to sulfur with subsequent ring opening of the ring. Subsequent tautomerization of the intermediate $C_6H_5(OH)P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)SH)$ (Y) gives $C_6H_5PH(O)(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)SH)$ (Z), the second intermediate (C) in the overall hydrolysis reaction in Scheme 1.



Scheme 1

The reaction rate has been measured over a temperature range from 313 K to 328 K (Table III). An Arrhenius plot (ln k against 1/T) of the data is linear, and the slope gives a value of 10.4 k cal mol^{-1} for E_a. From an Eyring plot (ln k/T against 1/T), values of 9.6 k cal mol^{-1} for ΔH^*, and -45 cal mol^{-1} K^{-1} for ΔS^*, are found. This large negative entropy supports an associative pathway leading to the transition state.

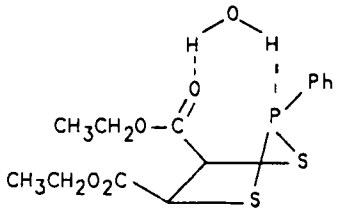
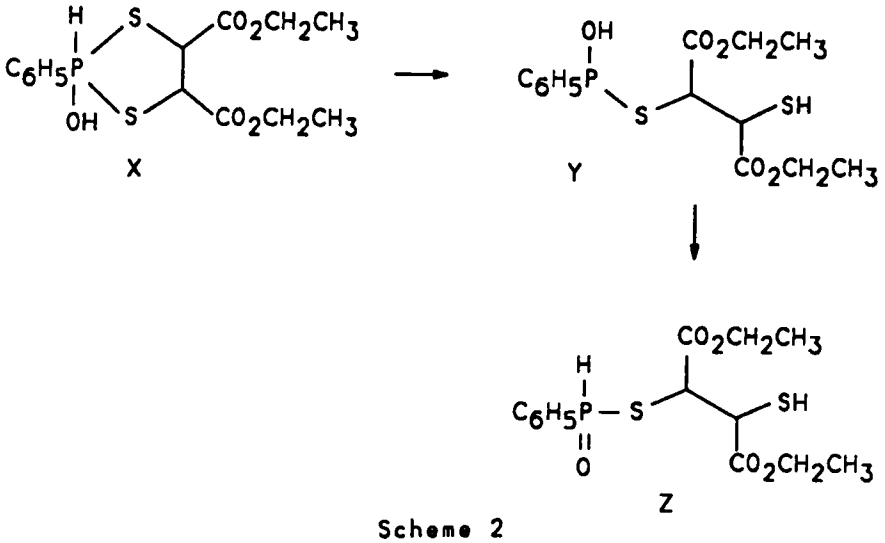


FIGURE 1 Proposed adduct between $C_6H_5P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)$ and water.



Scheme 2

TABLE III

Kinetic data for the hydrolysis of the cyclic phenylphosphonodithioite over the temperature range of 313 K to 328 K

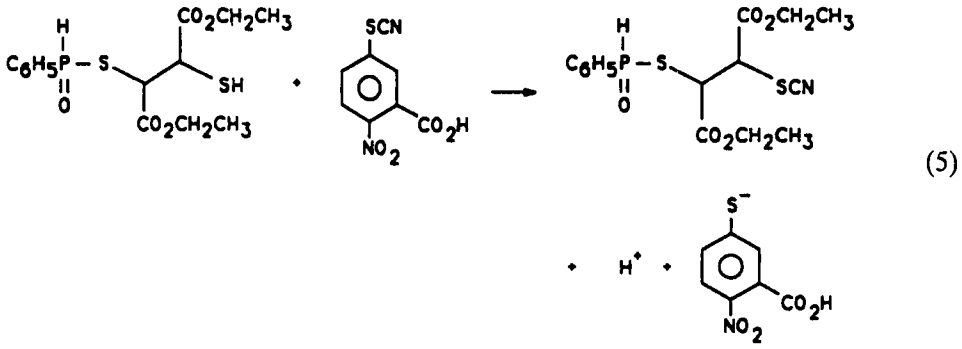
Temperature (K)	313	318	323	325	328
k (X 10^{-4})	1.83	2.36	3.00	3.34	3.92
1/T (X 10^{-3})	3.195	3.145	3.096	3.077	3.049
ln (k)	-8.61	-8.35	-8.10	-8.00	-7.84
-ln (k/T)	-14.35	-14.11	-13.87	-13.79	-13.64

Alternative explanations for the independence of the reaction rate on the water concentration are less satisfactory. One such explanation is that the phosphonodithioite undergoes a slow first order cleavage of a P—S bond, followed by rapid hydrolysis of this ring-opened intermediate. Such a pathway fits the rate law data, but it does not appear to be a realistic option, and also it does not provide a satisfactory explanation for the observed deuterium isotope effect when D_2O is used instead of H_2O. We therefore believe that our mechanism based on saturation kinetics provides the best explanation for the observed rate law and isotope effect.

Our proposal that the first step in the reaction pathway involves addition of a water molecule to the phosphorus center is based on two considerations. The first of these is the deuterium isotope effect. A value of 2.5 for the isotope effect k_H/k_D for reactions in H_2O and D_2O indicates that the cleavage of an O—H bond begins to occur prior or close to the formation of the transition state. Although this value of 2.5 is considerably less than the expected value of 11.6 if the slow step were to involve complete bond breakage, our value indicates that both O—H bond breaking and P—H bond making components are important in the pathway to the transition state. The second consideration comes from the known chemistry of phosphites, where hydrolytic cleavage of the P—O bonds involves initial attack by the water proton at phosphorus.[5,6]

The hydrolysis rate of phosphorous acid esters is faster than our cyclic phosphonodithioite. Thus, whereas the hydrolysis rate for our compound at 50°C is 3.00×10^{-4} M sec^{-1}, the comparable rate for triethyl phosphite is 3.7×10^{-2} M sec^{-1}.[7] For a cyclic phosphite, the hydrolysis rate appears to be faster than is observed for triethyl phosphite.[8] These observations can be usefully compared with those found for μ-monothiopyrophosphates, where the large rate enhancement induced by the replacement of oxygen by sulfur is attributed to the weakness of the P—S bond relative to the P—O bond.[9] This trend is not observed in the phosphite series, suggesting that a dissociative transition state with a high degree of bond cleavage between phosphorus and the leaving group is not operative in this case.

The possible presence of an intermediate such as that suggested in Equation 2 has been probed by carrying out the hydrolysis reaction in the presence of 2-nitro-5-thiocyanatobenzoic acid (NTCB). The compound NTCB is a selective cyanylation reagent that under neutral pH conditions reacts rapidly with free thiol groups. The products of this reaction are thiocyanate and thionitrobenzoate, which has a characteristic absorption band at 412 nm ($\in$ = 13,600 M^{-1} cm^{-1}).[10] If, therefore, the first step in the hydrolysis reaction results in the formation of an intermediate containing a free thiol group, in the presence of NTCB we will observe the cyanylation of this intermediate thiol in the early stages of the reaction, with thionitrobenzoate being formed stoichiometrically (Equation 5). When the hydrolysis reaction is carried out in the presence of NTCB, the appearance of a 412 nm absorption band due to the formation of thionitrobenzoate is observed. This rate of growth of this absorption band follows first order kinetics, and the maximum observed value occurs after one equivalent of NTCB has been consumed. This observation is in agreement with the reaction shown in Equation 5 and the mechanism shown in Scheme 1. Such an explanation is a viable one, because under the experimental conditions used with 5% aqueous acetonitrile solvent, the product obtained in Scheme 1, diethyl-2,3-dimercaptosuccinic acid, does not react with



(5)

NTCB. This reaction was carried out under the same experimental conditions (5% aqueous acetonitrile) as were used for the kinetic measurements. The failure to react was determined by the lack of any change in the intensity of the absorbance at 412 nm, or the peak for the SH resonances in the ^1H NMR spectrum. This failure of diethyl-2,3-dimercaptosuccinic acid to react with NTCB means that the observed loss of one equivalent of NTCB is in agreement with our proposed pathway for the hydrolysis.

EXPERIMENTAL

The compound $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ was prepared according to the literature procedure.[1] Acetonitrile was purified by distillation from lithium aluminum hydride, and the water purified by continuous distillation. Absorption spectra were obtained on a Hewlett-Packard diode array spectrometer with solutions contained in 1 cm quartz cells. NTCB (2-nitro-5-thiocyanatobenzoic acid) was purchased from Sigma chemicals. Nuclear magnetic resonance spectra were obtained on a GE Omega 400 spectrometer. Deuterium oxide (D_2O) was purchased from Aldrich Chemical Co. The kinetic data were obtained by collecting absorption data versus time for selected wavelengths with fixed time intervals between the absorption measurements. These data were then plotted using a kinetics software package to obtain the rate law and rate constants of the reactions. For the collection of the kinetic data, concentrations of the solutions of $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ in acetonitrile were in the range of 17.54–103.08 μmol. A Beer's law plot was obtained using three solutions of the compound in acetonitrile solvent having concentrations of 15.2 μM, 17.2 μM and 18.7 μM. The absorption spectra of these three solutions at 50°C were measured over the 200–400 nm range using in each case pure acetonitrile at 50°C as the reference solvent. The average optical density at 266 nm was measured for five solutions at each of these three concentrations. A plot of the absorbance at 266 nm against the solution concentration was linear with the line passing through the origin. A slope ($\in$) of 45,055 cm^{-1} mol^{-1} was obtained from this graph.

The initial rate method was used to determine the order of the reaction. In a typical kinetic run, 1 mL of a 5% aqueous acetonitrile solution was transferred to a quartz UV cell having a 1 cm path length. The cell was capped with a teflon stopper, and heated to 50°C. A reference spectrum was measured over the 200–400 nm range. Into this solution was transferred a portion of $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ in acetonitrile, and the absorption spectrum over the 200–400 nm range quickly measured. The solution concentration was obtained from the absorbance at 266 nm. The initial rate was measured from seven absorbance points at 266 nm with data being collected 30 seconds after mixing and terminating after 180 seconds. This procedure was repeated to obtain data for each of the nine concentrations shown in Table I.

A similar procedure was used to determine the rate order with varying water concentrations. Measurements were made on four solutions, each of which were prepared from a solution containing 18.7 mmol of $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ in 20 ml of acetonitrile. The other component was taken from four different aqueous acetonitrile solutions which contained 0.46, 1.70, 3.22 and 5.33 mmol of water in 10 mL of acetonitrile. The solutions for the measurements were prepared by transferring 0.1 mL of the first solution into 0.9 mL of each of the four solutions of aqueous acetonitrile.

The rate data that were collected to obtain the rate constants were determined using a similar procedure as for the rate order with the compound dissolved in 5% aqueous acetonitrile. The concentration of the compound was in the 10–12 μM range, and the concentration against time data were now collected for 6,000 seconds. The rate constant for each reaction run was calculated using the "Enzfitter" (Elsevier Biosoft) software routine, and then the rate constants obtained from each series of runs were averaged. The error in the reported rate constants reflect the range of values obtained in the separate rate runs.

The kinetic isotope effect was measured using two separate solutions of the compound, one of which contained H_2O and the other D_2O dissolved in the acetonitrile. Solutions were prepared containing either 10 mL of 5% H_2O in acetonitrile or 10 mL of 5% D_2O in acetonitrile. Each of these solutions were contained in 20 mL round bottom flasks under an atmosphere of nitrogen. These flasks were then placed in a stirred water bath controlled at a temperature of 50°C. After 10 min, an aliquot of 0.5 mL of $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$ was added to each solution by pipet. After 50 min, an aliquot of C_6D_6 was added to each solution, and the $^{31}P\{^1H\}$ NMR spectra were taken and integrated.

The reactions with 2-nitro-5-thiocyanatobenzoic acid (NTCB) were carried out by first preparing a solution (100 mL volume) containing potassium phosphate (0.12 g, 0.87 mmol) and disodium phosphate (0.43 g, 3.03 mmol) in aqueous acetonitrile (100 mL). To this solution was added NTCB (6.2×10^{-3} g, 27.5 μmol), and this stock solution was stored in a refrigerator. For each measurement, 1 mL of this solution was transferred into a quartz cell, which was stoppered and allowed to heat to 50°C for 5 min. A baseline reference spectrum was measured over the 200–500 nm range. To this solution was added an aliquot of solution containing $C_6H_5\overline{P(SCH(CO_2CH_2CH_3)CH(CO_2CH_2CH_3)S)}$, and the concentration of this compound was measured by its absorbance at 266 nm. Immediately after mixing, the absorbance at 412 nm was measured up to 5,000 seconds with each measurement timed for 120 sec intervals. This procedure was repeated five times with the concentration of the cyclic phosphonodithioite ranging from 7.8 to 8.5 μmol. The rate constants were calculated using the "Enzfitter" software routine, and the values were averaged to give a final value.

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