Phosphorus-31 Nuclear Magnetic Resonance Study of the Mechanism and Kinetics of the Hydrolysis of Zinc(II) *O,O*-Diethyl Dithiophosphate and Some Related Compounds

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^{31}P NMR spectroscopy has been used to investigate the mechanism and kinetics of hydrolysis of Zinc(II) *O,O*-diethyl dithiophosphate (**1**) (ZDTP) in 1,2-dimethoxyethane solution at 85 °C with ten equivalents of water. All major intermediates and products have been identified and the individual reaction rates determined. ZDTP was found to be hydrolysed ($k = 2.35 \times 10^{-4}$ s^{-1}) to phosphoric acid (**7**) *via* *O,O*-diethyl *S*-hydrogen dithiophosphate (**3**) ($k_{hyd} = 1.35 \times 10^{-2}$ s^{-1}) and thiophosphoric acid (**6**) ($k_{hyd} = 0.78 \times 10^{-5}$ s^{-1}). *O*-Ethyl *O,O*-dihydrogen and *O,O*-diethyl *O*-hydrogen phosphorothioates (**8**), (**9**), and ethyl dihydrogen phosphate (**10**) were produced as by-products of the reaction. From a study of the order of appearance of the intermediates and products, a detailed mechanism for the hydrolysis of ZDTP has been proposed. *O*-Ethyl *O,S*-dihydrogen phosphorodithioate (**4**) and dithiophosphoric acid (**5**) are found to be intermediates.

Zinc(II) bis(*O,O*-dialkyl dithiophosphates), $Zn[S_2P(OR)_2]_2$, often referred to as 'normal' or 'neutral' zinc *O,O*-dialkyl dithiophosphates, have been used extensively as lubricant oil-additives[1] for many years, owing to their dual ability to function as both anti-oxidant and anti-wear agents. While improving the performance of base oils, they themselves are subject to eventual oxidation,[2–5] thermal degradation[6–12] and hydrolysis.[13] The former aspects have been studied extensively, but so far little is known about the nature of their hydrolysis other than that they can give rise to unknown acidic oil-soluble and oil-insoluble products[14] which lead to degradation and loss of performance.

In this paper, we report a detailed investigation of the hydrolysis of 'normal' zinc(II) *O,O*-diethyl dithiophosphate (ZDTP), $Zn[S_2P(OEt)_2]_2$ (**1**) using ^{31}P NMR spectroscopy as a tool for the identification of intermediates and final products, and for elucidation of the mechanism of hydrolysis. Kinetic data were obtained, where appropriate, to confirm the sequence of reactions involved in the hydrolysis. Compound (**1**) was chosen for these hydrolysis studies because it is a simple homologue even though it was known to exist in a dimeric–monomeric equilibrium mixture in solution.[15] 1,2-Dimethoxyethane (DME) was chosen as the reaction medium because its miscibility with water and its boiling point (85 °C) allowed a homogenous-phase hydrolysis of ZDTP to be studied at a reasonable rate.

Results and Discussion

In quantitative work, and in some of the qualitative work, freshly prepared $Zn[S_2P(OEt)_2]_2$ (**1**) and distilled water were mixed in a 1:10 mole ratio in 1,2-dimethoxyethane (DME) and the solution was heated at 85 °C until completion of hydrolysis. The ^{31}P NMR hydrogen-decoupled spectrum was monitored for the disappearance of the starting material as well as for the initial formation, maximum concentration, and decay of any intermediates, and for the appearance of products. Identification of intermediates and products was based on the 'peak enhancement' technique by addition of authentic samples to the reaction mixtures and by matching of phosphorus–hydrogen spin–spin coupling constants and multiplicities in the ^{31}P NMR hydrogen-coupled spectrum.

Hydrolysis of Zinc(II) O,O-*Diethyl Dithiophosphate* (**1**) (*ZDTP*).—Mechanistically, it can be assumed that attack by water on ZDTP (**1**) (+101 ppm) could occur at one or more sites, including the α-carbon of the ethyl group,[16] the phosphorus atom,[17] and the metal atom.[18] From ^{31}P NMR spectra of the hydrolysis (see Figure 1) initial attack of water was found to occur exclusively at the metal atom as evidenced by the appearance of *O,O*-diethyl *S*-hydrogen phosphorodithioate, $(EtO)_2P(S)SH$ (**3**) (+84.6 ppm) as the primary hydrolysis product.[18]* As shown in Figure 1 subsequent hydrolysis of (**3**) yielded firstly phosphorothioic *O,O,O*-acid (**6**) (+58.7 ppm), and then phosphoric acid (**7**) (0.0 ppm), followed by *O*-ethyl *O,O*-dihydrogen phosphorothioate (**8**) (+61.3 ppm), *O,O*-diethyl *O*-hydrogen phosphorothioate (**9**) (+64.1 ppm) and ethyl dihydrogen phosphate (**10**) (−0.3 ppm), in that order.

Formation of (**3**) as the key intermediate in the hydrolysis of (**1**) was confirmed by the fact that under the same conditions of hydrolysis, an authentic sample of (**3**) produced the same products in identical proportions. Since the conversion of (**3**) into (**6**) involves a radical change of structure it was reasonable to assume the stepwise loss of the functional groups as shown in Scheme 1 whereby *O*-ethyl *O,S*-dihydrogen phosphorodithioate (**4**) and phosphorodithioic *O,O,S*-acid (**5**) are formed as intermediates. Under the original conditions of hydrolysis (85 °C and 10 equiv. of water) these compounds were not observed by ^{31}P NMR spectroscopy as intermediates, but monitoring of the hydrolysis of (**3**) to (**6**) at a lower temperature (25 °C) revealed the involvement of two phosphorus-containing species at +78.1 and +71.3 ppm [Figure 2(*a*)]. The identity of these two intermediates as the dithiophosphate (**4**), and dithiophosphoric acid (**5**), respectively, was established from the ^{1}H-coupled spectrum [Figure 2(*b*)] which showed a quintet for (**3**), triplet for (**4**) and singlets for (**5**) and (**6**) as expected ($^{3}J_{PH}$ = *ca.* 10 Hz).

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* The observation of (**3**) as the primary hydrolysis product points to the concomitant formation of a zinc complex, perhaps (**2**), (see Scheme 2) although the latter was not detected *per se*, in solution (*vide infra*).

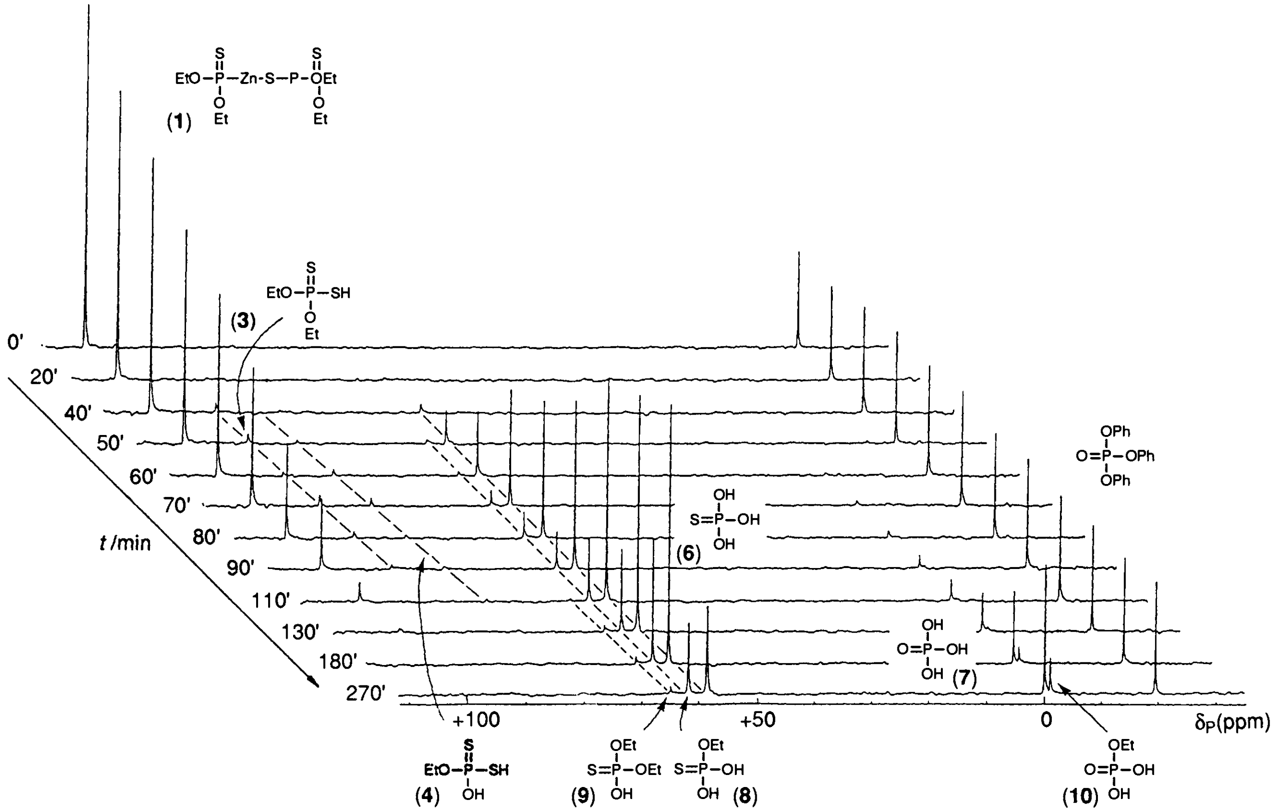
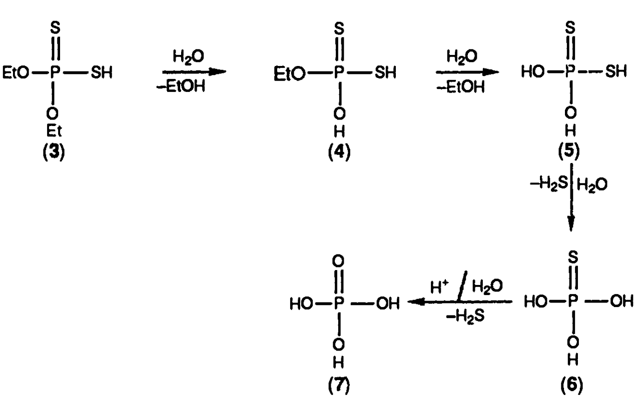


Figure 1. ^{31}P NMR spectra of the hydrolysis of ZDTP (**1**) as a function of time in DME at 85 ± 1 °C with 10 equiv. of water.



Scheme 1. Pathway for the hydrolysis of *O,O*-diethyl *S*-hydrogen phosphorodithioate (**3**).

Table 1. Rate constants (k) for hydrolysis of (**1**), (**3**), and (**6**) under pseudo-first-order conditions (10 equiv. of water and 85 ± 1 °C in DME).

Compound	$k_{obs}/10^{-4}$ s^{-1}
(**1**)	2.35
(**3**)	135.0
(**6**)	0.078

Of the final products (**7**), (**8**), (**9**), and (**10**), from the hydrolysis of both ZDTP (**1**) and diethyl dithiophosphoric acid (**3**), only (**7**) arises directly by hydrolysis. Reference to Figure 1 shows that (**8**), (**9**), and (**10**) are produced in that order, only *after* the formation of (**6**). The question as to their origin was answered by kinetic investigations into the relative rates of hydrolysis of ZDTP (**1**), its primary hydrolysis product (**3**) and the subsequently obtained phosphorothioic acid (**6**).

Kinetic Studies.—Kinetic analyses for the hydrolyses of ZDTP (**1**), diethyl phosphorodithioate (**3**) and phosphorothioic acid (**6**) were carried out individually under identical conditions, *viz.* 85 °C/DME and 10 equiv. of water, by monitoring their respective rates of disappearance using ^{31}P NMR spectroscopy. It was necessary to use triphenyl phosphate as an inert * internal standard and the ^{1}H-decoupled spectra were obtained under conditions in which the T_1 values of the various species were taken into account,† so that their signal intensities were proportional to their respective concentrations. In the case of ZDTP (**1**), it was found to be essential to use freshly prepared samples otherwise induction periods were observed, arising from surface hydrolysis and the formation of coatings of zinc(II) oxide. All the hydrolyses were found to follow pseudo-first-order kinetics (Figure 3); in the case of ZDTP (**1**) the plot was linear for only *ca.* two half-lives of the disappearance of substrate. During this period the only products to be observed were (**3**) and (**6**), *i.e.* before the formation of (**8**), (**9**), and (**10**), and the pH of the hydrolysis mixture decreased from 4.5 to 1.0. Thereafter the plot for the hydrolysis of (**1**) showed an exponential increase presumably due to acid catalysis since no change occurred in the rate profile, even in the presence of large excesses of water (30 equiv.).

The calculated pseudo-first-order rate constants (k_{obs}) for each species are presented in Table 1, and clearly establish that

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* Control experiments showed that triphenyl phosphate is not hydrolysed under the kinetic conditions.

† T_1 values were obtained using the inversion–recovery method and calculated from a least-squares logarithmic plot of the data using a JEOL FX90Q program (see the Experimental).

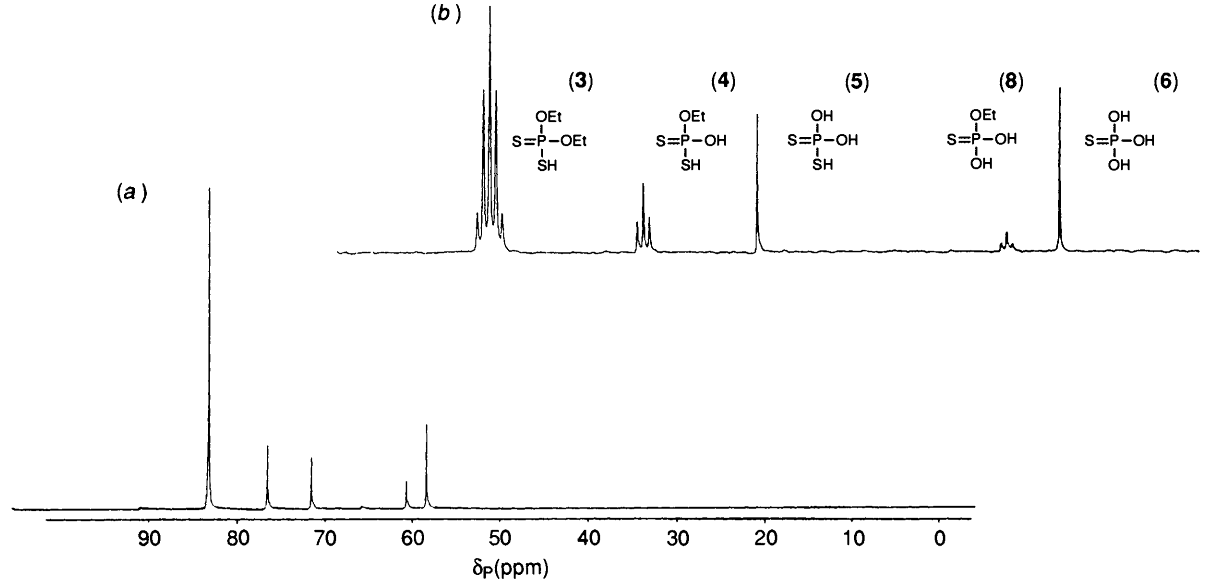


Figure 2. ^{31}P NMR spectra of the room temperature hydrolysis of *O*,*O*-diethyl *S*-hydrogen phosphorodithioate acid (**3**) in DME with 10 equiv. of water: (*a*) ^{1}H-decoupled; (*b*) ^{1}H-coupled.

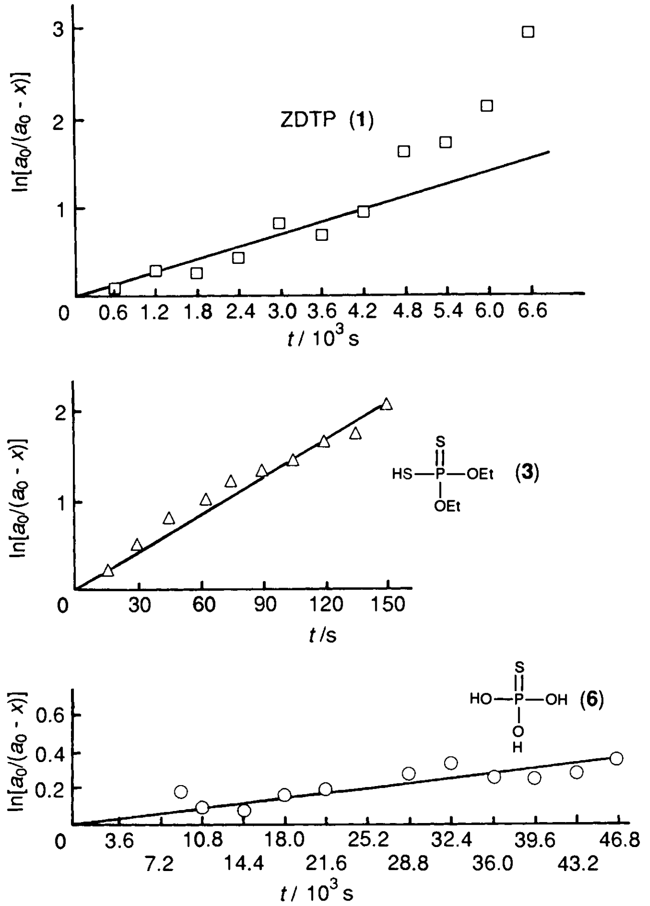


Figure 3. Plots of pseudo-first-order decay of (**1**), (**3**), and (**6**) at 85 ± 1 °C in DME with 10 equiv. of water.

the rate of hydrolysis of the phosphorothioic acid (**6**) is *very slow* compared with that of its precursor the *O*,*O*-diethyl phosphorodithioate (**3**) which in turn is hydrolysed at a *faster* rate than ZDTP (**1**) itself. This leads to a build-up in the concentration of (**6**) in the hydrolysis mixture (Figure 1) and suggests that both monoethyl thiophosphate (**8**) and diethyl thiophosphate (**9**) originate from the esterification of (**6**) with (**3**) and/or ethanol which is a product of the hydrolysis of (**3**). This assumption was verified when thiophosphoric acid (**6**) and *O*,*O*-diethyl *S*-hydrogen phosphorodithioate (**3**) were mixed in a 1:2 molar ratio in anhydrous DME and, upon being heated at 85 °C for 15 minutes, were found to produce (**8**) and (**9**) together with the transesterification by-product (**4**) (Figure 4). The same products could also be obtained from the esterification of (**6**) with ethanol under identical conditions but their rate of

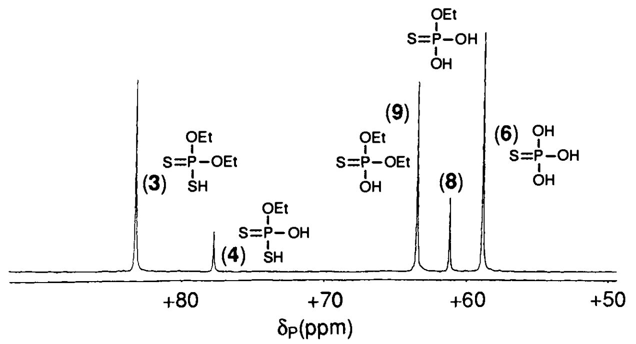


Figure 4. ^{31}P NMR H-decoupled spectrum of the reaction between phosphorothioic *O*,*O*,*O*-acid (**6**) and (**3**) in anhydrous DME at 85 ± 1 °C after 15 min.

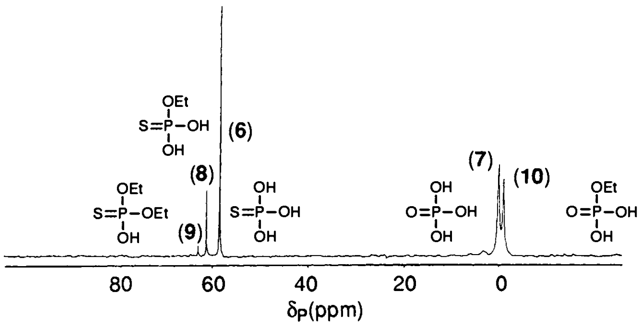
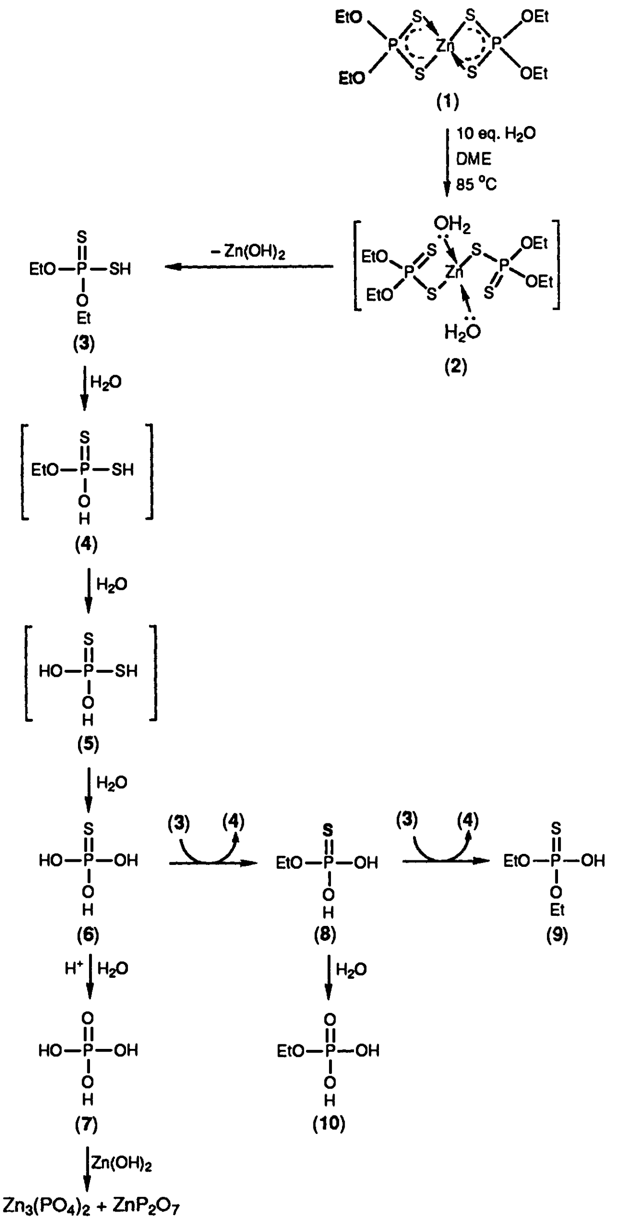


Figure 5. ^{31}P NMR H-decoupled spectrum of the reaction of (**6**) with ethanol in anhydrous DME at 85 ± 1 °C after 3 days.



Scheme 2. Mechanism for the hydrolysis of zinc(II) *O,O*-diethyl dithiophosphate (**1**).

Table 2. Elemental analysis of a precipitate from the hydrolysis of ZDTP (**1**).

Element	% Weight	Elemental ratio
Zn	41.0	1
S	7.6	0.38
P	16.9	0.87
C	1.3	0.18
H	1.5	2.38
O	31.7	3.18

formation was found to be much slower and even after 3 days most of (**6**) remained unconverted (Figure 5). As to the mechanism of the conversion of (**6**) into (**8**) and (**9**), we note that in none of these reactions are any *S*-ethyl species observed among the products. This implies that the conversion of (**6**) into (**8**) and subsequently (**9**), involves transfer of an ethoxy group rather than direct ethyl-group transfer, which would be expected to lead to some *S*-ethylation.

Further proof that (**8**) and (**9**) did not arise by the direct hydrolyses of (**4**) and (**3**) respectively, was obtained by monitoring the hydrolysis of (**3**) at room temperature to completion, whence (**8**) and (**9**) were observed *only after* the formation of (**6**). Thus, it can be concluded that the rate of esterification of (**6**) to (**8**) is much faster than its hydrolysis to (**7**) and that the subsequent hydrolysis of (**8**) gave rise to the formation of (**10**) as depicted in Scheme 2 which summarises the overall breakdown of ZDTP (**1**).

Finally, turning to the ultimate fate of the zinc in (**1**), we note that hydrolysis is accompanied by the gradual formation of a colourless precipitate. We assumed that the initially formed zinc complex (**2**) was transformed into insoluble zinc hydroxide, but the yield of precipitate was considerably higher than that expected (154% based on zinc hydroxide). An explanation for this ambiguity is that the zinc hydroxide undergoes further reactions with hydrogen sulphide and phosphoric acid formed during hydrolysis. This viewpoint is supported by the elemental analysis of a typical precipitate (Table 2) which showed that its composition is probably best formulated as a mixture of zinc hydroxide, zinc oxide, zinc sulphide, and zinc phosphates. Indeed, treatment of the precipitate with mineral acid resulted in evolution of hydrogen sulphide indicating the presence of a metal sulphide. In addition, ^{31}P NMR analysis of a solution of the precipitate in 2 mol dm^{-3} sodium hydroxide solution showed signals at +6.3 and +4.1 ppm which are identical with those for authentic samples of sodium phosphate and pyrophosphate, respectively. No NMR signals for sodium thiophosphate and/or pyrothiophosphate were observed. The yield of precipitate and soluble products increased and decreased, respectively, with time in keeping with the increase in concentration of phosphoric acid. The elemental ratios for the precipitate also changed with time, although it is important to note that the recovery of zinc from (**1**) in the precipitate was almost quantitative (96.25 ± 0.05%) regardless of its composition. This fact further reinforces the mechanism shown in Scheme 2 wherein attack of water occurs at the zinc centre, and in consequence does not give rise to any metal-containing soluble products.

Experimental

Melting points were determined on a Gallenkamp m.p. apparatus. Combustion analyses were carried out on Perkin-Elmer 240 or Carlo Erba 1106 elemental analysers. ^1H NMR spectra were recorded with a Bruker WP80 spectrometer operating at 33 °C or with a JEOL PMX60 spectrometer operating at 30 °C; ^{13}C NMR spectra with a Bruker WP200 SY instrument operating at 28 °C; and ^{31}P NMR spectra with a JEOL FX90Q spectrometer operating at 27 °C with an internal C_6D_6 capillary lock. ^{31}P chemical shifts are quoted with reference to 85% H_3PO_4; shifts to high frequency are positive in sign. The spectral window for kinetic measurements was 5 200 Hz with 8 K data, giving a digital resolution of 0.635 Hz per point. A pulse width of 4 μs (20°) was used with acquisition time of 0.787 s and a pulse delay of 5 s; and accumulations over 100 scans per spectrum gave a typical signal:noise ratio of $\geqslant 10:1$. Mass spectra were recorded with a Kratos Ms50 instrument. Solvents obtained from Aldrich, May and Baker, and Fisons were purified before use; chemicals and reagents from Aldrich, Sigma, and BDH were used without further purification.

Relaxation-time Measurements.—^{31}P spin–lattice (T_1) relaxation times were determined from proton-decoupled inversion–recovery Fourier transform (IRFT) spectra using a $(-T-180°-\tau-90°-)_n$ pulse sequence.[19] The 90 and 180°

Table 3. ^{31}P NMR spin-lattice (T_1) relaxation times for the compounds observed in the ZDTP hydrolysis studies.

Compound	T_1/s	Compound	T_1/s
Triphenyl phosphate	18.2	(**6**)	6.1
(**1**)	7.1	(**7**)	2.4
(**3**)	10.2	(**8**)	16.9
(**4**)	13.4	(**9**)	14.2
(**5**)	15.6	(**10**)	3.5

pulse times were 20.5 and 41 μs; T was 60 s; and typical values of τ were 0.02, 0.08, 0.5, 1, 2, 3, 4, 5, 7, 15, and 20 s. The T_1 values were calculated with the JEOL T_1 program which uses a least-squares fit to equation (1). Duplicate measurements

$$(M_o - M_z)/2M_o = \exp(-\tau/T_1) \qquad (1)$$

suggest a precision of ±10%. The results are summarised in Table 3.

O,O-*Diethyl* S-*Hydrogen Phosphorodithioate* (**3**).[20]—Ethanol (46 g, 1 mol) was added dropwise to a well stirred slurry of phosphorus pentasulphide (55.57 g, 0.25 mol) in toluene (500 cm^3) and the mixture was boiled under reflux for 3–5 h. The liberated hydrogen sulphide was led into saturated aqueous sodium hydroxide solution and/or aqueous $FeCl_3$ solution. On being cooled to room temperature, the reaction mixture deposited a viscous layer; the brown solution was decanted and solvent removed *in vacuo* to yield (**3**) (77.7 g, 83%), which was further purified by distillation, b.p. 54–55 °C at 0.5 mmHg (lit.,[21] 65 °C at 0.75 mmHg) (Found: C, 25.9; H, 5.70. Calc. for $C_4H_{11}O_2PS_2$: C, 25.8; H, 5.95%); $\delta_H(CDCl_3)$ 1.33 (6 H, dt, $^4J_{PH}$ < 1 Hz, CH_3), 3.37 (1 H, s, SH), and 4.17 (4 H, dq, $^3J_{PH}$ 10.3 Hz, CH_2); δ_P(DME) 84.7 ppm; (neat) 84.6 ppm [lit.,[22] $\delta_P(CDCl_3)$ 84.5].

S-*Potassium* O,O-*Diethyl Phosphorodithioate.*—Compound (**3**) (96.3 g, 0.52 mol) was neutralised with saturated aqueous $KHCO_3$ solution (pH 6–7) and the solution was extracted with ether (3 × 50 cm^3). Removal of water from the aqueous layer after separation yielded the potassium salt (80.4 g, 72%) which was dried *in vacuo* over phosphorus pentaoxide overnight and recrystallised from acetone/ether, m.p. 194–195 °C [lit.,[23] 152–153 °C (ether/ethanol)] (Found: C, 20.8; H, 4.5. Calc. for $C_4H_{10}KO_2PS_2$: C, 21.4; H, 4.5%); $\delta_P(D_2O)$ 110.6 ppm (lit.,[22] δ_P 110.5 ppm).

'*Normal*' *Zinc*(II) O,O-*Diethyl Phosphorodithioate* (**1**).—Potassium *O,O*-diethyl phosphorodithioate was mixed with zinc(II) sulphate in a 2:1 mole ratio in aqueous solution in a separating funnel with vigorous shaking. The solution was extracted with ether and the extract was evaporated to dryness *in vacuo* to yield (**1**) (90%) which was recrystallised from n-heptane, m.p. 79–80 °C (lit.,[24] 77 °C) (Found: C, 22.25; H, 4.8. Calc. for $C_8H_{20}O_4P_2S_4Zn$: C, 22.4; H, 4.6%); $\delta_H(CDCl_3)$ 1.37 (12 H, dt, $^4J_{PH}$ < 1 Hz, ^3J_H 7.1 Hz, CH_3) and 4.23 (8 H, dq, $^3J_{PH}$ 9.7 Hz, CH_2); $\delta_C(CDCl_3)$ 15.66 (d, $^3J_{PC}$ 8.3 Hz, CH_3) and 64.47 (d, $^2J_{PC}$ 6.7 Hz, CH_2); δ_P(DME) 101.5 ppm; ($CDCl_3$) 96.5 ppm.

Phosphorothioic Acid O,O,O-*Acid* (**6**).[25]—Distilled water (100 cm^3) was added dropwise to a vigorously stirred slurry of phosphorus pentasulphide (111.1 g, 0.5 mol) in acetone (200 cm^3) cooled to 0 °C. The reaction temperature was maintained at below 10 °C and after completion of the addition the mixture was stirred for 1.5 h and the temperature allowed to reach 25 °C. The mixture was filtered and cooled to below 0 °C and refiltered through Celite under nitrogen. Solvent was removed *in vacuo* from the filtrate to yield (**6**) (95 g, 83%) which was then stored in dry methanol at below −20 °C. The di-anilium salt of (**6**) decomposed at 124–126 °C without melting, (methanol/ether) (unreported); $\delta_H[(CD_3)_2SO]$ 5.65 (7 H, s, NH_3^+/H^+), 6.25 [6 H, m, $-(CH)_3-$], and 6.75 [4 H, m, $-(CH)_2-C-N$]; $\delta_C[(CD_3)_2SO]$ 116.37 [s, $-(\mathit{C}H)_2-C-N$], 118.89 [s, $-(\mathit{C}H)-(CH)_2-C-N$], 129.23 [s, $(\mathit{C}H)-(CH)-C-N$], and 144.77 (s, $-C-N$); $\delta_P[(CD_3)_2SO]$ 57.48 ppm; (CD_3OD) 47.59 ppm; (CH_3OD) 47.99 ppm; m/z 301 [(M + 1), 2%] FAB. The free acid gives $\delta_H(D_2O)$ 3.42 (s); $\delta_P(D_2O)$ 55.3; (DME) 58.7 ppm.

O-*Ethyl* O,O-*Dihydrogen Phosphorothioate* (**8**).[26]—Ethyl dichlorothiophosphate (10 g, 0.056 mol) was added dropwise to a vigorously stirred solution of aqueous sodium hydroxide (100 cm^3, 10%) and dioxane (15 cm^3) kept at 90 °C. Stirring was continued for 30 min after the mixture had become homogeneous and it was then cooled and neutralised with hydrochloric acid. After removal of the solvent, the residue was extracted with hot methanol (3 × 20 cm^3) and the extracts were concentrated to *ca.* 10 cm^3. On addition of acetone, the disodium salt (7.75 g, 90%) crystallised out, 240–242 °C (decomp.); $\delta_H(D_2O)$ 1.35 (3 H, t, ^3J_H 7.2 Hz, CH_3) and 4.00 (2 H, dq, $^3J_{PH}$ 6.8 Hz, CH_2); δ_P(MeOH) 51.5, (D_2O) 42.8 ppm [lit.,[27] $\delta_P(D_2O)$ 42.02 ppm]; m/z 187 [(M^+ + 1), 50%] FAB. Compound (**8**) was obtained by treatment of the disodium salt with DOWEX-50W resin in DME overnight (Found: C, 16.5; H, 4.9. Calc. for $C_2H_7O_3PS$: C, 16.9; H, 5.0); $\delta_H(D_2O)$ 1.22 (3 H, t, ^3J_H 7.2 Hz, CH_3), 3.85 (2 H, dq, $^3J_{PH}$ 9.2 Hz, CH_2), and 4.65 (1 H, s, OH); δ_P(DME) 61.3 ppm.

O,O-*Diethyl* O-*Hydrogen Phosphorothioate* (**9**).[28]—Prepared by the acidification of *N,N,N*-triethyl ammonium *O,O*-diethyl phosphorothioate, made by boiling a mixture of diethyl phosphite (14.8 g, 0.107 mol), sulphur (3.4 g, 0.106 mol), and triethylamine (10.3 g, 0.102 mol) in ether (40 cm^3) for 3.5 h. $\delta_H(CDCl_3)$ 1.25 (1 H, s, NH), 1.45 (15 H, dt, ^3J_H 7.2 Hz, CH_3), 3.25 (6 H, q, NCH_2), and 4.10 (4 H, dq, $^3J_{PH}$ 8.3 Hz, OCH_2); $\delta_P(CDCl_3)$ 57.2 ppm; (DME) 56.5 ppm. Treatment with hydrochloric acid and extraction with ether gave (**9**) (14.8 g, 81%) (Found: C, 28.2; H, 6.8. Calc. for $C_4H_{11}O_3PS$: C, 28.2; H, 6.5%); $\delta_H(CDCl_3)$ 1.50 (6 H, t, ^3J_H 7.2 Hz, CH_3), 4.30 (4 H, dq, $^3J_{PH}$ 9.3 Hz, CH_2), and 7.80 (1 H, s, OH); $\delta_P(CDCl_3)$ 57.5 ppm; (DME) 63.5 ppm [lit.,[29] δ_P(neat) 58.1 ppm].

O-*Ethyl* O,O-*Dihydrogen Phosphate* (**10**).[30]—Phosphorus acid (0.88 g, 0.011 mol) was boiled under reflux at 87 °C for 15 min with vigorous stirring in the presence of mercury(II) chloride (2.72 g, 0.010 mol), ethanol (15 cm^3) and triethylamine (5 cm^3, 0.036 mol). The reaction mixture was filtered twice and solvent removed to yield (**10**) (1.08 g, 80%), derivatised as the dicyclohexyl ammonium salt, m.p. 205–206 °C (ethanol) [lit.,[31] 205–206 °C (aq. Me_2CO)] (Found: C, 51.5; H, 10.4; N, 8.3. Calc. for $C_{14}H_{33}N_2O_4P$: C, 51.8; H, 10.3; N, 8.6%); $\delta_H(D_2O)$ 1.1 (2 H, s, NH^+), 1.25 [12 H, s, $-(CH_2)_3-$], 1.35 (3 H, t, ^3J_H 7.2 Hz, CH_3), 1.85 [12 H, m, $-(CH_2)_2-C-NH_2$] 3.2 (2 H, m, $-CHN$) and 3.85 (2 H, dq, $^3J_{PH}$ 7.7 Hz, $-CH_2O-$); $\delta_P(D_2O)$ 3.8 ppm; free acid (DME) −0.6 ppm.

Phosphorodithioic O,O,S-*Acid* (**5**).[32]—2-Methylpropan-2-ol (t-butyl alcohol) (14.8 g, 0.199 mol) was added dropwise to a vigorously stirred mixture of phosphorus pentasulphide (4 g, 0.018 mol) in DME (15 cm^3) under nitrogen at 45 ± 1 °C for 5 h. The resultant *O,O*-di-t-butyl dithiophosphoric acid (*ca.* 80%) [δ_P(DME) +64.2 ppm] was neutralised with saturated aqueous $KHCO_3$ solution and dried *in vacuo*. The dried potassium salt [$\delta_P(D_2O)$ +91.3 ppm; (DME) +93.8 ppm] was treated with aqueous lead(II) acetate solution (5.5 g in 25 cm^3 H_2O) to yield the lead(II) salt (8.9 g, 72.6%) which was dried and recrystallised from di-isopropyl ether, m.p. 88–92 °C (decomp.) [lit.,[32] 109 °C (decomp.)] (Found: C, 27.6; H, 5.2. Calc. for $C_{16}H_{36}O_4P_2PbS_4$: C, 27.9; H, 5.3%); $\delta_H(CDCl_3)$ 1.75 (36 H, br s); $\delta_C(CDCl_3)$ 30.48 (d, $^3J_{PC}$ 4.2 Hz, CH_3) and 86.1 [d, $^2J_{PC}$ 11.98 Hz, $C(CH_3)_3$]; $\delta_P(CDCl_3)$ +76.5 ppm. The free acid (**5**) was obtained by treating either the crude *O,O*-di-t-butyl phosphorodithioate or the potassium salt, in DME, with 3 equiv. of trifluoroacetic acid (TFA) at room temperature. This reaction gave (**5**) (*ca.* 10% and several other by-products as observed by ^{31}P NMR spectroscopy.

Hydrolysis of 'Normal' Zinc(II) O,O-*Diethyl* S-*Hydrogen Phosphorodithioate* (**1**).—Compound (**1**) (1.55 g, 3.55 mmol) was mixed with triphenyl phosphate (0.546 g, 1.67 mmol) and distilled water (0.642 g, 35.6 mmol) in DME (10 cm^3). The resultant solution was transferred to a series of 5 mm NMR tubes which were heated in a water-bath maintained at constant temperature (85 ± 1 °C). Kinetic measurements were obtained by monitoring the ^{31}P NMR (hydrogen-decoupled) spectrum for the disappearance of ZDTP at various time intervals when an NMR tube was removed and immersed in an ice-bath to quench the reaction. The rate constants were reproducible to within $\pm 10\%$.

Hydrolysis of O,O-*Diethyl* S-*Hydrogen Phosphorodithioate* (**3**).—Compound (**3**) (0.656 g, 3.52 mmol) was mixed with triphenyl phosphate (0.553 g, 1.69 mmol) and distilled water (0.661 g, 36.7 mmol) in DME (10 cm^3). Hydrolysis and kinetic measurements were carried out as previously described for the hydrolysis of ZDTP.

Hydrolysis of Phosphorothioic O,O,O-*Acid* (**6**).—Triphenyl phosphate (0.554 g, 1.70 mmol) was mixed with (**6**) (0.438 g, 3.84 mmol) and distilled water (0.694 g, 38.5 mmol) in DME (10 cm^3). Hydrolysis and kinetic measurements were carried out as described for the hydrolysis of ZDTP.

Reactions of Phosphorothioic O,O,O-*Acid* (**6**).—(*a*) *With* O,O-*diethyl* O-*hydrogen phosphorodithioate* (**3**).—Compound (**3**) (0.661 g, 3.5 mmol) was mixed with (**6**) (0.810 g, 7.10 mmol) and triphenyl phosphate (0.620 g, 1.90 mmol) in anhydrous DME (10 cm^3).

(*b*) *With ethanol.*—(**6**) (0.405 g, 3.55 mmol) was mixed with ethanol 0.327 g, 7.10 mmol) and triphenyl phosphate (0.587 g, 1.80 mmol) in anhydrous DME (10 cm^3). Both reactions were monitored as described in the hydrolysis of ZDTP.

Acknowledgements

We thank Professor R. F. Hudson FRS for helpful discussions.

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Paper 9/03703I
Received 12*th January* 1989
Accepted 10*th January* 1990