# PHOSPHORUS - 31 NUCLEAR MAGNETIC RESONANCE STUDY OF THE MECHANISM AND KINETICS OF THE HYDROLYSIS OF ZINC (II) O,O' - DIALKYL DITHIOPHOSPHATE, ITS BASIC SALT AND SOME RELATED COMPOUNDS.

A Thesis Submitted for the Degree of Doctor of Philosophy

at the

UNIVERSITY OF EDINBURGH

by

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April 1990

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University of Edinburgh

*To my Mum and Dad*

*for their love, support and encouragement*

*throughout the years.*

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**Published Papers** - ref. 106, J. Chem. Soc., Perkin Trans. 2, 1990, 753-8, covering the contents of Chapter 3;
another paper covering the contents of Chapter 4 has been submitted for publication in the same journal.

Paper 0/00387E

## Declaration

I declare that this thesis is entirely my own composition, that the work of which it is a record has been carried out by myself, and that it has not been submitted for a Higher Degree. Proper acknowledgement is given where due as regards pieces of work carried out by other persons.

## Postgraduate Lecture Courses

The following is a statement of the courses attended during the period of research:-

Organic Research Seminars (three years attendance),
Mass Spectrometry - Prof. K.R. Jennings (5 lectures),
Business Management - Prof. S. Coke (4 lectures),
Modern Methods of N.M.R. - Dr. I.H. Sadler (5 lectures),
Recent Advances in Organic Chemistry - Prof. R. Ramage et al. (5 lectures),
2D - Nuclear Magnetic Resonance - Drs. R.L. Baxter, I.H. Sadler & B. Birdsall (5 lectures),
Medicinal Chemistry - staff of M.,S. & D.(Terling's Park, U.K.) (5 lectures),
Current Topics in Organic Chemistry - Prof. R. Ramage et al. (5 lectures).

## German Language Test

I have passed the stipulated Departmental German Language Test.

## Abstract

$^{31}P$ n.m.r. spectroscopy was used to investigate the mechanism and kinetics of hydrolysis of zinc (II) O,O'-dialkyl dithiophosphates (ZDTP's) in aqueous 1,2-dimethyoxyethane solution at 85°C. All the major intermediates and products were identified and the relative reaction rates of the key steps in the hydrolysis determined. Diethyl ZDTP was found to be hydrolysed ($k=2.35 \times 10^{-4}\ s^{-1}$) to phosphoric acid *via* O,O'-diethyl dithiophosphoric acid ($k_{hyd}=1.35 \times 10^{-2}\ s^{-1}$) and thiophosphoric acid ($k_{hyd}=0.78 \times 10^{-5}\ s^{-1}$); O-ethyl dithiophosphoric acid and dithiophosphoric acid were found to be intermediates; O-ethyl, O,O'-diethyl thiophosphoric and O-ethyl phosphoric acids 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's has been proposed.

The relationship between the 'normal' salt of a ZDTP and its 'basic' form was also studied and the isopropyl derivative was found to dissociate in a variety of organic solvents (including xylene, toluene, diethyl ether, chloroform, 1,2-dimethoxyethane, acetone, dimethyl formamide and dimethyl sulphoxide) *via* a facile equilibrium into its 'normal' salt and zinc (II) oxide. The dissociation was promoted by increasing temperature and solvent polarity and by increasing the water content in aqueous 1,2-dimethoxyethane. This equilibrium in favour of the 'normal' salt and zinc (II) oxide was also acid-catalysed. Zinc (II) oxide arising from the dissociation of the 'basic' form was found to inhibit the hydrolysis of 'normal' zinc (II) O,O'-diisopropyl dithiophosphate by reaction with its primary hydrolysis product, O,O'-diisopropyl dithiophosphoric acid . Eventual hydrolysis occurred after all the zinc (II) oxide was consumed.

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## Symbols and abbreviations

| | |
|---|---|
| mol $dm^{-3}$, mol $cm^{-3}$ | moles / litre, moles / cubic centimetre |
| ml or mL | millilitre(s) |
| $^{o}C$ | degree(s) Celsius |
| m.p. | melting point |
| b.p. | boiling point |
| h, min., s | hour(s), minute(s), second(s) |
| NMR | nuclear magnetic resonance [spectroscopy] |
| $\delta_{[\ ]}$ p.p.m. | chemical shift (delta)[nucleus], parts per million |
| (s,d,t,q,m,dt,etc.) | singlet, doublet, triplet, quartet, multiplet, doublet of triplets |
| m/s | mass spectroscopy |
| M+ | molecular ion mass |
| tlc | thin layer chromatography |
| $^{3}J_{PH}$ | (no. of bonds) coupling constant (coupled nuclei) |

# CHAPTER 1

METAL DITHIOPHOSPHATES AND THEIR ROLE AS LUBRICATING OIL ADDITIVES


| | | |
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*'If you can keep your head when all about you*
*Are losing theirs.....*
*.....If you can dream - and not make dreams your master;*
*If you can think.....'*

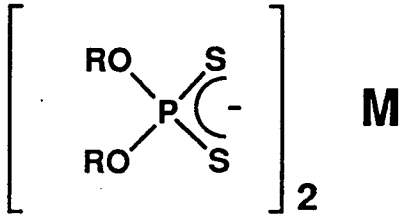
*R. Kipling*

# CHAPTER 1

# METAL DITHIOPHOSPHATES AND THEIR ROLE AS LUBRICATING OIL ADDITIVES

## 1.1 The nature of lubricating oils and the function of oil additives.

Since about the middle of the nineteenth century, chemical compounds have been used as lubricant additives when mixing petroleum oils and fatty acid soaps produced lubricating greases.[1] The arrival of motor vehicles at the end of the nineteenth century found plain mineral oils, solid fats and fatty oils unsatisfactory for the lubrication problems which arose. For example, the need for lubricating greases which would not become rancid and corrosive towards metal surfaces was met by the use of mineral oils thickened with fatty acid soaps as mentioned earlier. Progressive advances in engine and gear design have placed increasingly severe demands on lubricants, demands which are not satisfied by uncompounded mineral oils and succeeding years have seen the growing use of a wide variety of chemicals as additives.[2] Thus, additives are mixed with lubricating base oils to economically achieve specific performance goals since lubricating oils are often expected to operate under diverse conditions and to satisfy many different requirements. Lubricating base

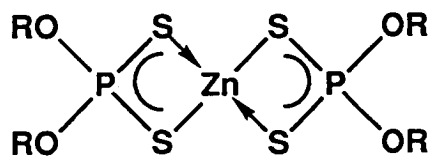



(1)

R = alkyl, aryl or alkylaryl

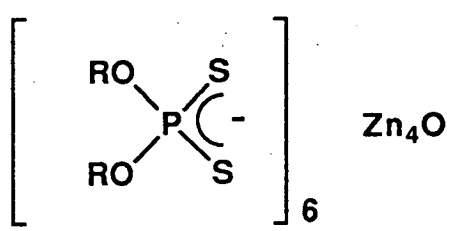
M = Zn, Cd, Ni, Mo, Pb or Sb

oils consist of straight chain and cyclic hydrocarbons (typically 70-85%), aromatics (15-30%) and a very small amount of polar heteroatoms (nitrogen, sulphur and oxygen) (ca. 0.5-2.0%).[3] The ability of base oils to respond to friction and wear and its stability towards oxidation are often dependent on the total concentration of the heteroatoms and the distribution of the heteroatom in various functional forms. There are many different types of additives in use today for oxidation inhibition, friction and wear control, corrosion and rust prevention, engine cleanliness, and foaming. Moreover, a single type of additive may perform more than one function. For example, basic phenates are used as acid neutralisers but also possess the ability to function as detergents.[4] Similarly, metal dithiophosphates (MDTP's) (1) are used as anti-oxidants and anti-wear agents.[2,3,5]




(2)

R = alkyl, aryl or alkylaryl



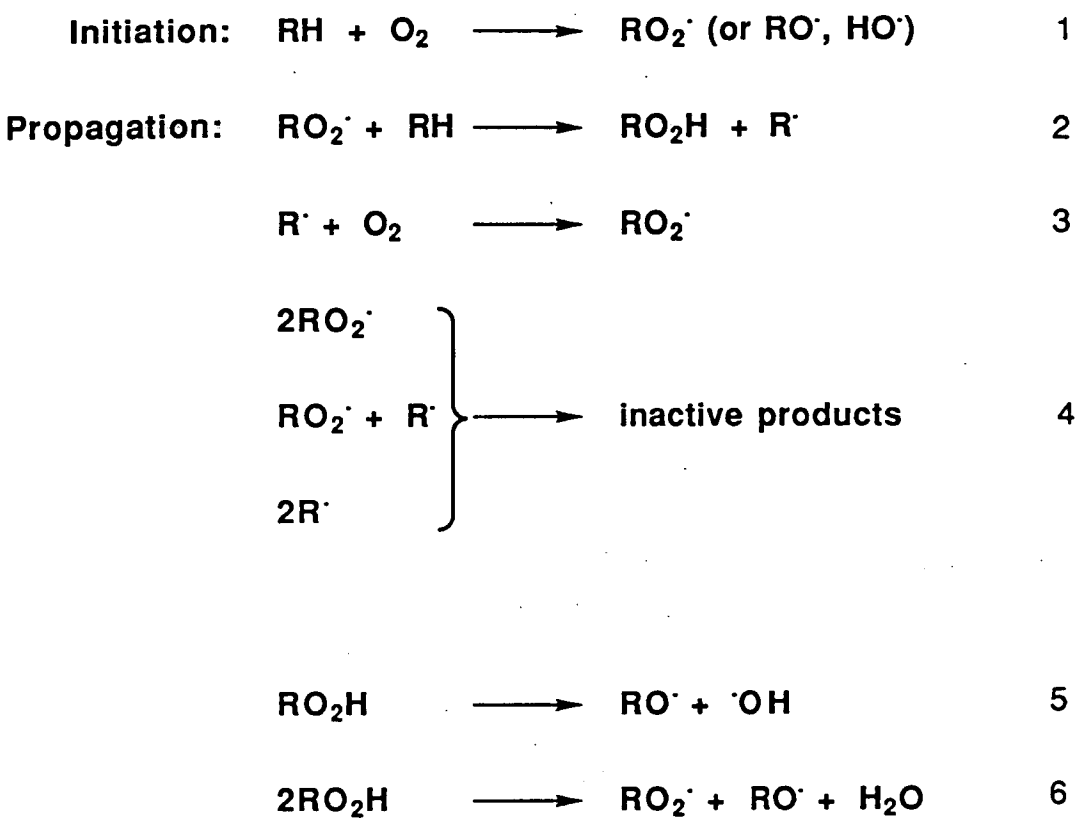

(3)

R = alkyl, aryl or alkylaryl

## 1.2 Zinc dithiophosphates as anti-oxidant and anti-wear agents.

The best known and most widely used of the MDTP's are the zinc dithiophosphates (ZDTP's) (2). ZDTP's are classified as alkyl, primary or secondary, or aryl, depending upon the alcohol from which they are derived. Based on their relative performance levels, the ZDTP's are selected for particular applications[6]. For example, in diesel engine oils aryl ZDTP's are very much favoured because of their outstanding thermal stability. Primary ZDTP's are used extensively in both engine oils and hydraulic oils whilst secondary ZDTP's are selected for hydraulic oils, transmission and gear oils. Primary and secondary ZDTP's have been selected owing to their relatively good anti-wear performance, good anti-oxidant qualities and low cost. Commercial ZDTP's usually contain mixed alkyl groups and are used normally in conjunction with other additives depending upon the particular engine requirements. Both the anti-wear and thermal stability properties of the 'alkyl' - type ZDTP's vary with different alkyl substituents.

ZDTP's as a general class of compounds are known to exist in two forms, referred to as normal (2) and basic (3). Commercial ZDTP's usually contain both types because the manufacturing process for the normal salt from zinc (II) oxide and $(RO)_2PS_2H$ (R = alkyl or aryl or


Initiation: RH + O2 → RO2· (or RO·, HO·) 1
Propagation: RO2· + RH → RO2H + R· 2
R· + O2 → RO2· 3
2RO2·
RO2· + R·
2R·
→ inactive products 4
RO2H → RO· + ·OH 5
2RO2H → RO2· + RO· + H2O 6

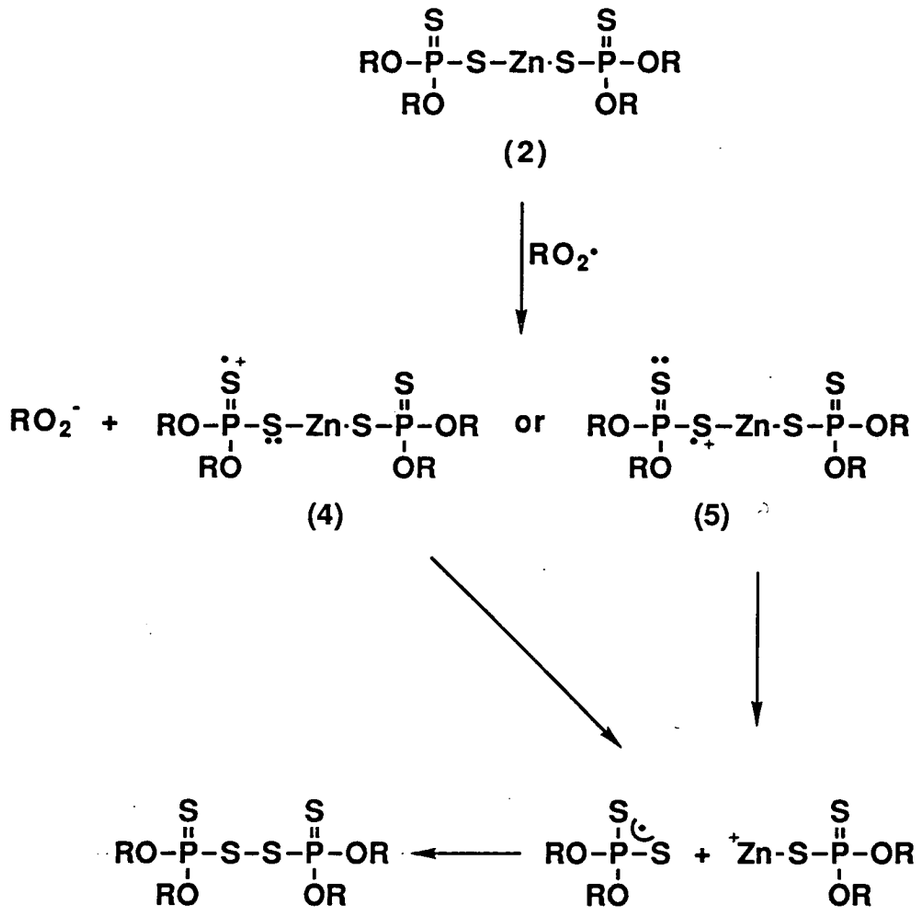
SCHEME 1

alkylaryl) leads to the formation of the basic salts as by-products to varying extents.

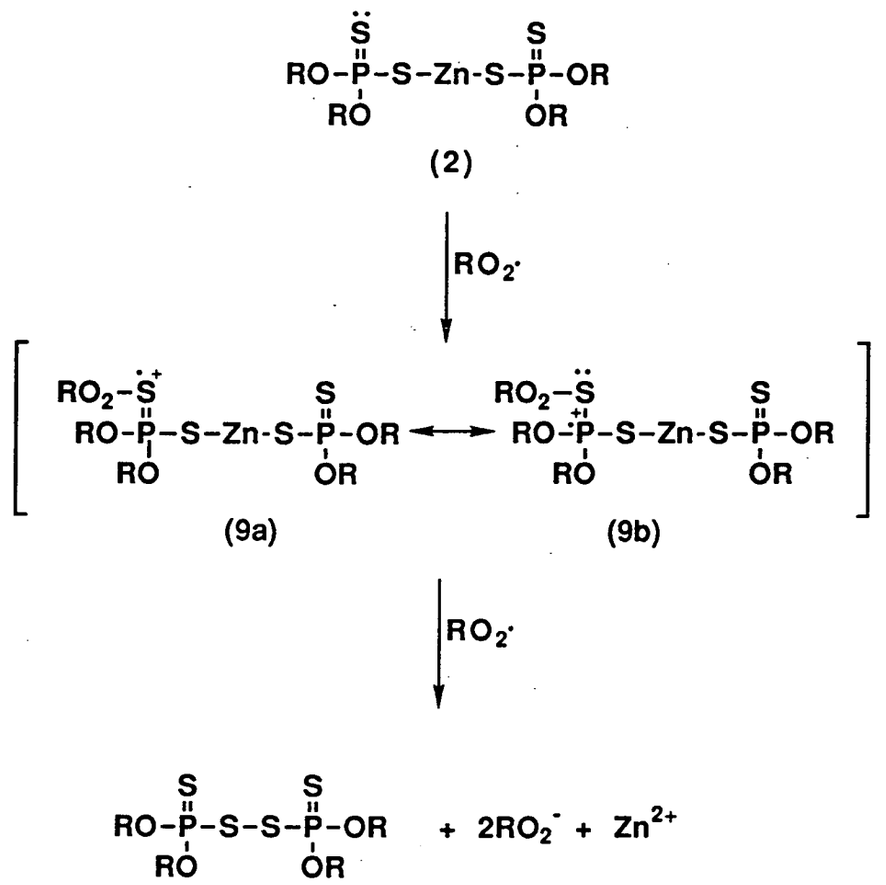
Inspite of having been used for over four decades as anti-oxidant and anti-wear additives the mode of action of ZDTP's in both fields is still a controversial subject. ZDTP's in a formulated oil decompose as a result of exposure to a variety of influences whilst performing under operating conditions, (a) oxidation, (b) thermal degradation, (c) reaction at metal surfaces, (d) interactions with other additives, and (e) hydrolysis. These different[6a] modes of decomposition of ZDTP's are discussed in the following sections.

In order to put into perspective the operation of ZDTP's in mineral lubricating oils, particularly its role as anti-oxidant, it is useful to be aware of the manner in which lubricating oils are oxidised. In the temperature range of operation, it has been well established[7] that hydrocarbons (RH) oxidise by a free-radical chain mechanism as shown in Scheme 1. However, it is known that, with most of the types of hydrocarbons occuring in lubricating oils, at a very early stage in the oxidation the primary oxidation product, the hydroperoxide $RO_2H$, decomposes to give radicals which provide the major source of initiation (equations 5 and 6). The decomposition of the hydroperoxide (and subsequent oxidation and interaction of the products) is the major source of the observed oxidation products. The hydroperoxide also

accounts for the auto-catalytic behaviour of oxidizing hydrocarbons, i.e. oxidation rate increases with extent of oxidation. In reality the relative contributions of equations 1, 5 and 6 of initiation is largely unknown, except that these can be catalysed by metals such as copper or iron.[7,8]



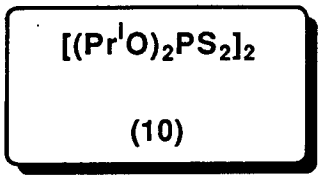

SCHEME 2

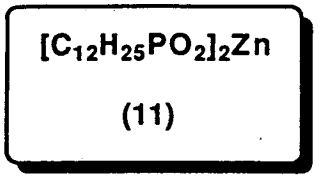



SCHEME 3

## 1.3 Degradation of ZDTP's by oxidation

Anti-oxidants can be broadly classified by their mode of action. They can function either as "chain-breaking" inhibitors by scavenging chain-propagating alkyl peroxy radicals ($RO_2\cdot$) or as "peroxide-destroyers", reacting rapidly with the hydroperoxide ($RO_2H$) by a non-radical mechanism. MDTP's have been shown to react by both ways. Colclough and Cunneen[9] had proposed that the ZDTP's react with $RO_2\cdot$ radicals via an electron transfer mechanism summarised in Scheme 2, in which the peroxy radical is converted into a peroxy-anion by electron abstraction from the electron-rich sulphur atom, resulting in the formation of the disulphide (8) by the rapid decomposition of (4) and (5) followed by mutual recombination. Burn[10] showed this to be inadequate and proposed that the electron-transfer mechanism involved a stabilised peroxy intermediate (9), which on attack of a second peroxy radical led to intramolecular dimerization of the incipient dithiophosphate radicals (6), (illustrated by Scheme 3) eventually resulting in disulphide (8) formation. He suggested that the function of the metal in Scheme 3 was to provide an easy route for the heterolysis of the intermediate peroxy radical-zinc complex (9). Evidence in support of this mechanism was obtained from experiments which showed that both the disulphide (10) and the zinc dialkyl phosphate (11),




$$RO_2^{\cdot} + [(RO)_2PS_2]_2Zn \longrightarrow ROO\text{-}Zn\text{-}S_2P(OR)_2 + (RO)_2PS_2^{\cdot} \quad 7$$

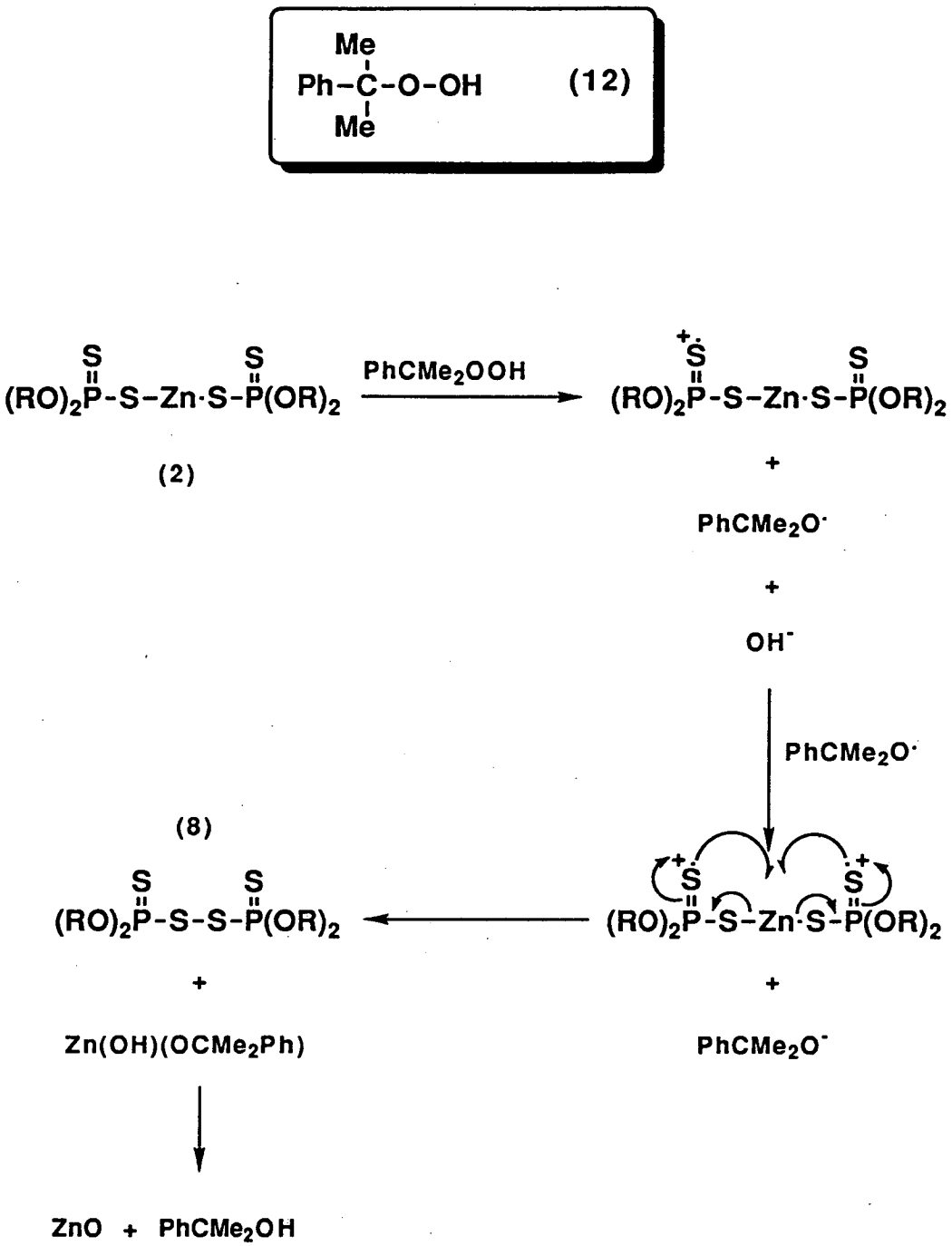
(6)

$$(RO)_2PS_2H + RO_2^{\cdot} \longrightarrow (RO)_2PS_2^{\cdot} + RO_2H \quad 8$$

containing no metal and sulphur respectively, do not react with tert-butyl peroxy radicals.

Howard et al.[11] later argued that alkyl peroxy radicals react with ZDTP's and related complexes at the metal by an electron transfer mechanism generating the dithiophosphate radical (6) (equation 7).
They showed that dialkyl dithiophosphoric acids, $(RO)_2PS_2H$, react rapidly with $Bu^tOO\bullet$ preventing auto-oxidation of styrene. The probable mechanism for the observed inhibition involves hydrogen abstraction from the -SH group by $RO_2\bullet$, the resulting $(RO)_2PS_2\bullet$ being less reactive than $RO_2\bullet$ towards propagation (equation 8). The disulphide (8) has been identified and confirmed recently as the major product.[12]

On a different tack, the anti-oxidant activity of ZDTP's has been shown[13,14] to involve heterolytic hydroperoxide decomposition. The presence of ZDTP's caused the formation of phenol from cumene hydroperoxide (12). Unable to ascertain a clear mechanism for this ionic decomposition of hydroperoxide (12), the authors concluded that it was the intermediates from the decomposition of ZDTP's that were responsible. Burn et al.[15] observed that catalytic decomposition of cumene hydroperoxide (12) occurred in three stages. An initial fast stage involving the formation of the disulphide (8)

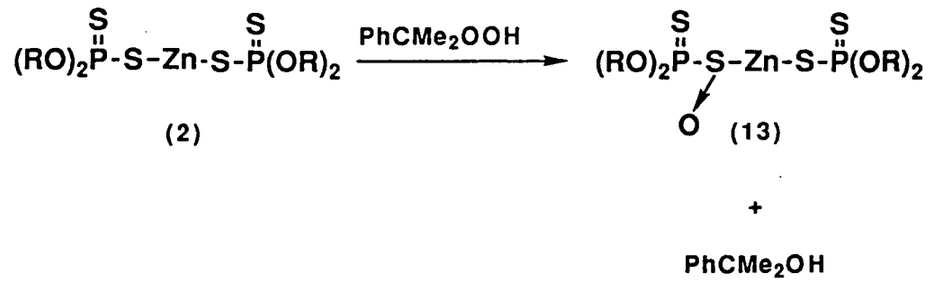

Me
Ph–C–O–OH
Me
(12)
PhCMe2OOH
(RO)2P-S-Zn·S-P(OR)2
(2)
PhCMe2O·
OH⁻
PhCMe2O·
(8)
(RO)2P-S-S-P(OR)2
Zn(OH)(OCMe2Ph)
ZnO + PhCMe2OH

SCHEME 4

followed by a slow second stage (induction period) probably involving the formation of the unknown active catalytic intermediate. The fast third stage involved the decomposition of the hydroperoxide (12) giving products characteristic of ionic decomposition.

Since the disulphide (8) was formed at the first stage, it was concluded that initially the reaction was primarily the reduction of cumene hydroperoxide (12) to dimethyl benzyl alcohol with the concomitant oxidation of the ZDTP's to the corresponding disulphide (8). The proposed major mechanism is outlined in Scheme 4. This work was subsequently confirmed by other groups.[16-21] The products derived from the cumene hydroperoxide were identified as acetone, phenol, $\alpha$-methylstyrene, $\alpha$,$\alpha$-dimethyl benzyl alcohol & acetophenone.

The other possible mechanisms[15] (minor) in operation during the first stage are summarised in Scheme 5 and Scheme 6. The type of oxygenation reaction shown in Scheme 5 is well established for sulphides and for phosphites and phosphines.[23] However, only Scheme 4 accounts for the production of the disulphide (8) and is considered the main initial reaction. Product yield studies indicated that the formation of phenol and acetone occur mainly in the third stage, this being the stage corresponding to the catalytic decomposition reported previously.[13,14,24,25,26] Scheme 7 depicts the general




SCHEME 5

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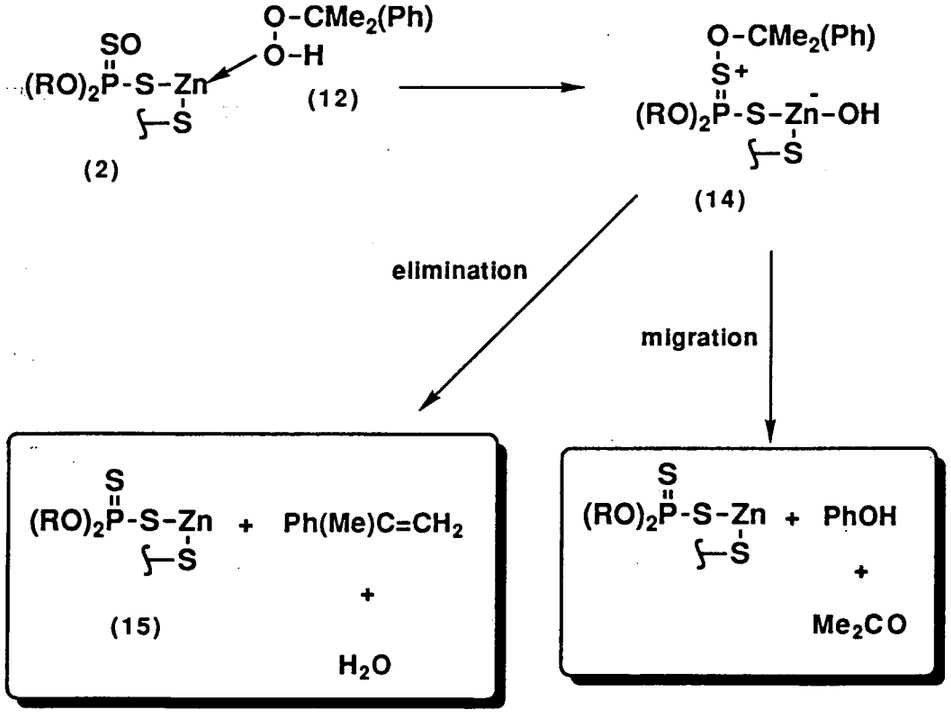



SCHEME 6

$PhCMe_2OOH + X \longrightarrow PhCMe_2O^+ + XOH^-$

$PhCMe_2O^+ \longrightarrow PhOC^+Me_2$

$PhOC^+Me_2 + PhCMe_2OOH \longrightarrow PhOH + Me_2CO + PhCMe_2O^+$

$PhOC^+Me_2 + XOH^- \longrightarrow PhOH + Me_2CO + X$

e.g.- X= $H^+$, $SO_2$, $FeCl_3$.

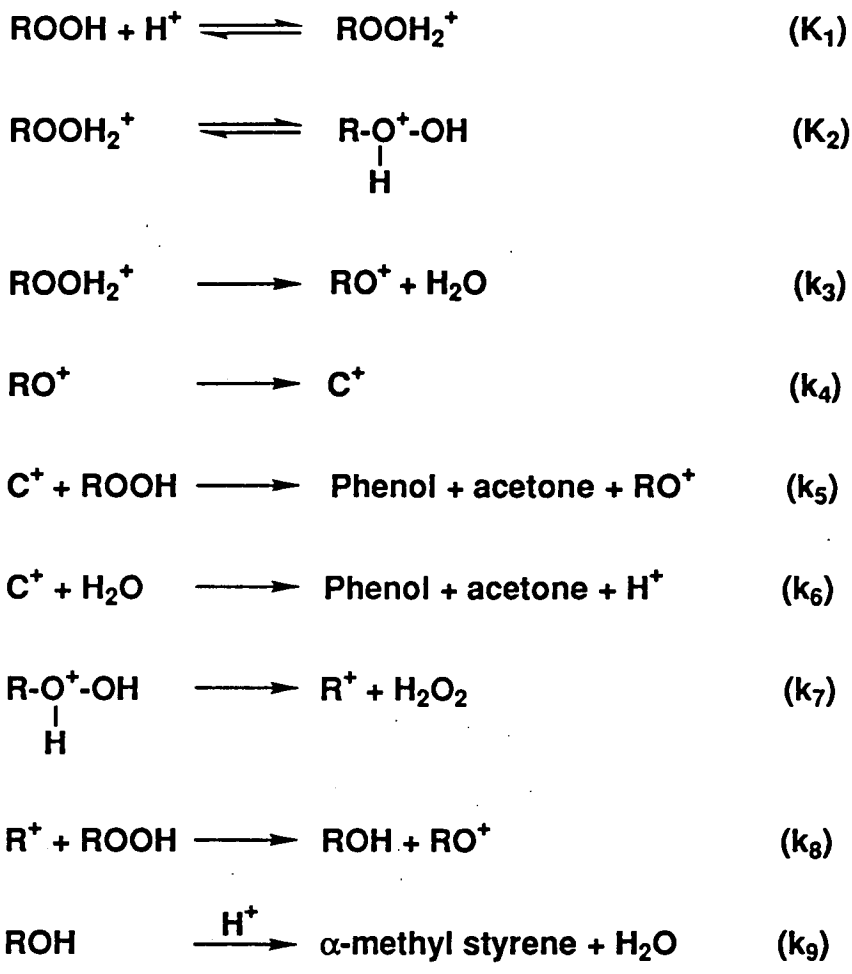
SCHEME 7

---

$[(RO)_2PS_2]_2Zn + R'OOH \longrightarrow [(RO)_2PS_2]_6Zn_4O + [(RO)_2PS_2]_2 + R'OH$

mechanism which is well established [27,28] as a rearrangement reaction catalysed by various electrophilic species (X) which accounts for the observed formation of these type of products. However, the nature of the catalyst which caused this heterolytic decomposition has been the subject of much debate.[14,15,21,24,29,30,31,32-39]

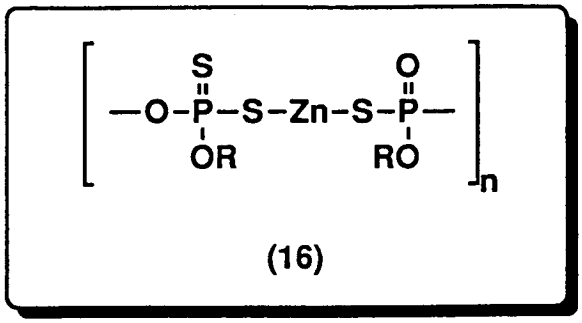
Recent works by Bridgewater et al.[21&39] have taken into account the varied observed data and they have rationalised and explained the complex product formation, nature of the catalyst and the influence of the basic salt (3) in the ionic decomposition of cumene hydroperoxide (12). The latter point (represented by equation 9) was observed by Burn et al.[15] and others[16,35-37,40-42] since but not fully rationalised. In summary, Bridgewater et al. have shown that the catalyst is the acid $(RO)_2PS_2H$, and that the phenol and ( $\alpha,-\alpha$ -dimethyl benzyl alcohol & $\alpha$-methylstyrene) were formed via an ionic mechanism while the acetophenone was formed via a free radical decomposition of the hydroperoxide that was independant of the ZDTP. The acid catalyst, $(RO)_2PS_2H$, formed from the ZDTP, catalysed the decomposition of the hydroperoxide by protonating both oxygen atoms of the hydroperoxide thereby initiating an ionic chain reaction (Scheme 8).



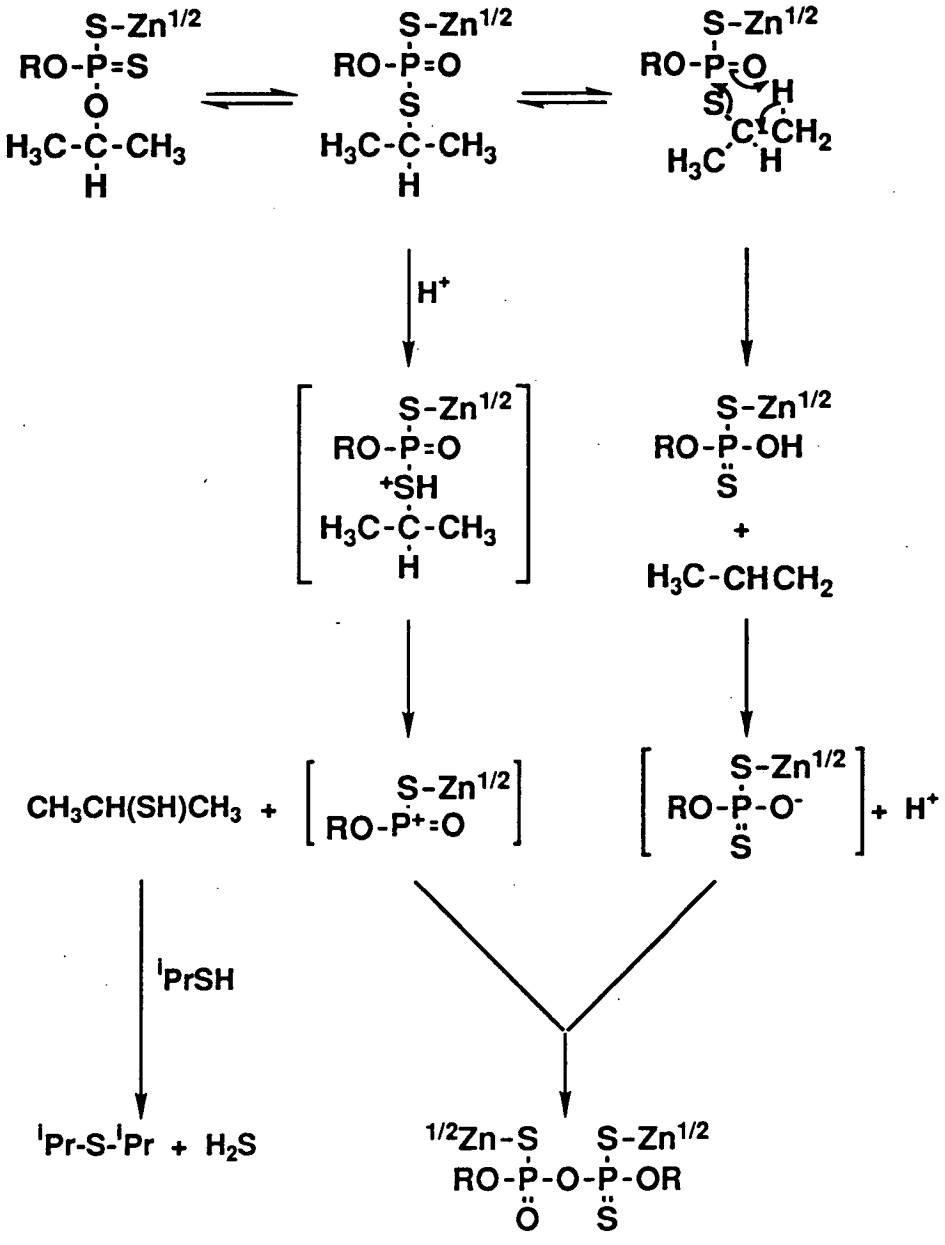

R= Ph–C(Me)(Me)

C= Ph–O–C(Me)(Me)

SCHEME 8



(16)

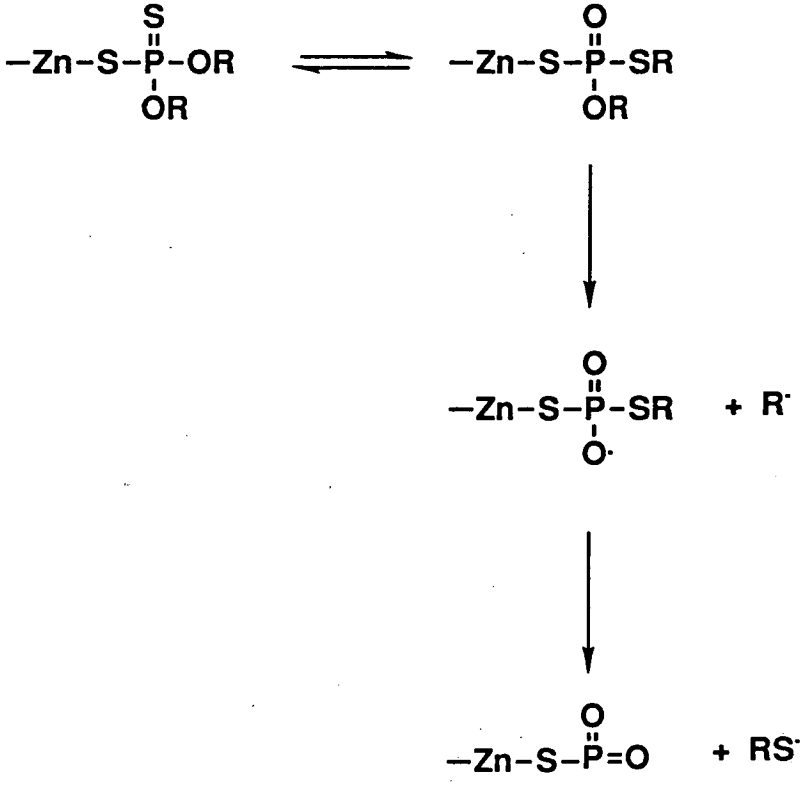


SCHEME 9

## 1.4 Thermal degradation of ZDTP's

The anti-wear behaviour of ZDTP's is generally attributed to the reaction between their thermal decomposition products and metal surfaces. Dickert and Rowe[43] proposed the intramolecular elimination mechanism shown in Scheme 9 whilst investigating the thermal decomposition of ZDTP's. They concluded that the order of product formation was alkene, thiol and hydrogen sulphide; leaving behind a polymeric residue, the structure of which was suggested as shown in (16).

It was also concluded that the temperature of decomposition depended on the structure of the alkyl group and on the size of the metal cation (for a series of divalent metals). Specifically, the decomposition rate increased with increasing number of hydrogens on the $\beta$-carbon atoms in the alkyl groups and with decreasing metal cation size. Earlier Feng and coworkers[44,45] and Gallopoulos[46] had attempted to rationalise a mechanism which postulated that the rate determining step was an intramolecular $\beta$-elimination of an alkene. On the other hand Luther and Sinha[47] had proposed a radical mechanism (Scheme 10) for the degradation of ZDTP's but later[48] observed that the reactions were accelerated by the addition of polar substances but not by radical initiators. This fact lent support to the heterolytic mechanism as advanced by previous workers. Ashford



$$R^{\cdot} \longrightarrow \text{alkene} + H^{\cdot}$$
$$R^{\cdot} + RS^{\cdot} \longrightarrow RSR$$
$$RS^{\cdot} + H^{\cdot} \longrightarrow RSH$$
$$RSH \longrightarrow \text{alkene} + H_2S$$

SCHEME 10

et al.[49] believed that the mechanism involved both radical and ionic species. Spedding and Watkins[5] favoured a hydrolytic mechanism and identified a complex mixture of sulphides, a range of (thio)phosphoric acids and esters, confirming the works of Grishina[37,50] and Kuzmina[51,52], Brazier and Elliot[53] and Coy and Jones[54].

## 1.5 Reactions at metal surfaces

The degradation of ZDTP's discussed in the preceeding section leads to the formation of zinc polyphosphates and mixed alkyl sulphides (RSH, RSR, RSSR). Their subsequent interaction[5] with metal surfaces provides the anti-wear function of ZDTP's. Watkins[5] demonstrated that zinc polyphosphate was physically adsorbed on the mating metal surface in the engines by a combination of temperature and stress; he suggested that its presence there as a fluid glass allowed lubrication of the surface. The mixed alkyl sulphides reacted with the surface oxide layer ($Fe_2O_3$) of the mating metal parts, and were oxidised to sulphur. This then reacted with the iron metal to produce iron sulphide (FeS) which formed a ternary eutectic with iron oxide; this eutectic formed a fluid surface film under extreme wear conditions and provided the anti-wear function.

Previous workers[55] had observed that films containing zinc, phosphorus and sulphur are formed on the surfaces of

cams and tappets when lubricated with ZDTP-containing oils. Larson[14] suggested that the decomposition of the ZDTP's left a largely inorganic residue as a film on the metal.

However, it is pertinent to note that there is no correlation[56] between thermal stability and extreme pressure effectiveness. Baumgarten[57] explained the possibility that adsorption of ZDTP's was dependent on the particular metal substrate. Nevertheless, Watkins' work[5] using esca (electron spec. for chem. analysis) has provided the best insight so far into the interaction of ZDTP products with metal surfaces.

## 1.6 Interactions with other additives

It is known[3,58-60] that both the anti-wear performance and anti-oxidant properties of ZDTP's are greatly impaired by the presence of other additives. In the case of amines, it has been shown that complexation occurs between the ZDTP's and the polyamine ashless dispersants[60]. This area has been the subject of recent investigations[61-65]. Shiomi and coworkers[60] investigated the anti-wear properties of these ZDTP : amine complexes. They suggested that an equilibrium state probably exists between free ZDTP, free amine and their complexes in oil solution. They concluded that the (1:1) ZDTP : amine complex's lower adsorptivity (relative to free ZDTP) accounted

for the poorer anti-wear function observed. Previously, Gallopoulos and Murphy[59] had investigated the complexation between ZDTP's and a host of dispersants and had concluded that chemical reactions are also likely to occur. Thus, additive synergistic and antagonistic interactions all take place to varying degrees for many combinations of lubricating oil additives - for example, ZDTP's act synergistically with chain-breaking oxidation inhibitors[13]. With dispersants, their thermal stability is increased at the loss of their anti-wear performance[60,66]. In spite of the work already carried out, the mechanisms of additive effectiveness and additive - additive interactions are complex and little understood.

## 1.7 Hydrolysis of ZDTP's

It has been long recognised [5,6,6a,67] that a hydrolytic mechanism exists for the decomposition of ZDTP's. Water is a common contaminant which causes degradation of mineral lubricating oils. The major source of water in the engine system comes from the combustion of petroleum itself. This water having gained entry into the system usually collects in the sump region where it eventually causes most damage. Operating the system regularly at temperatures much higher than 100°C can to a limited extent reduce the amount of degradation. Studies involving the hydrolysis of ZDTP's have not received much attention[5,6,6a]

even though it is "common knowledge" that ZDTP hydrolysis can give rise to unknown acidic oil-soluble and oil-insoluble products which in the course of time can curtail the lubricating properties of mineral oils. To this end, hydrolytic studies on ZDTP additives could help in the identification of sludge contaminants and oil-soluble viscous products. Moreover, it could also lead to the identification of potentially usefully load-carrying additives for water-based fluids.

## CHAPTER 2

PHOSPHORUS - 31 FOURIER TRANSFORM NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AND ITS USE AS AN ANALYTICAL TOOL IN CHEMICAL REACTIONS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*'....You get an ology you're a scientist.'*

*Beattie.*

CHAPTER 2

# PHOSPHORUS - 31 FOURIER TRANSFORM NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY AND ITS USE AS AN ANALYTICAL TOOL IN CHEMICAL REACTIONS

## 2.1 Introduction

The immediate objective of this project was the determination of the detailed mechanism of the hydrolysis of zinc dithiophosphates, both normal (2) and basic (3) salts, under conditions relevant to their usage in mineral lubricating oils. Taking into account the complex structure of ZDTP's and the feasibility of different modes of nucleophilic attack by water, it was appreciated that the hydrolysis could produce a multitude of phosphorus - containing intermediates and their subsequent decomposition products. Thus, it was logical to employ $^{31}$ P FOURIER TRANSFORM (FT) - NUCLEAR MAGNETIC RESONANCE (NMR) spectroscopy as the best general purpose analytical 'tool' to elucidate both the rate of formation and structural identification of these intermediates and their products.

As an instrumental technique, $^{31}$P FT-NMR spectroscopy has had an explosive impact on organophosphorus chemistry [68-74] over the last three decades (particularly since around

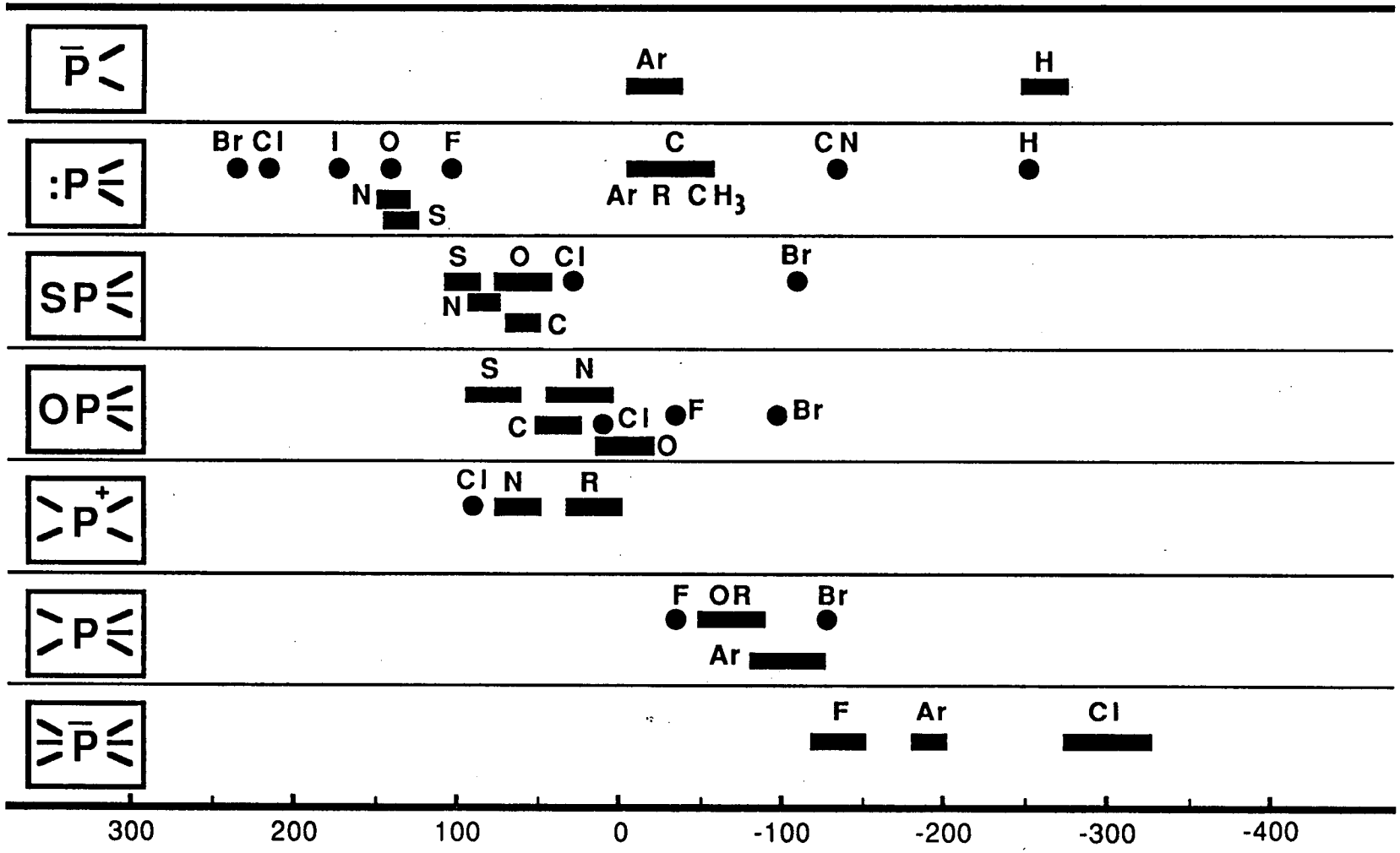


**Figure 1.** **Phosphorus - 31 N.M.R. Chemical Shifts (p.p.m.) for variously coordinated nuclei.**

the
mid-1960's - the advent of signal-averaging, Fourier-Transform (FT) and high-field superconducting-magnets). The latest, routine, multinuclear FT-NMR spectrometers (80-500 MHz, proton frequency) have largely overcome the one serious drawback to the widespread usage of $^{31}P$ NMR, which is the low sensitivity of the phosphorus nucleus (6.6% at constant field compared to $^{1}H$ NMR). Other convenient NMR properties of the $^{31}P$ nucleus suitable for FT NMR include spin I = ½ (thus, avoiding problems associated with quadrapolar nuclei), 100% natural abundance, moderate relaxation times (providing relatively rapid signal averaging and sharp lines), and a very wide range of chemical shifts (>600ppm) ( Figure 1). Linking together $^{1}H$ and $^{13}C$ NMR data to $^{31}P$ information for organophosphorus compounds forms a very powerful investigative probe for the chemist in structure determination, kinetic analyses, reaction mechanisms and product purity. Strangely enough these techniques have not been applied to characterise phosphorus containing additives used in lubricants to any great extent.[71-77] A short discussion of the qualitative and quantitative aspects of $^{31}P$ NMR work relevant to this project follows.

## 2.2 Chemical Shifts and $^{31}P$

Most phosphorus - 31 chemical shifts are referenced relative to the signal for 85% phosphoric acid and follow the IUPAC convention[78] so that positive values are to high frequency (low field):

$$\delta = [\nu - \nu_{ref} / \nu_{ref}].10^6 \qquad 10.$$

where $\nu$ is the frequency of the signal of interest and $\nu_{ref}$ the frequency of the 85% $H_3PO_4$ reference standard.[1*] Reported $^{31}P$ chemical shifts from early literature (pre-1975) tend to use the OPPOSITE sign convention. Even though extremely accurate information can be obtained from organophosphorus compounds when studied under a given set of conditions, $^{31}P$ chemical shifts are dependent on concentration, temperature, pH, H-bonding solvent effects and the presence of other compounds. Variations are often within 1 ppm but it is not uncommon to observe larger variations for phosphoryl and related compounds. However, these environmental effects are generally smaller than the intrinsic effects discussed below.[68]

---

1* When expressed in ppm, the chemical shift is independent of the particular magnetic field, $H_o$, employed in the measurement.

The basic N.M.R. phenomenon as applied to $^{31}P$ chemical shifts is described as follows:

The interaction of the electron cloud around the phosphorus nucleus with an external applied magnetic field $H_o$ results in a local magnetic field. This induced field shields the nucleus, with the shielding proportional to the applied field $H_o$ so that the effective field $H_{eff}$ experienced by the nucleus is represented thus,

$$H_{eff} = H_o(1-\sigma) \qquad 11.$$

where $\sigma$ is the shielding constant. The difference in chemical shift $\delta$ between two lines is the difference in shielding constants of the nuclei giving rise to the two lines. Increased shielding corresponds to more negative chemical shifts. (equation 10) Since the charge distribution is not spherically symmetrical, the major contribution to the $^{31}P$ chemical shift comes from the paramagnetic term in the shielding constant.[79] The chemical shift will thus be affected by changes in bond overlap and hybridisation, and changes in atomic charges. It has been shown in one of the more successful theoretical approaches to $^{31}P$ chemical shifts by Letcher and Van Wazer [80, 81], that three factors appear to dominate $^{31}P$ chemical-shift differences $\Delta\delta$ :

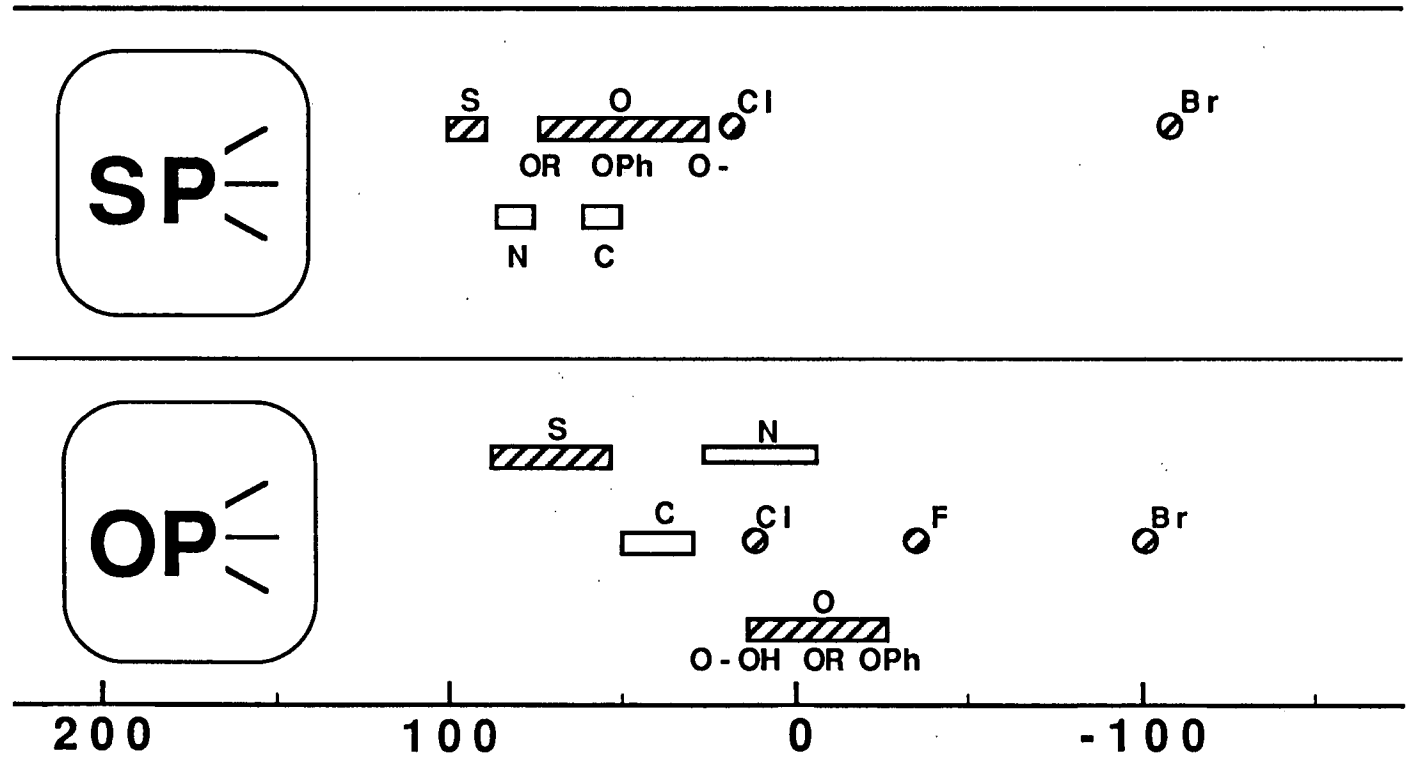


**Figure 2.** Phosphorus-31 Chemical Shifts (p.p.m.) for (thio)phosphoryl compounds.

$$\Delta\delta = -C\Delta\chi_x + k\Delta n_\pi + A\Delta\theta \qquad 12.$$

where $\Delta\chi$ is the difference in electronegativity in the P-X bond, $\Delta n_\pi$ the change in the $\pi$ electron overlap, $\Delta\theta$ the change in the $\sigma$ bond angle, and C, k and A are constants. In this project, it is the relation of $^{31}P$ shift changes to structural and electronic parameters as applied to (thio)phosphoryl compounds that is of interest. As can be seen from Figure 2, (thio)phosphoryl derivatives can be found in the range from +100 to -50 ppm, with the exception of a few compounds such as $OPBr_3$ at -103 ppm. Generally speaking, thiophosphoryl structures appear somewhat down field (higher frequency) from their phosphoryl analogues.

## 2.3 Spin-spin coupling constants

A magnetically active nucleus associated with a given resonance can interact through the electronic structure with other magnetically active nuclei in the molecule. This results in the splitting of the $^{31}P$ resonance into smaller multiplet peaks which when added together, give the same total intensity. The magnitude of this coupling is measured in terms of a spin-spin coupling constant, J, which is independent of the field strength when expressed in hertz (Hz). The patterns of spin-spin splitting commonly found can be divided into: (i) simple or first-order splitting and (ii) complex, second-and higher-order splitting.[71] Simple first-order splitting is obtained when the coupling constant (in Hz) is small compared to the relative chemical shift (also in Hz) between the observed nucleus and the other nuclei in question. The number of peaks observed from such splitting is equal to (2nI + 1) where I is the nuclear spin of the n coupled nuclei and the observed nucleus has a spin of ½. For $^{31}P$ - $^{1}H$ coupling, ie.-I = ½, the relative intensities of the split resonances (n+1) are given by the binomial coefficients, following the rules of combinatorial analysis.

Thus, scalar spin-spin coupling patterns and constants can supply important information regarding the

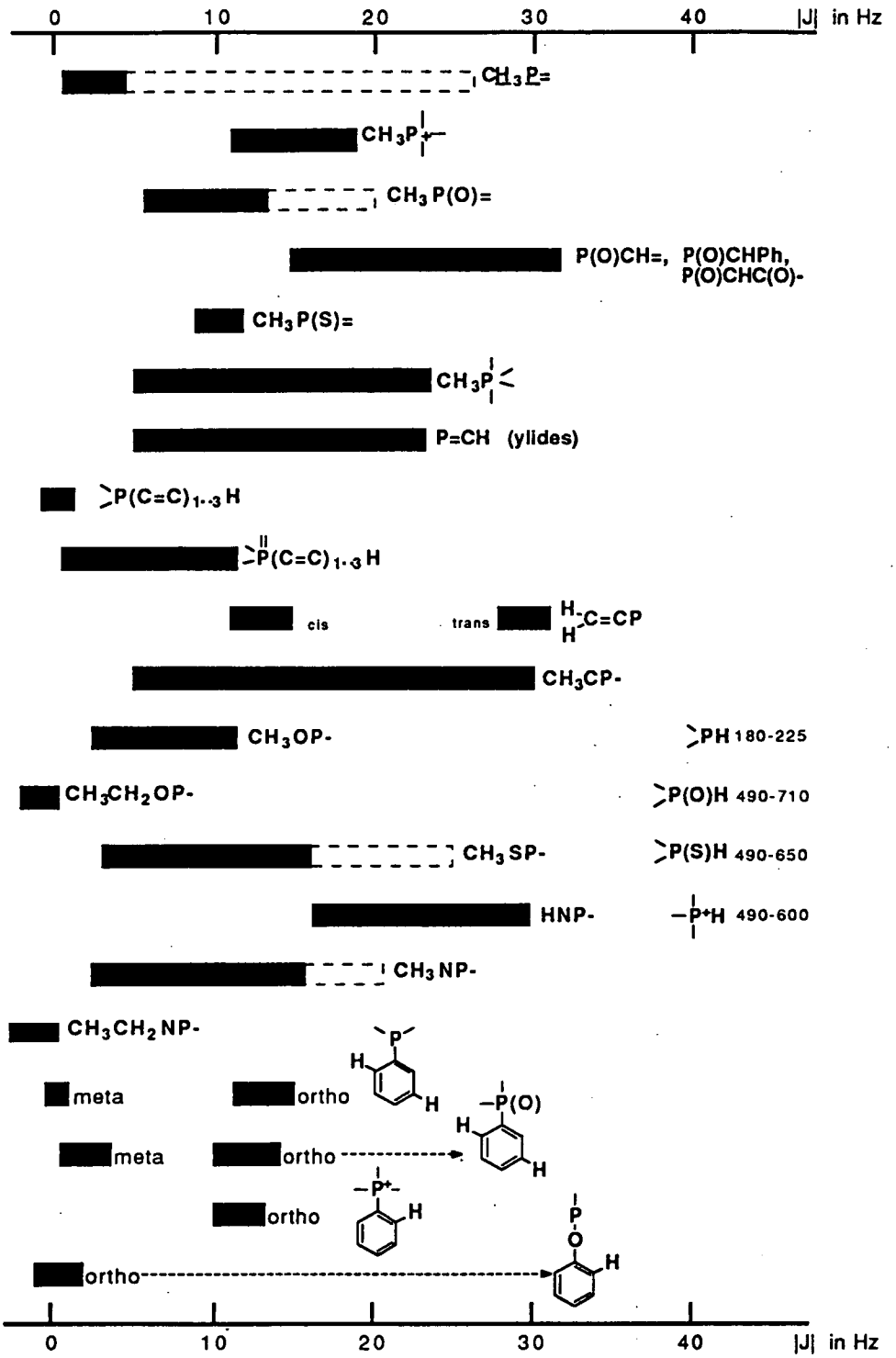


**Figure 3. Phosphorus-hydrogen coupling constants.**

nature of bonding and structure in organophosphorus molecules. The absolute values of coupling constants between phosphorus and other nuclei cover a large range from near zero to ca. 3500 Hz [69]. Figure 3 illustrates the range of the absolute values of coupling constants between phosphorus and hydrogen for various classes of compounds commonly studied. In this project, it was the use of three-bond coupling constants, $^3J_{PX}$, that provided the greatest amount of information. In particular, $^3J_{POCH}$, and the resultant splitting patterns obtained were key factors in unravelling the complex reactions studied. (It was possible to ascertain the number of alkyl groups attached to a given (thio)phosphoryl moiety by studying the $^{31}P-^1H$ coupled spectrum. This was true for most of the compounds examined in this project.)

## 2.4 Kinetic studies, $T_1$ relaxation times and nuclear Overhauser enhancement effects

In the preceeding sections the discussion has been based on the qualitative information that can be gleaned from $^{31}P$ NMR spectroscopy. For quantitative work, it is necessary to consider additional factors such as relaxation effects, peak area/peak integral measurements, nuclear Overhauser effects and a variety of operation modes/observation parameters. Precise details of the

latter can be found in the Experimental chapter but for now discussion will briefly rationalise the salient features relevant to this project.

When obtaining and processing data for kinetic studies, differences in relaxation times[2*] often produce non-linear relationships.[69] Particularly in this project when dealing with the many and varied phosphorus compounds it was essential to known the spin-lattice relaxation times ($T_1$)[2*] and under conditions relevant to the overall study. $T_1$ values can be strongly dependent on solvents and temperature, and as such for this project they were obtained using the authentic hydrolysis mixtures. Moreover, for quantitative work in general it was normal to minimise the sweep width and to accumulate a

---

2* Spin-lattice or longitudinal relaxation refers to the way in which the Boltzmann population distribution of nuclear spins between the energy levels is established when a sample is placed in an applied magnetic field (ie - a spectrometer) or this population is re-established after being perturbed by a radio frequency pulse. $T_1$ can be considered as a measure of the time taken for this to happen. Since NMR is a form of emission spectroscopy, this emission being dependent on the difference between the population of the energy levels, knowledge of $T_1$ values can prevent 'saturation' from occurring, which would result in loss of the nmr signal. $T_1$'s also govern the choice of pulse angle $\theta$ and acquisition time (PI) required in the accumulation of the free induction decay (FID) data. The importance of this being that optimum signal to noise is obtained in a given time if these three quantities are related by equation 13. A variety of methods for $T_1$ measurement are available: progressive saturation method; saturation recovery and inversion recovery methods; see also refs 82-84.

$$\cos\theta = \exp(PI / T_1) \qquad 13.$$

'reasonable' number of FID's.

Minimising sweep width has the effect of improving signal resolution, increasing the number of data points defining each signal and increasing the acquisition time. Increase in baseline noise can be compensated by increasing the window weighting function in conjunction with reducing sweep width. Each signal peak should be defined by at least five data points, preferably eight or more. 'Zero-filling' can also enhance the accuracy of the measurements; this is a readily applied manipulation which involves the interpolation of additional data point(s) between each consecutive data point defining the FID. Accumulating a number of FID's improves signal to noise as does apodisation; another very common manipulation of FID's, involving the multiplication of the FID by a changing (usually decreasing) weighting function. Thus reduces the contribution of the 'tail' of the FID to the transformed spectrum and increases the signal to noise ratio but at the cost of some line broadening.

Providing that saturation is negligible, the areas of various peaks in an NMR spectrum are proportional to the number of magnetically active nuclei giving rise to the particular resonances [85]. Integration via the data-reduction function gives reliable results and good quality data can be obtained even when S/N ratio is as low as 5:1.

NMR experiments utilising Nuclear Overhauser effects (NOEs) have been very effective in elucidating structure in complex molecular systems. However, in $^{31}P$ NMR the use of this technique currently is very limited.[69] The most routinely available method is the phosphorus-hydrogen NOE pioneered by Hart,[86,87] as applied to conformational analyses of ATP and nucleoside monophosphates. A study of phosphorus-phosphorus NOE of ATP by two-dimensional cross-relaxation NMR has also been carried out.[88] In relation to this project, NOEs ought to be removed (by gated decoupling techniques)[76] to ensure correct signal intensities especially in strict quantitative measurements. When comparing integrals of peak areas/heights of aryl ZDTPs and alkyl ZDTPs with normal or broad-band proton decoupling, the values for the aryl ZDTP's will be smaller.[75] The NOE (dominated by dipole-dipole interactions) is greater in alkyl ZDTPs (having protons in 3-bond distance) than in aryl ZDTPs (protons in 4-bond distance) However, in semi-quantitative work or when dealing with systems containing ONLY alkyl OR aryl ZDTP's this consideration is less important. Nevertheless, due care must be taken when interpreting such spectra (ie-those without the gated decoupling technique).

## CHAPTER 3

HYDROLYSIS OF 'NORMAL' ZINC (II) O,O'-DIETHYL DITHIOPHOSPHATE


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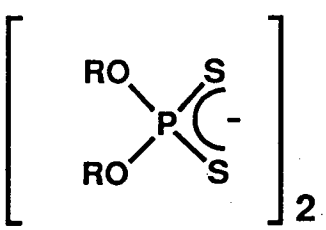
*'One Ring to rule them all, One Ring to find them,*
*One Ring to bring them all and in the darkness bind them.'*

*from The Fellowship of the Ring,*
*J.R.R. Tolkien*

$$4\ EtOH + P_2S_5 \longrightarrow 2(EtO)_2PS_2H + H_2S \qquad 14.$$




M

(1)

R = alkyl, aryl or alkylaryl

M = Zn, Cd, Ni, Mo, Pb or Sb

# CHAPTER 3

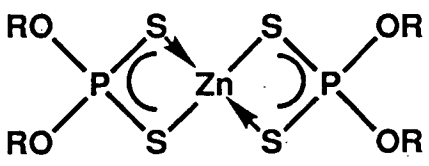
# HYDROLYSIS OF 'NORMAL' ZINC (II) O,O'-DIETHYL DITHIOPHOSPHATE

## 3.1 Introduction

Metal dithiophosphates (MDTP's) (1), also known as 'metal dithiophosphoridates' and 'metal phosphoridithioates', are derived from O, O'-dialkyl (aryl) dithiophosphoric acids, $(RO)_2PS_2H$. The latter compounds were first aluded to by Pistschimuka[89] when he postulated their formation (where R=Et) in the reaction between ethanol and phosphorus pentasulphide (equation 14). Little more was achieved with this reaction until 1945 when Mastin and co-workers[90] verified equation 14 and synthesized the mercuric salt of O, O'-diethyl dithiophosphoric acid by reacting the potassium derivative of the latter with mercuric chloride. In establishing this route, a variety of metal salts of different dithiophosphoric acids could be prepared and subsequently both the MDTP's and their parent acids have found wide usage.[2]

In 1956 Wystrach and co-workers[91] synthesized the normal zinc dithiophosphates ZDTP's (2) from the sodium salts of their parent acids by reaction of the former with zinc

$$2(RO)_2PS_2Na + ZnCl_2 \longrightarrow [(RO)_2PS_2]_2Zn + 2NaCl \qquad 15.$$




(2)

a; R = Et; b; R = $^{i}$Pr

(II) chloride in aqueous solution (equation 15). They showed that in a basic reaction medium, basic ZDTP's (3) were formed as by-products. Zinc (II) sulphate is used in preference to zinc chloride, nowadays, even in neutral media for normal ZDTP synthesis.

In the present work, the normal ZDTP's (2) were made using zinc sulphate in place of zinc chloride in equation 15 and the resultant salts purified by repeated recrystallisations. Purity was confirmed by elemental analysis and sharp m.p's as well as complementary $^{1}H$ and $^{31}P$ NMR data. Thus, in the proton-decoupled $^{31}P$ NMR spectra, the normal diethyl ZDTP (2a) and isopropyl ZDTP (2b) showed signals at + 101.5 p.p.m. and + 98.5 p.p.m., (lit.[75], + 94.7 p.p.m. $CDCl_3$), in 1, 2-dimethoxyethane (DME) solution, respectively. These chemical shifts are relative to 85% $H_3PO_4$ and use an internal $C_6D_6$ capillary lock.

The normal MDTP's in their solid-state can be represented typically by the simple structure (Figure 4) determined[92] for the isopropyl ZDTP (2b) by X-ray crystallography. The zinc complex has a binuclear structure and associated with each metal atom are two dithiophosphate ligands, one of which chelates exclusively to the metal atom while the other bridges the two metal atoms of the dimer

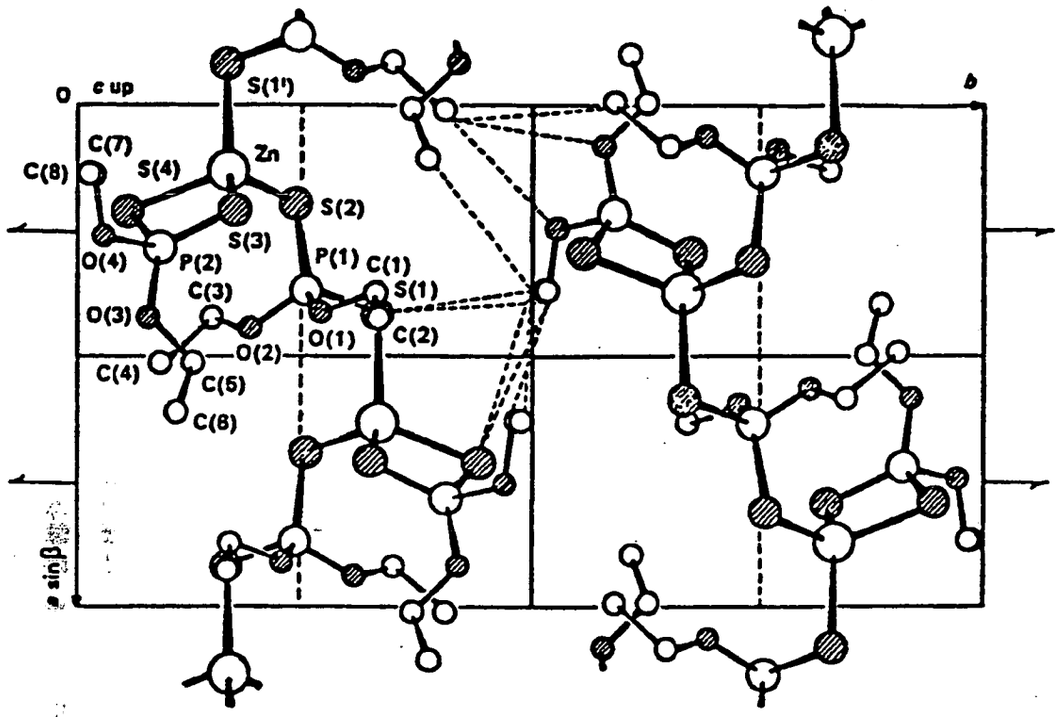



Figure 4. X-ray analysis showing unit cell of zinc diethyl dithiophosphate.

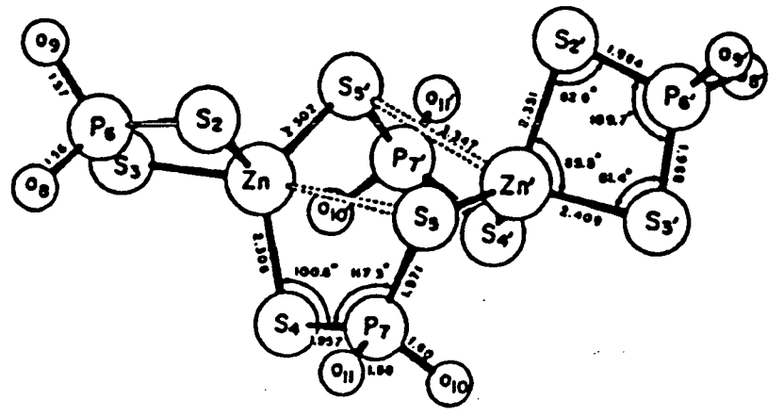



Figure 5.1. Selected bond distances and angles in dimer of zinc diisopropyl dithiophosphate.

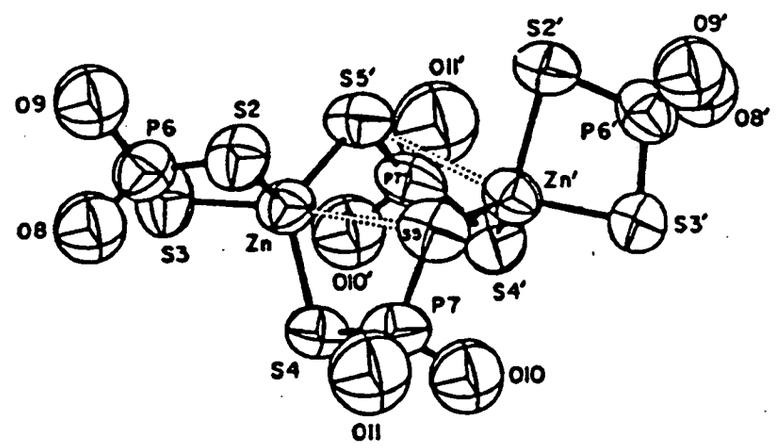


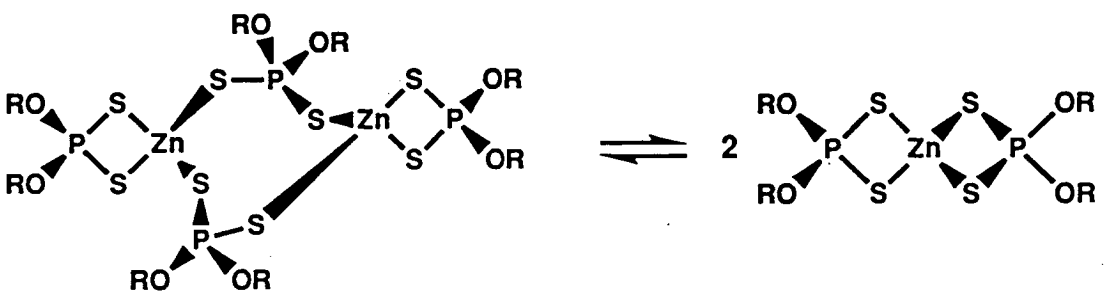

Figure 5.2. Dimer of zinc diisopropyl dithiophosphate, illustrating the root-mean-square thermal displacements of atoms in the inner coordination sphere. The ellipsoid boundaries are at the 60% probability level.

unit. On the other hand, the diethyl ZDTP (2a) (Figure 5) shows a one-dimensional polymeric structure[93] rather than dimeric, but the two dithiophosphate ligands still show the same chelation and bridging pattern along the chain. In both cases, the zinc atoms exhibit a distorted tetrahedral coordination polyhedron.

It has been shown[94] that ZDTP's (2) in solution comprise an equilibrium mixture of dimeric and monomeric molecules. (page 47) Tendency towards association into dimers decreased with increasing chain length for higher homologues, and no association was found to occur for the $C_{18}$ derivative. An NMR study[65] of the equilibrium has also been carried out.

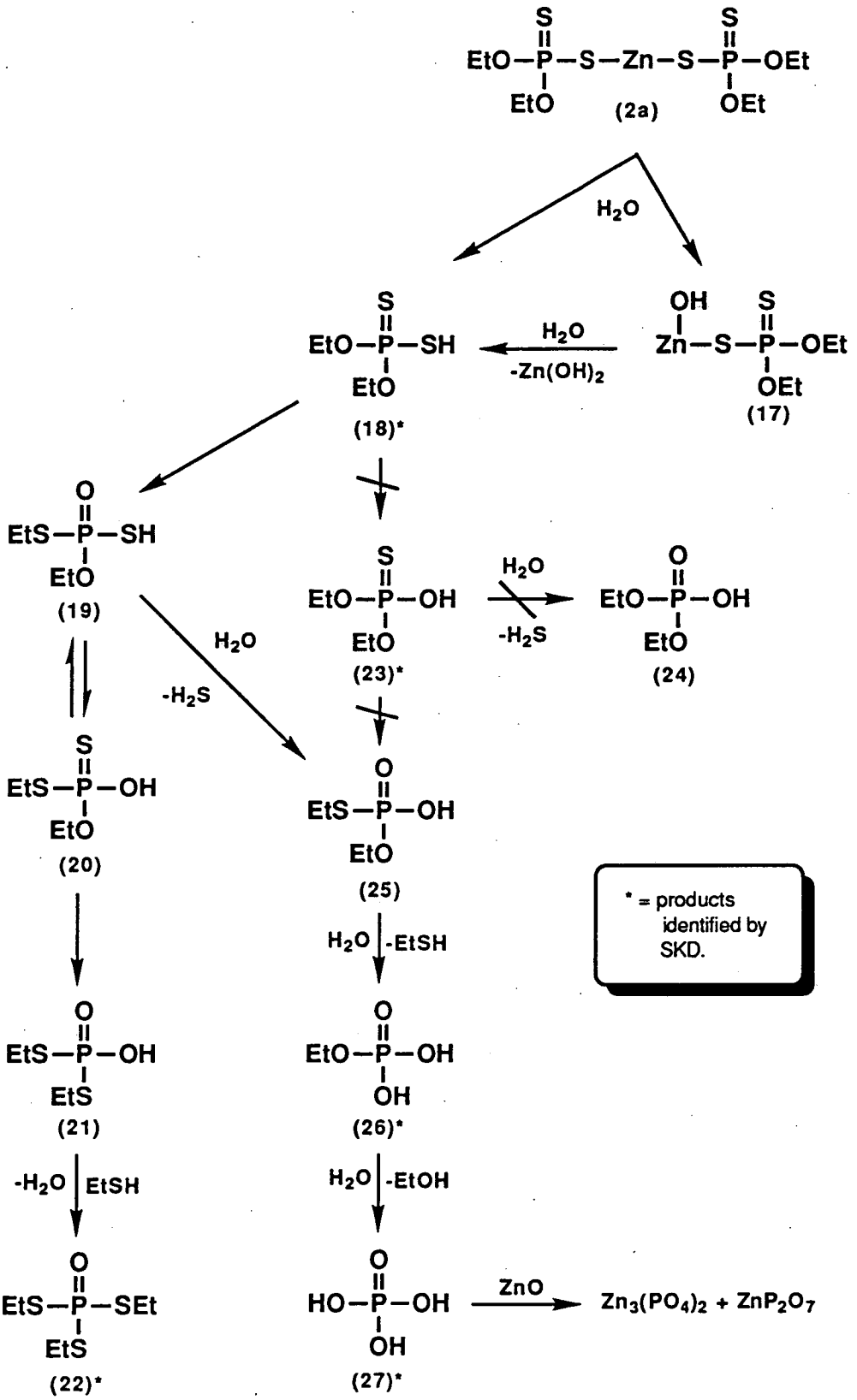
### 3.2 Previous work reviewed

The work carried out by Dewan[95] represents the first major detailed investigation into the hydrolytic mechanism of the degradation of ZDTP's. Scheme 11 (page 49) summarises the results achieved in 1986 and though most of the products had been identified, the exact mechanism was not established unequivocally. This present work was a direct continuation of that effort. It had been ascertained[95] that the intermediacy of O, O' - dialkyl dithiophosphoric acids preceeds the formation of the products. However, the


RO
OR
S
P
Zn
RO
OR
2

identification of the product with $\delta$ + 61.3 p.p.m. as S,S',S"-triethyl trithiophosphate (22) with no corroborative evidence posed a mechanistic dilemma. (It had also been shown that no P-O-C to P-S-C rearrangements occur under the hydrolysis conditions studied). Furthermore, it was not known how O, O - diethyl thiophosphate (23) was formed except that it was not by direct hydrolysis. The formation of ethyl phosphate (26) and phosphoric acid (27) was also ambiguous in the light of no P-O-C to P-S-C rearrangements. Moreover, a product at $\delta$ + 58.7 p.p.m. was not identified and the precise sequence in which the products appeared after O, O, - diethyl dithiophosphoric acid (18) was unclear.

In view of all these uncertainties it seemed prudent to review the facts as known and reassess the possibilities. That the O, O' - dialkyl dithiophosphoric acids were the primary intermediates was certain[95]. Thereafter, the mechanism required a lot of clarification. It was logical to concentrate on the hydrolysis of diethyl ZDTP (2a) because it was a simple homologue and its hydrolysis occurred over the shortest duration. Diisopropyl ZDTP (2b) was later included in the study so that there were representative examples of straight chain primary and secondary metal complexes.


(2a)
$H_2O$
$H_2O$
$-Zn(OH)_2$
(18)*
(17)
(19)
(20)
(21)
(22)*
(23)*
(24)
(25)
(26)*
(27)*
$H_2O$
$-H_2S$
$H_2O$
$-H_2S$
$H_2O$ -EtSH
$-H_2O$ EtSH
$H_2O$ -EtOH
ZnO
$Zn_3(PO_4)_2 + ZnP_2O_7$
* = products identified by SKD.

SCHEME 11

## 3.3 Initial studies and confirmation of intermediacy of 0, 0' - diethyl dithiophosphoric acid in the hydrolysis pathway

1, 2 - Dimethoxyyethane (DME) was chosen as the reaction medium after earlier studies[95] had ruled out water and tetrahydrofuran (THF). It was a suitable solvent because its miscibility with water and its boiling point (85°C) allowed a homogenous phase hydrolysis of ZDTP's to be studied at a reasonable rate. The DME/water solvent system fortuitously allowed the intermediates and products of diethyl ZDTP (2a) to be 'seen' by $^{31}P$ NMR. Analytical reagent (AR) grade DME was dried over activated 4Å molecular sieves or sodium wire, after percolation through a column of alumina (to remove peroxides which if present, caused the formation of the basic salt and in so doing retarded the hydrolysis, see Chapter 4).

It should be mentioned at this point that all $^{31}P$ NMR spectra were recorded with $^{31}P$-$^{1}H$ spin-spin decoupling, except where stated. This heteronuclear decoupling mode of operation allowed discrete signals to be observed for the variously coordinated phosphorus nuclei. Subsequently, unambiguous identification of all phosphorus containing species was achieved by addition of an authentic sample of

the suspected compound to the reaction mixture in an NMR tube. This technique referred to as the 'peak enhancement' method was used in the present work unless otherwise stated. In the course of this work, no less than nine hundred spectra were recorded but for clarity and conciseness, only the more significant have been included in the thesis.

Virtually all the studies involved preparative scale (ca. 0.0033 mole) hydrolyses (of the ZDTP's under investigation) in thermostated baths (± 2°C or better) maintained at 85°C, with ten equivs of water in 10$cm^{-3}$ DME. Later experiments involving 0, 0' diethyl dithiophosphoric acid (18) were carried out on small scale (ca. 0.0003 mole) in NMR tubes as well as preparative scale hydrolyses (ca. 0.0033 mole). The reaction vessels used for the hydrolyses were either 25 $cm^{-3}$ Quickfit round-bottomed (r.b.) flasks equipped with magnetic stirrers or 5 mm NMR tubes into which the 'stock' reaction solutions were introduced (0.4 $cm^{-3}$). In the former case, aliquots (ca. 0.4 $cm^{-3}$) were withdrawn from time to time for $^{31}P$ NMR analysis after the reaction had been quenched by cooling the NMR tubes in an ice-bath. The $^{31}P$ NMR spectra were obtained within 4 hours of hydrolysis.

Preliminary studies[95] had indicated that the formation of a colourless precipitate occurred when hydrolysis took place. Control experiments conducted in the absence of

Figure 6. The formation of diethyl dithiophosphoric acid (18) from the hydrolysis of diethyl ZDTP (2a) in aqueous DME at 85°C as seen by $^{31}P$ NMR.

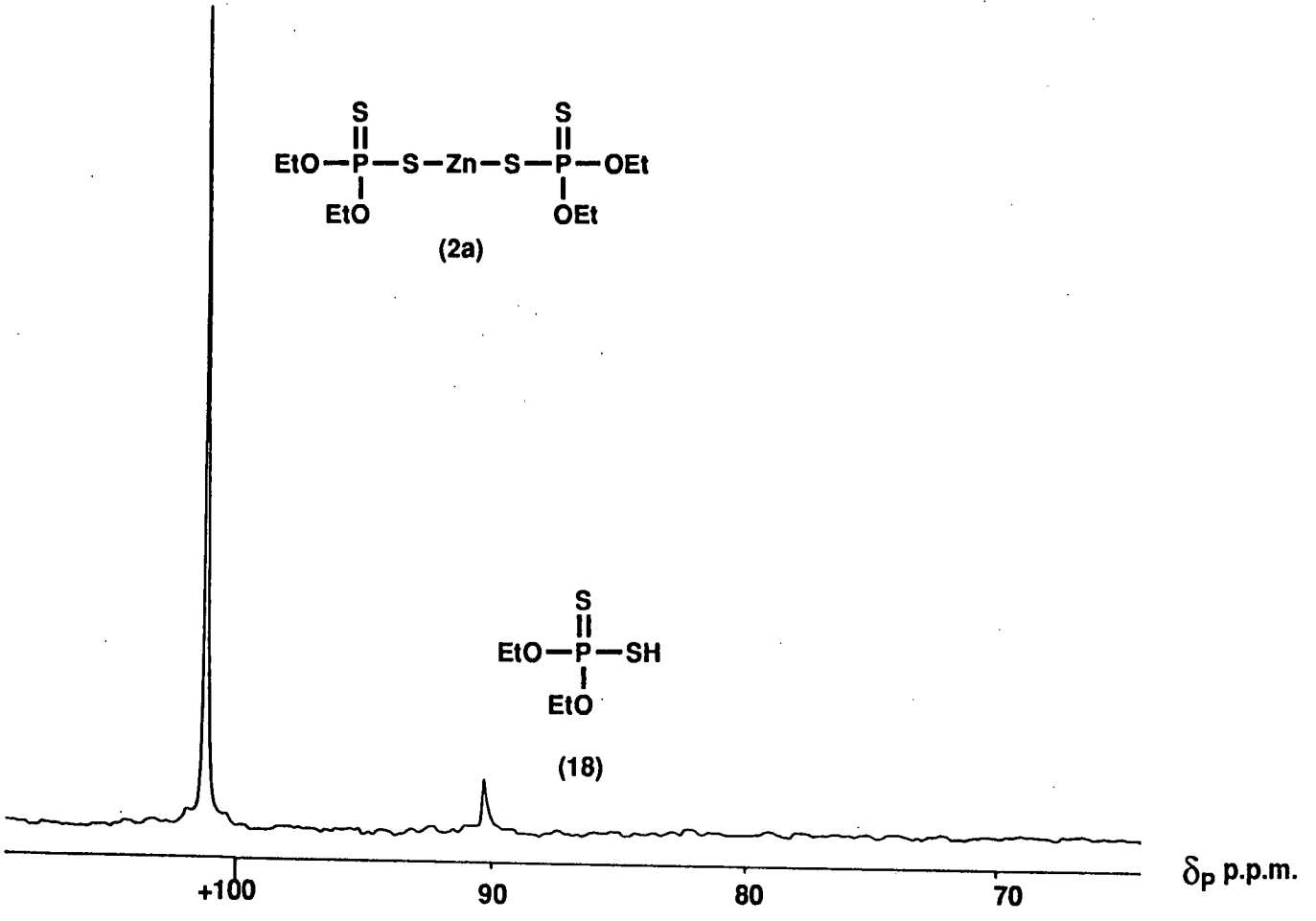


Figure 7. $^{31}P$ NMR spectrum of the hydrolysis products of ZDTP (2a) in aqueous DME at 85°C, at t= 300 minutes.

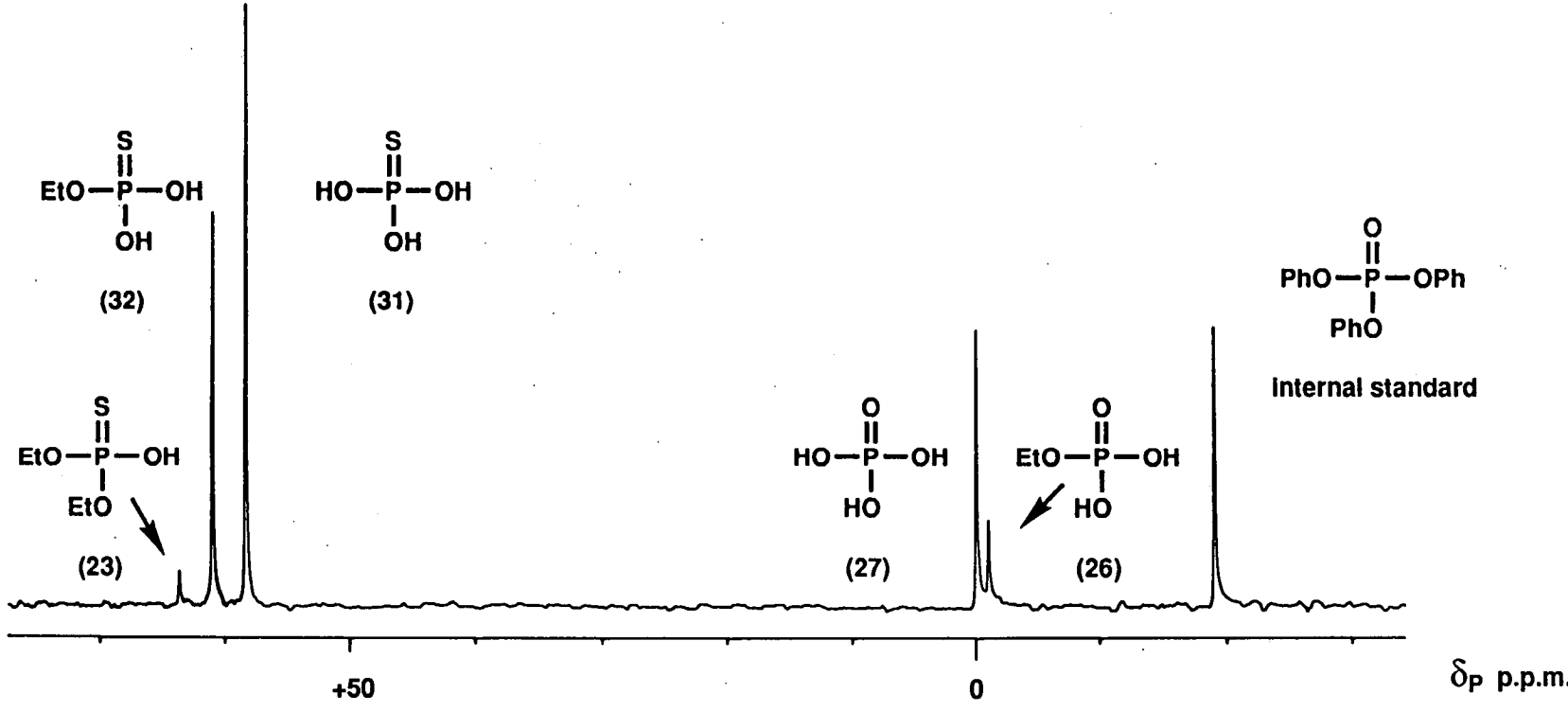
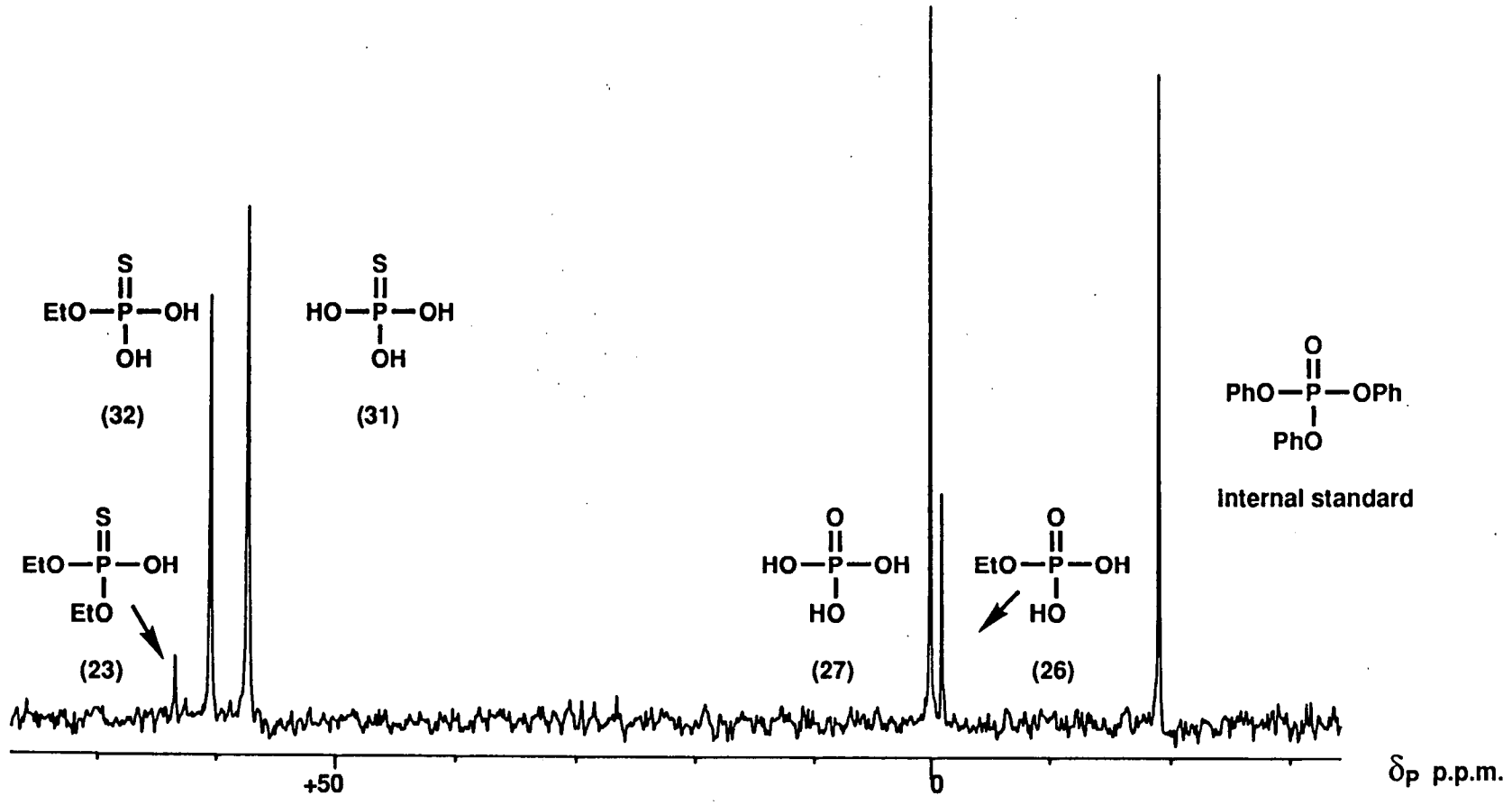
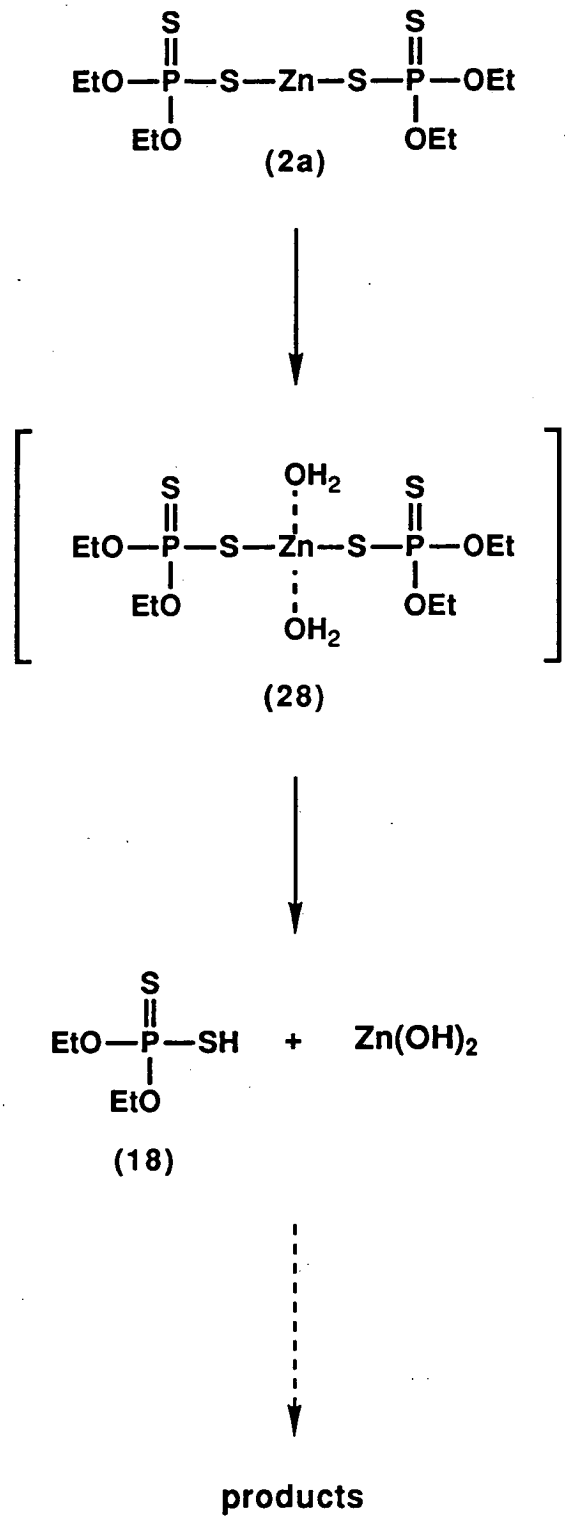


Figure 8. $^{31}P$ NMR spectrum of the hydrolysis products of $(EtO)_2PS_2H$ (18) in aqueous DME at 85°C, at t= 5 minutes.



water monitored by $^{31}P$ NMR had also shown that no thermal degradation occurred and no precipitate was observed. These facts were reaffirmed by repeat studies in the present work. Thus, when diethyl ZDTP (2a) (0.0033 mole) was heated with ten equivs of water at 85°C in 10 $cm^{-3}$ DME, the formation of a colourless precipitate was observed within 20 minutes of hydrolysis and became more dense as the reaction progressed. The formation of this precipitate coincided with the formation of O, O' - diethyl dithiophosphoric acid (18) in the reaction mixture as observed by $^{31}P$ NMR (Figure 6). This signal at $\delta$ + 88.7 p.p.m. was confirmed as (18) by peak enhancement. That diethyl dithiophosphoric acid (18) was THE primary intermediate[95] in the ZDTP hydrolysis was reconfirmed by a further experiment in which an authentic sample $(EtO)_2PS_2H$ (18) (0.0029 mol) was hydrolysed, at 85°C with ten equivs of water, in 10$cm^{-3}$ DME solution. The products of the reaction were the same type and of comparable distribution (Figures 7 and 8) to the products from the ZDTP hydrolysis, which also argued that (18) must be the intermediate from which the other products stem.




SCHEME 12

Mechanistically speaking, it can be assumed that attack by water on diethyl ZDTP (**2a**) could have occurred at one or more sites, including the $\alpha$-carbon of the ethyl group[96], the phosphorus atom[97] and the zinc atom. As evidenced by the results of the two experiments described above, initial attack of water was found to occur exclusively at the metal atom. No other soluble phosphorus containing species were detected by $^{31}P$ NMR during the early stage (0-40 minutes) of hydrolysis. An explaination for this preference for zinc over phosphorus and carbon atoms as the site for attack by water could be gleaned if one considers an analogous situation involving the hydrolysis of a diethyl nickel complex[95]. Theoretical charge distribution calculations showed[98] that the charge on nickel, phosphorus and carbon in the complex amounted to +0.583e, +0.136e and +0.016e respectively. From this data, it is evident that attack by water is more likely to occur at the metal moiety rather than at phosphorus or carbon.

The observations of 0, 0' - diethyl dithiophosphoric acid (**18**) as the primary hydrolysis product points to the concomitant formation of a zinc complex, perhaps (**28**) (see Scheme 12), which is insoluble in the reaction mixture and hence not detected by $^{31}P$ NMR. As can be seen from Figures 7 and 8 there were five major intermediate(s)/products from

the hydrolysis of diethyl ZDTP (2a), giving signals at $\delta$ +64.1, +61.3, +58.7, 0.0 p.p.m. and -0.3 p.p.m. All but one of these peaks had been identified by Dewan[95], thus the resonance at $\delta$ +64.1 p.p.m. corresponded to O, O' - diethyl thiophosphoric acid (23); 61.3 p.p.m. (tentatively), S,S',S" -triethyl trithiophosphate (22); 0.0 p.p.m., phosphoric acid (27); and -0.3 p.p.m., O-ethyl phosphoric acid (26).

## 3.4 Identification of intermediate $\delta$ +58 p.p.m. and further clarification of hydrolysis mechanism

As mentioned earlier in Section 3.2, the precise order in which the products appeared in the $^{31}P$ NMR spectrum after the formation of the primary intermediate diethyl dithiophosphoric acid (18) was not explained clearly by Dewan.[95] It seemed pertinent at this juncture that the sequence of product formation had to be known so that the identification of the $\delta$ +58.7 p.p.m. intermediate could be made easier. The importance of knowing this product formation sequence lay in the fact (mentioned earlier in 3.3) that all the final intermediates and products are derived from diethyl dithiophosphoric acid (18).

To achieve this goal the hydrolysis of O, O' - diethyl dithiophosphoric acid (18) in DME solution was monitored by

$^{31}P$ NMR at very short intervals. These hydrolytic studies were carried out under a range of conditions: (i) with ten equivs of water at 85°C; (ii) with ten equivs of water at room temperature; and (iii) with two equivs of water at 85°C. It was expected that with the data generated from these experiments a further attempt at extracting answers from the reaction about its mechanism would be made possible.

It is also relevant at this point to mention the introduction of the use of $^{31}P$-$^{1}H$ spin-spin coupling information in endeavours to elucidate the nature and type of 'ligands' coordinating around the phosphorus nuclei. This data can be obtained from the original signal resonance by recording the $^{31}P$ NMR spectrum in the NON-decoupled mode. As described earlier in Section 2.3 it was the three-bond phosphorus hydrogen coupling, P-O-C-H or P-S-C-H, and resulting splitting of the $^{31}P$ resonance signal (i.e. the multiplicity) which proved to be of greatest benefit in unravelling the nature of bonding and structure around the phosphorus nucleus in question.

In the first experiment, diethyl dithiophosphoric acid (18) (0.0032 mole) was hydrolysed with ten equivs of water at 85°C in DME solution ($10cm^{-3}$); $^{31}P$ NMR analysis showed that the sequence in which the final products arose was in the

Figure 9. $^{31}P$ NMR stack plot of the hydrolysis of diethyl dithiophosphoric acid (18), in aqueous DME at 85°C.

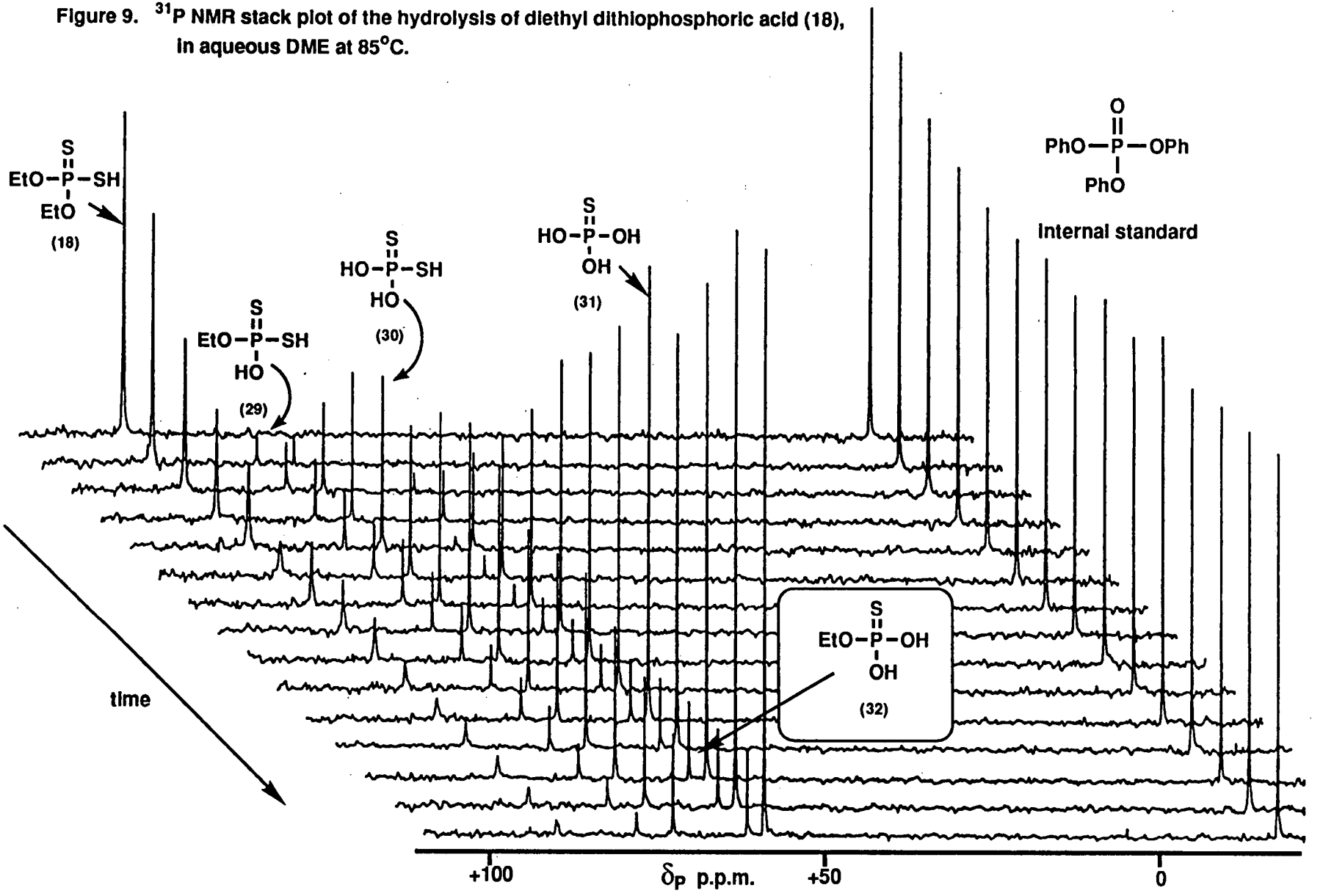
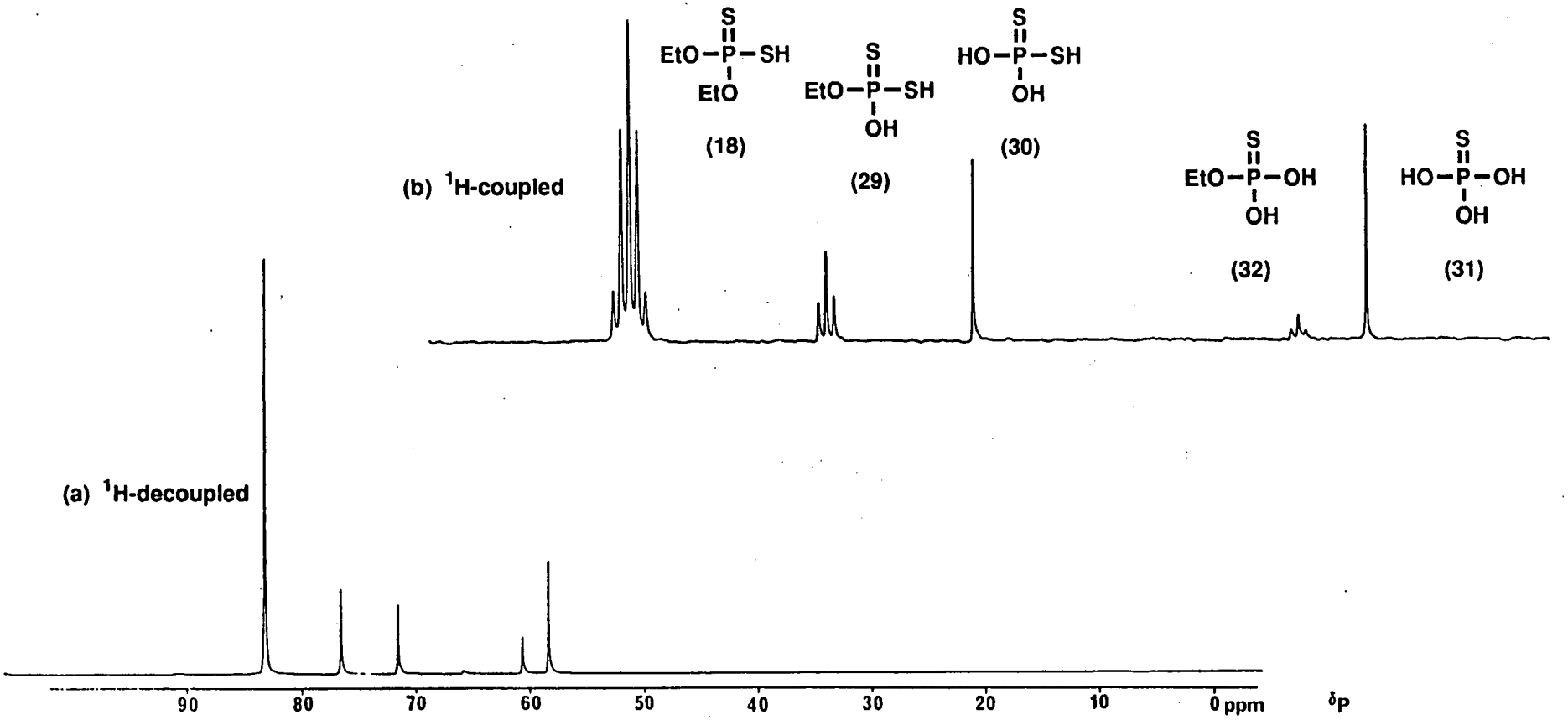


Figure 10. Room temperature hydrolysis of diethyl dithiophosphoric acid (18), $^{31}P$ NMR spectra $^{1}H$-coupled (a) and decoupled (b).



order: $\delta$ + 58.7 p.p.m. first, followed by $\delta$ +61.3 p.p.m. (see Figure 9). More importantly, it revealed for the first time, the involvement of two additional soluble phosphorus containing species, at $\delta$ +78.1 p.p.m. and +71.3 p.p.m. in that order, respectively. The signals for the latter intermediates arose directly after the signal for diethyl dithiophosphoric acid (18) at ca $\delta$ + 86 p.p.m. began to decay. All this took place prior to the development of the signal for the product at $\delta$ + 58 p.p.m.

It had been known[95] that the hydrolysis of (18) with ten equivs of water at room temperature, though a much slower process, gave rise to a single major product at $\delta$ 58 p.p.m. identical with that obtained at 85°C. With that in mind and in the effort to identify the species at $\delta$ 58 p.p.m. the second experiment involving the hydrolysis of (18) (0.008 mole) with ten equivs of water at room temperature in DME solution (25cm$^2$) was carried out to probe the mechanism of these reactions. The resultant $^{31}$P NMR spectrum (Figure 10a, taken from the middle of the sequence monitoring the course of the reaction) confirmed the involvement of the intermediates at $\delta$ +78 p.p.m. and +71 p.p.m. before the product at $\delta$ +58 p.p.m. was formed. NMR monitoring also revealed that a small amount of the product at $\delta$ + 61.3 p.p.m. was generated in this reaction compared to the larger

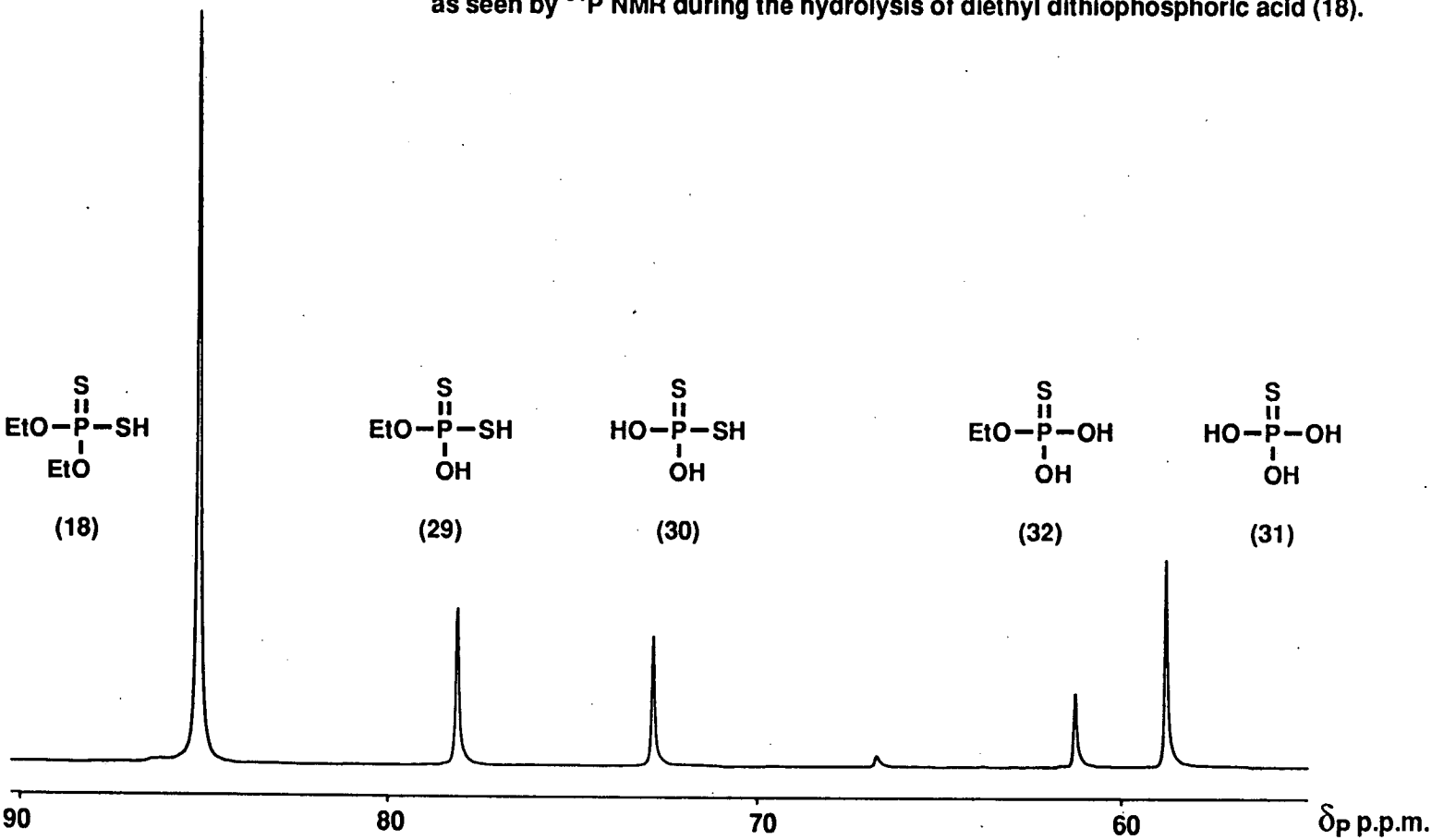
amounts created by reaction at 85°C. Moreover, at this point, the 'normal' $^{1}H$-decoupled $^{31}P$ NMR spectrum was supplemented with a $^{31}P$ NMR $^{1}H$-spin-spin coupled spectrum. (Figure 10b) This created a NEW dimension to the $^{31}P$ NMR analysis not possible previously and allowed the monitoring of the fate of the alkyl groups attached to the (thio) phosphoryl nucleus as well as added recognition of the coordination around the phosphorus atom.

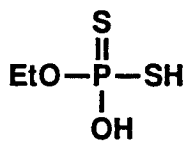
As can be seen from Figure 10b, the signal for diethyl dithiophosphoric acid (**18**) at $\delta$ +86 p.p.m. was split into a 1:4:6:4:1 multiplet (a quintet). This was rationalised by considering the spin-spin splitting caused by the three-bond coupling of the $^{31}P$ nucleus to the protons on the methylene ($-CH_2-$) units of the ethoxy groups ($^{3}J_{PH}$ ca. 10 Hz)[1*]. With the acid (**18**), the two ethoxy groups (and the 4 methylene protons) gave rise to the observed quintet (see Chap 2, Section 2.3) signal. Consequently, the 1:2:1 triplet centred at $\delta$ +78 p.p.m. must imply that only ONE ethoxy group was attached to that phosphorus nucleus (coupling with only TWO methylene protons). In addition, taking into account the chemical shift value ( $\delta$ +78 p.p.m.) that phosphorus nucleus must also be attached to at least two

---

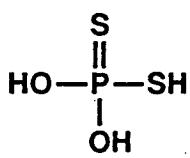
1* $^{4}J_{PH}$ ca 0.5 Hz, too small to be resolved properly.

Figure 11. Formation of O-ethyl dithiophosphoric acid (29) and dithiophosphoric acid (30) as seen by $^{31}P$ NMR during the hydrolysis of diethyl dithiophosphoric acid (18).

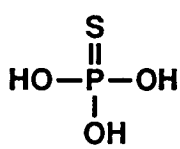




(29)



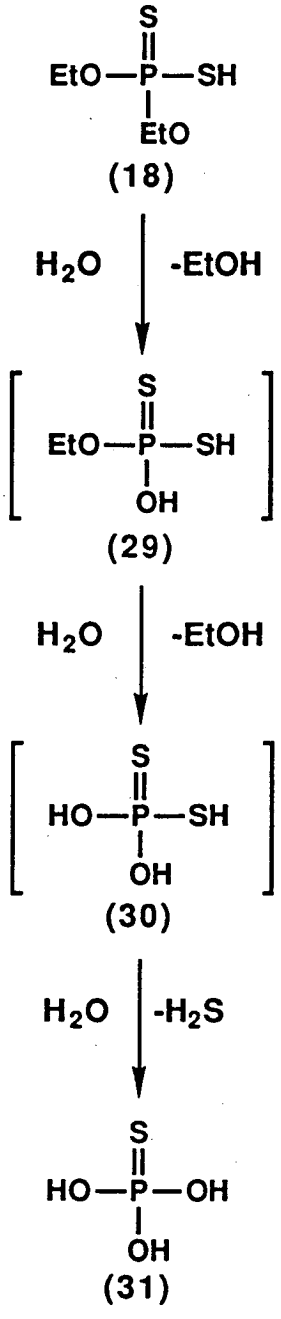
(30)



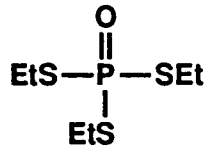
(31)

sulphur atoms, one of which must be P=S (c.f. - Figure 2, Section 2.2). Furthermore, the alkyl group must be coordinated to the phosphorus via the oxygen atom (ie - EtO) rather than the sulphur (ie - EtS) because its value for $^{3}J_{PH}$ is 10.3 Hz and is identical to the value for diethyl dithiophosphoric acid (18) which is also 10.3 Hz and corresponds to ethoxy attachment. Correlating all this information, one must conclude that the most reasonable structure for the intermediate at $\delta$ +78 p.p.m. is shown (29). Subsequently, the singlets at $\delta$ +71 p.p.m. and $\delta$ +58 p.p.m. must imply that NO ethoxy/thioethoxy groups are attached to those phosphorus nuclei and accounting for their $\delta$ values, proposed structures (30) and (31) fit the criteria.

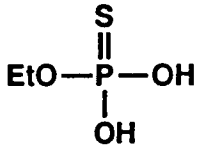
Confirmation that structure (31) was indeed that hitherto unknown intermediate/product at $\delta$ +58 p.p.m. was obtained when an authentic sample of thiophosphoric acid (31) was prepared[99] and verified by peak enhancement. This identification represented a major breakthrough in the understanding and unravelling of the complexities of this hydrolytic mechanism under study. Scheme 13 summarises the deduced mechanism of hydrolysis of diethyl dithiophosphoric acid (18) leading up to the formation of thiophosphoric acid (31) which was ascertained at this point in the project.


S
EtO—P—SH
EtO
(18)
H2O
-EtOH
S
EtO—P—SH
OH
(29)
H2O
-EtOH
S
HO—P—SH
OH
(30)
H2O
-H2S
S
HO—P—OH
OH
(31)

SCHEME 13



(22)



(32)

At the same time as the preceeding two experiments were being studied, a third experiment was carried out in which diethyl dithiophosphoric acid (18) (0.001 mole) in DME solution ($5cm^{-3}$) was hydrolysed with two equivs water at 85°C. The resulting $^{31}P$ NMR analysis (Figure 11) provided corroborative evidence in support of the mechanism outlined previously in Scheme 13, that thiophosphoric acid (31) was produced from the hydrolysis of (18) *via* ethyl dithiophosphoric acid (29) and dithiophosphoric acid (30).

## 3.5 Verification of product $\delta$ +61 p.p.m. and further elucidation of the source of product $\delta$ +64 p.p.m.

The product at $\delta$ +61.3 p.p.m., had earlier been tentatively identified by Dewan[95] as S,S',S" - triethyl trithiophosphate (22); did not show NMR signals compatible with such a trialkylated phosphorus moiety (see Figure 10b).

Interpreting the signal centred at + 61.3 p.p.m.; the 1:2:1 triplet with $^{3}J_{PH}$ *ca*. 9.5 Hz in THAT range of values suggests that structure (32) is MORE CONSISTENT with the known experimental facts.

In order to explain this discrepancy and ascertain the facts, the synthesis of (22) by a known method [100] was carried

**Figure 12.** $^{1}$H-coupled $^{31}$P NMR spectrum of S,S',S''-triethyl trithiophosphate (22).

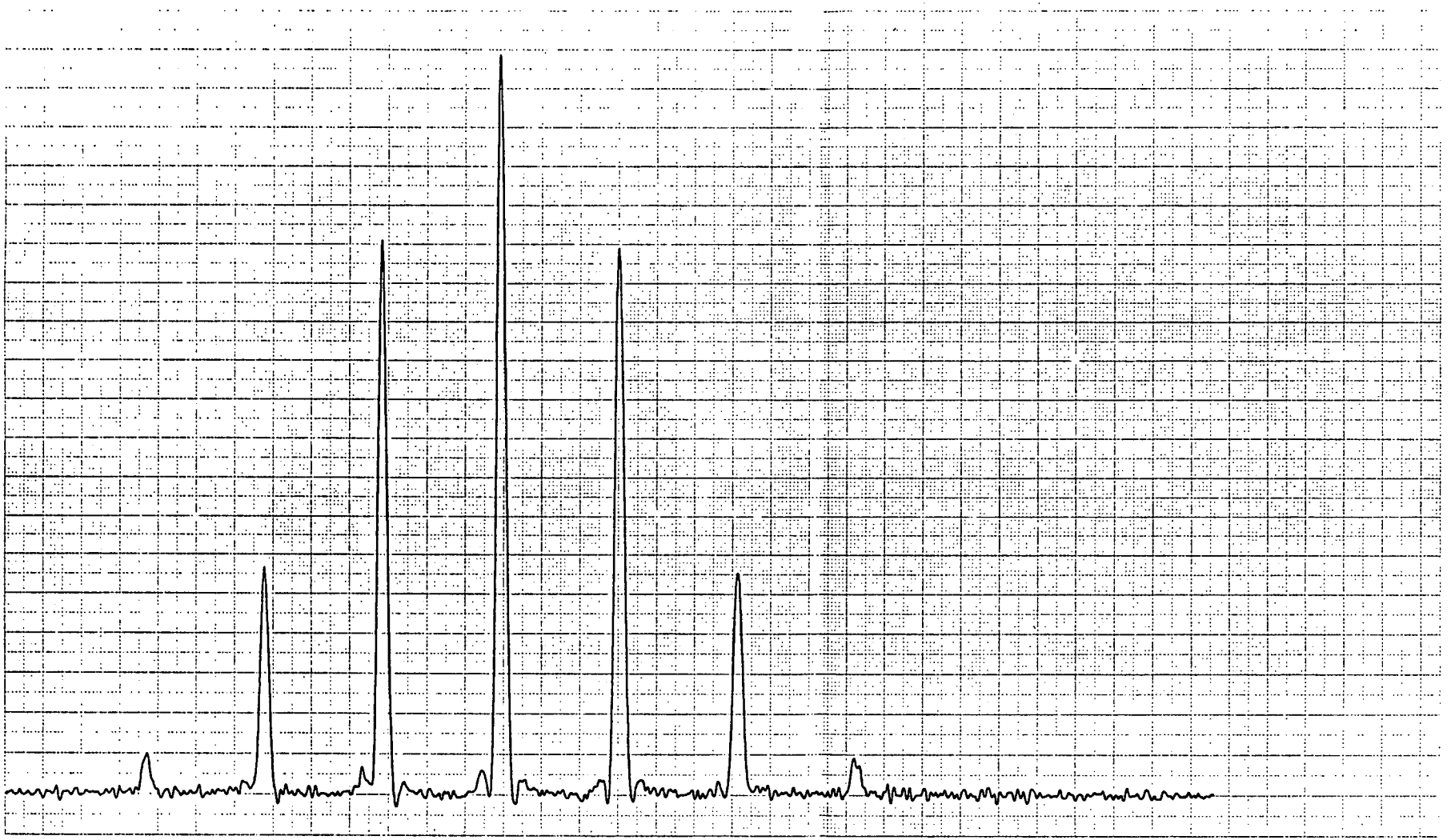


Figure 13. $^{31}P$ NMR spectra for O-ethyl thiophosphoric acid (32) at $\delta$+61.3 p.p.m.

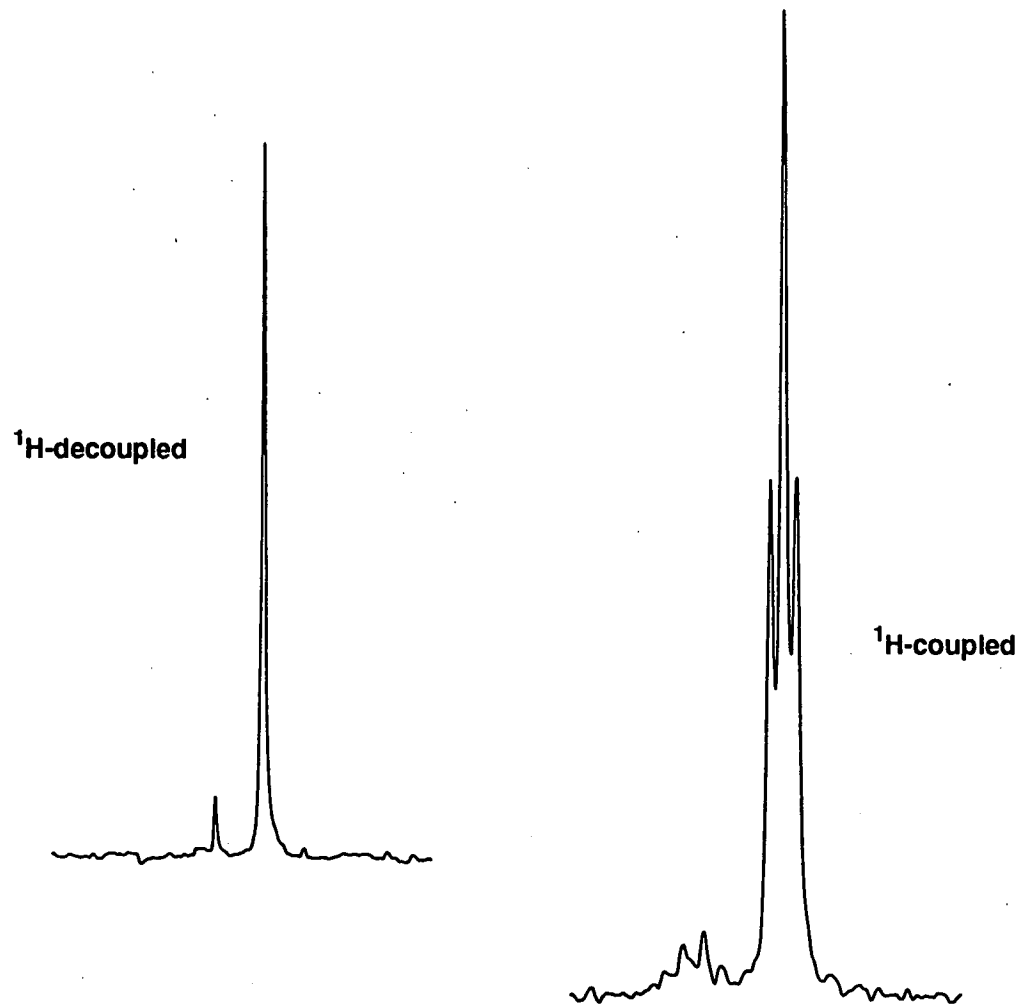
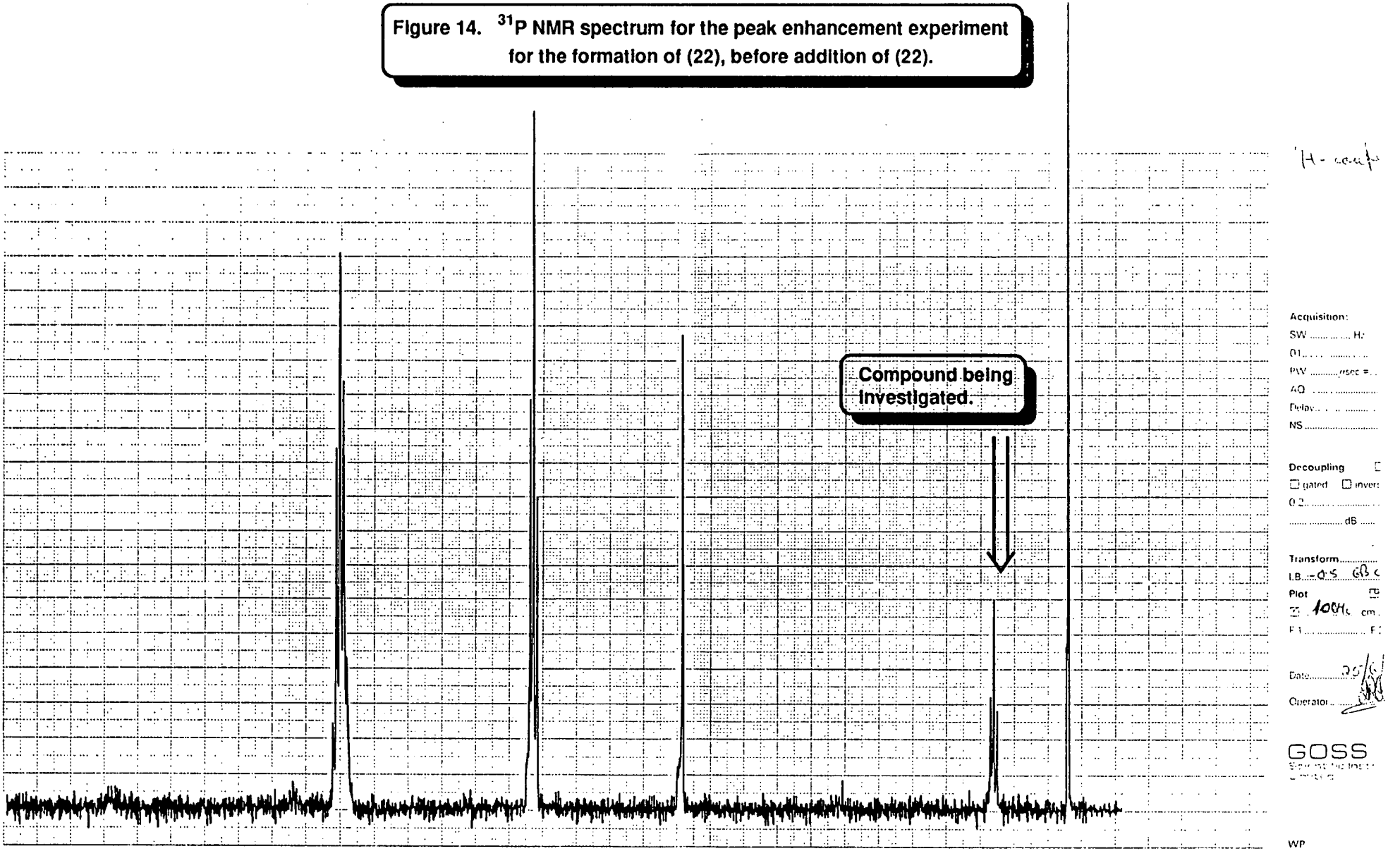


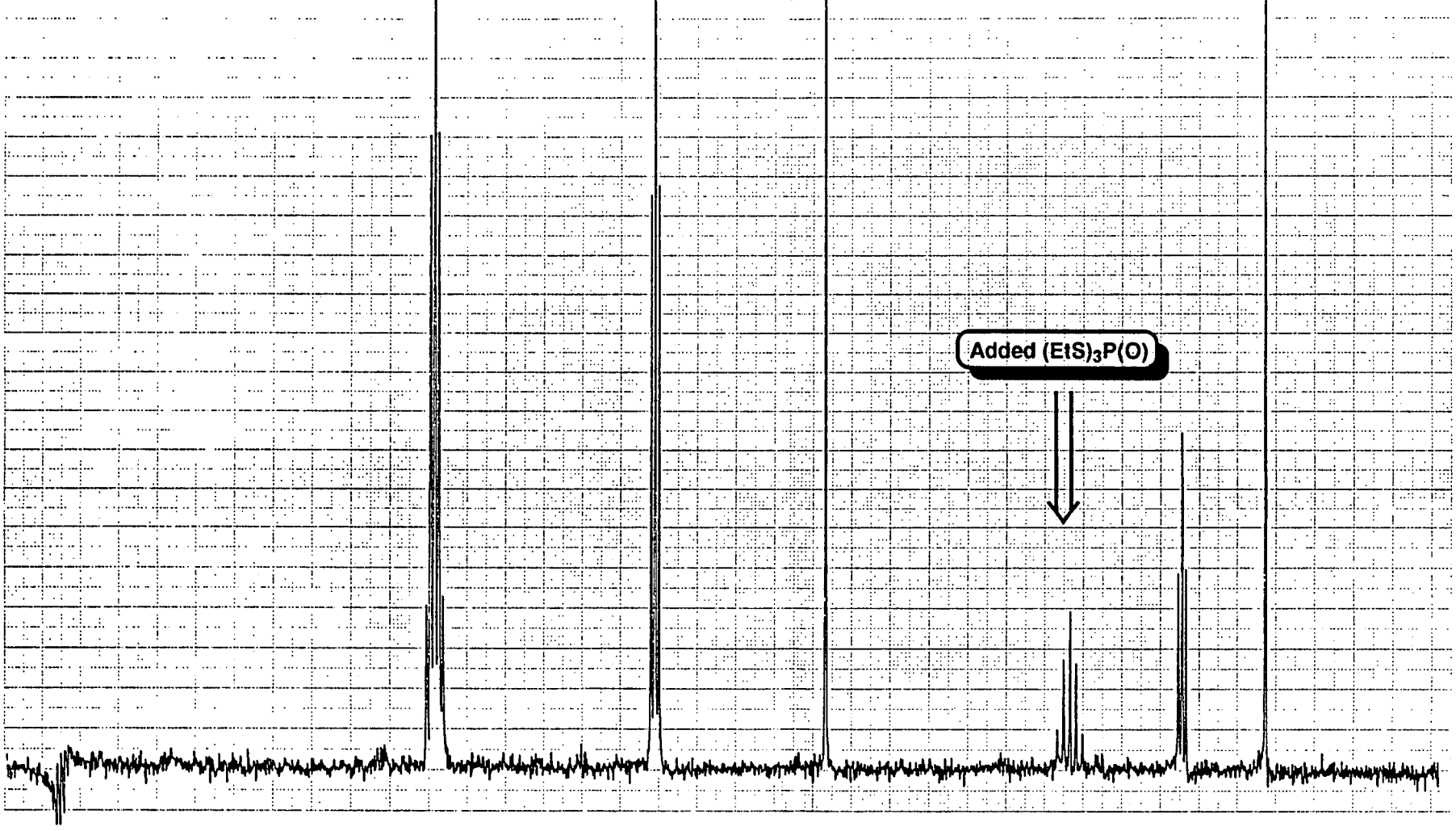
**Figure 14.** $^{31}P$ NMR spectrum for the peak enhancement experiment for the formation of (22), before addition of (22).



out. In the subsequent $^{31}P$ NMR analysis (Figure 12), the $^{1}H$-coupled spectrum showed a 1:6:15:20:15:6:1 multiplet centred at $\delta$ +61 p.p.m. ($CDCl_3$) $^{3}J_{PH}$ = 15.5 Hz, (a larger $^{3}J_{PH}$ value as might be expected for P-S-C-H coupling as opposed to P-O-C-H coupling which has a smaller value of the order of 10Hz). Similarly, the synthesis of **(32)** by an adaptation of known methods [101-102] was performed and $^{31}P$ NMR analysis carried out. Figure 13 shows the $^{1}H$-coupled $^{31}P$ NMR spectrum of **(32)**: a 1:2:1 triplet centred at $\delta$ +61.3 p.p.m. (DME) $^{3}J_{PH}$ = 9.5 Hz.

In the subsequent 'key' experiment, diethyl dithiophosphoric acid **(18)** (0.96 mole) was hydrolysed in DME solution (0.4$cm^{-3}$) on an NMR scale with 2 equivs of water at 85°C. $^{31}P$ NMR analysis after heating for 3 minutes gave the spectrum shown in Figure 14. The 'unknown' product in question (indicated by the arrow) resonates at +61.4 p.p.m.

**Figure 15.** $^{31}P$ NMR spectrum for the peak enhancement experiment for the formation of (22), with added (22)(arrowed).




1H- coup

Acquisition:
SW.....Hz
01.....
PW.....μsec =...
AQ.....
Delay.....
NS.....

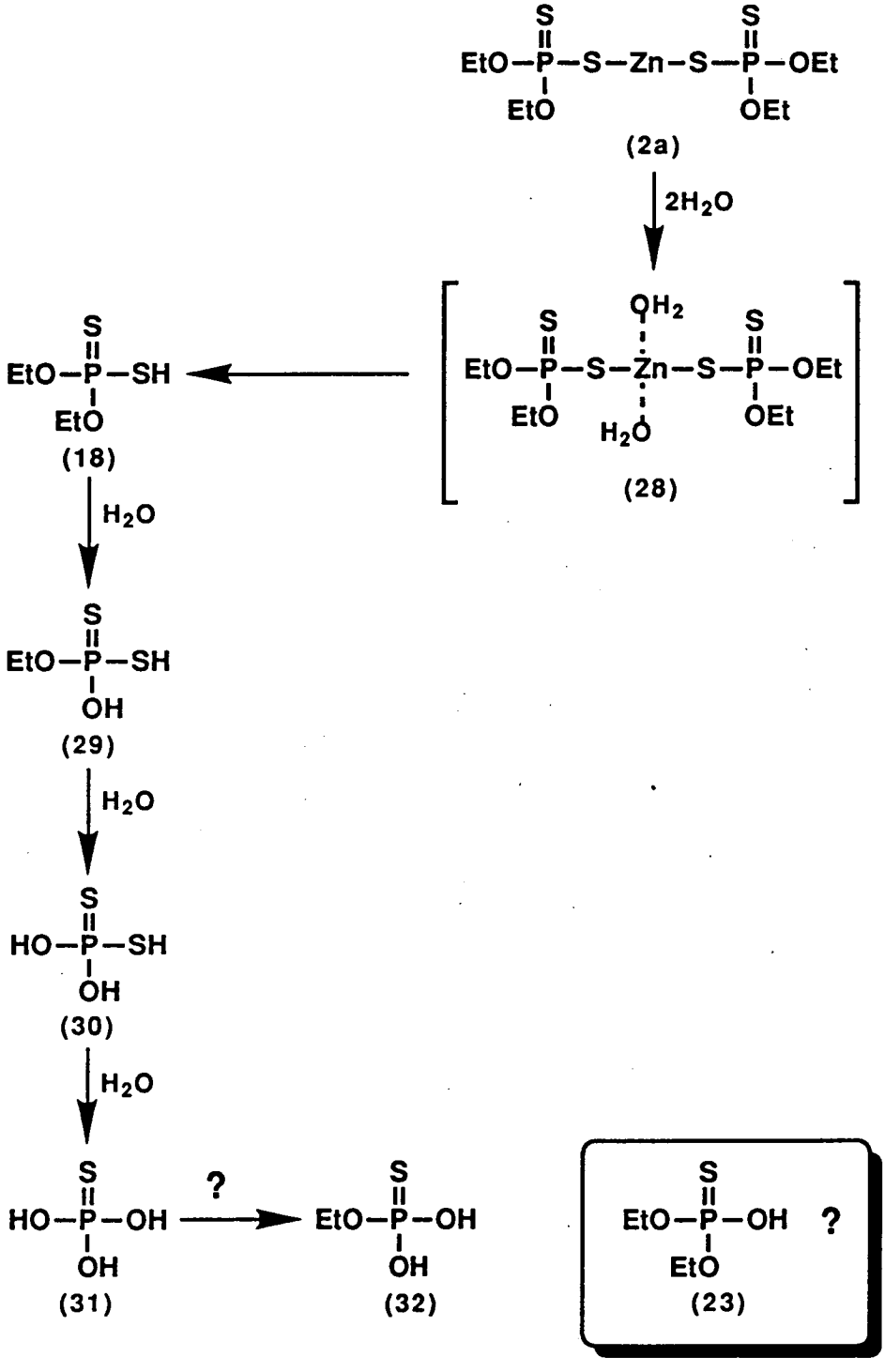
Decoupling
☐ gated ☐ inver
02.....
.....dB.....

Transform.....
LB.....
Plot ☐
☐ work ...cm
F1 ..... f

Date ..... 25/
Operator.....

GOSS

WP



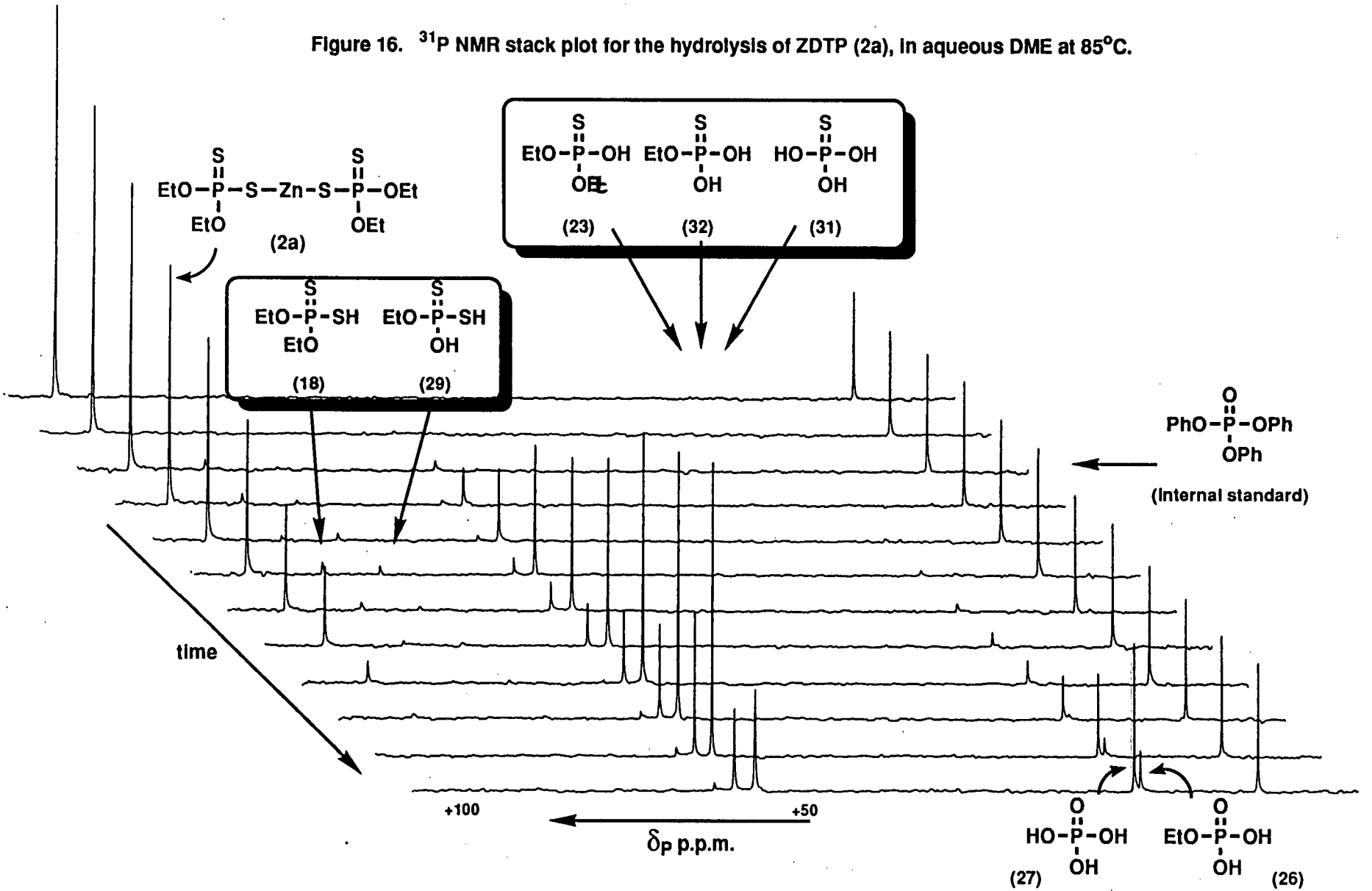

SCHEME 14

Upon addition of an authentic sample of $(EtS)_3P(O)$ (22), the spectrum shown in Figure 15 was obtained. Clearly the 'unknown' product IS NOT $(EtS)_3P(O)$ (22) which now appears at $\delta$ +64 p.p.m! When an authentic sample of ethyl thiophosphoric acid (32) was added instead the required 'peak enhancement' was observed.

Scheme 14 summarises the various steps in the ZDTP hydrolysis pathway as determined and confirmed at this point in the investigation. It superceeds Schemes 11-13. Dewan had been unable to work out[95] the origin of the species at $\delta$ +64.1 p.p.m. in the original ZDTP hydrolysis spectrum (figures 7 and 8) which corresponded to O, O' - diethyl thiophosphoric acid (23). The present identification of ethyl thiophosphoric acid (32) as the compound at $\delta$ +61.3 p.p.m. made the product pattern more 'uniform' and plausible/sensible even if a few more questions were now raised.

From the experiments earlier (Figures 7, 8, 11 and 14) it was noted that ethyl thiophosphoric acid (32) formation was favoured by reducing the amount of water present for hydrolysis. Similarly a lower reaction temperature discourages its formation. This implied that the formation

Figure 16. $^{31}P$ NMR stack plot for the hydrolysis of ZDTP (2a), in aqueous DME at 85°C.



of (32) was due to reactions other than hydrolysis. If this was so, it seemed likely that diethyl thiophosphoric acid (23) was similarly formed (this would explain why Dewan was unable to find the precursor to (23)). Synthesis of (23) by an adaptation of a literature reaction[103] and a peak enhancement check reconfirmed the authenticity of diethyl thiophosphoric acid (23) in the reaction pathway.

At this stage a detailed study of the hydrolysis of ZDTP (2a) revealed the order of formation of the major intermediates and products; this information was not made clear previously by Dewan[95]. So, when ZDTP (2a) (0.0033 mole) in DME solution ($10cm^{-3}$) was hydrolysed with ten equivs of water at 85°C and monitored at short intervals by $^{31}P$ NMR over the course of its reaction (5 hours), the stack plot of spectra shown in Figure 16 was obtained. Subsequent analysis of the spectra confirmed the conclusions of the experiments with diethyl dithiophosphoric acid (18) regarding the sequence in which the products arose, as summarise in Scheme 14. Furthermore, the order in which the four final products occurred was also determined: ethyl thiophosphoric acid (32) before phosphoric acid (27), which in turn was formed before diethyl thiophosphoric acid (23) and finally ethyl phosphoric acid (26). The salient implication at this stage was that ~~hyrdo~~hydro lysis was not responsible directly for

the evolution of these products under the reaction conditions described. After all, hydrolysis of thiophosphoric acid (31) could only ever give rise to $H_3PO_4$ (27).

## 3.6 Kinetic studies on the hydrolysis of ZDTP (2a), diethyl dithiophosphoric acid (18) and thiophosphoric acid (31)

Even while the detailed qualitative investigations into the ZDTP hydrolysis mechanism were being carried out (described in preceeding sections), utilising and developing techniques of $^{31}P$ NMR analysis, it had always been envisaged that quantitative rate data (from kinetic experiments) could be extracted from these studies, with a view to applying relative rates of hydrolysis in the comparison of variously (aryl) alkylated ZDTP's. In this broader context, the use of $^{31}P$ NMR analysis in kinetic investigations was developed. This technique was applied to the study of the hydrolyses of ZDTP (2a), diethyl dithiophosphoric acid (18) and thiophosphoric acid (31) and is described in brief detail here. Technical factors involved when obtaining kinetic information in $^{31}P$ NMR analysis have been discussed in Section 2.4.

If the mechanism outlined in Scheme 14 is valid (ie-attack of water at the metal moiety of the MDTP's), then

the rate of the reaction is expected as a $S_N2$ type (ie- dependent on the concentration of both the MDTP and water), provided of course this is the rate determining step.

$$\frac{-d\,[substrate]}{dt} \propto [substrate]\,[H_2O] \qquad 16.$$

If water is present in large excess, the rate expression simplifies to:

$$\frac{-d\,[substrate]}{dt} \propto [substrate] \qquad 17.$$

that is,

$$\frac{-d\,[substrate]}{dt} = k\,[substrate] \qquad 18.$$

where k is the rate constant for the hydrolysis. In other words, the rate should follow a pseudo-first-order rate expression:

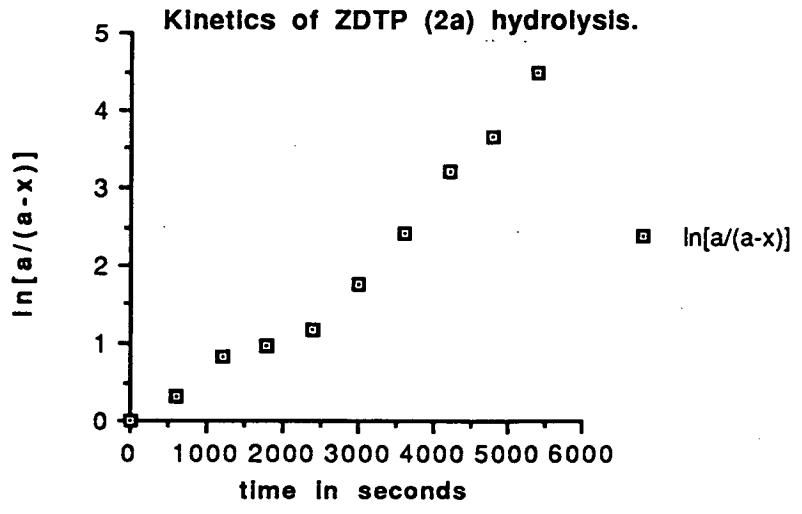
$$k = \ln\left[\frac{a_0}{a_0 - x}\right] . 1/t \qquad 19.$$

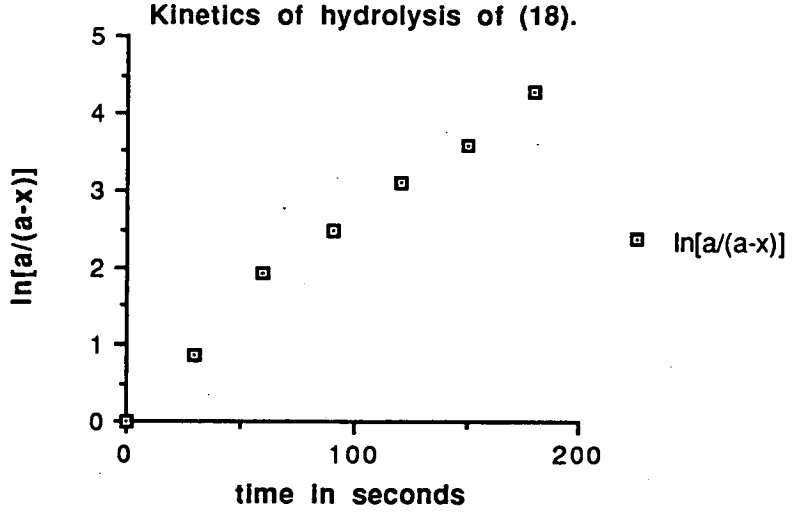
where $a_o$ is the initial concentration of substrate, and x is the amount consumed in time t.

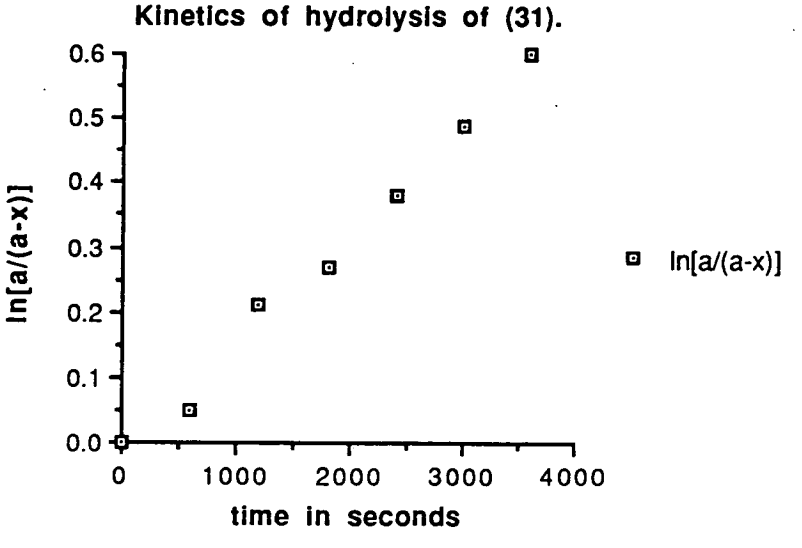
These assumptions were also applied to the hydrolyses of (18) and (31).

Kinetic analyses for the hydrolyses of ZDTP (2a)

Figure 17. Kinetic plots for the hydrolyses of (2a), (18) and (31).



(0.0034 mole), diethyl dithiophosphoric acid (18) (0.0029 mole) and thiophosphoric acid (31) (0.0035 mole) were carried out individually under identical conditions, viz 85± 1°C/DME ($10cm^{-3}$) and ten equivs of water, by monitoring their respective rates of disappearance using $^{31}P$ NMR spectroscopy. It was necessary to use triphenyl phosphate as an INERT[2*] 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[3*] so that their signal intensities were proportional to their respective concentrations. In this way, the ratio of signal peak height due to the substrate compared to that for the standard could be used for obtaining $(a_o-x)$ values. In the case of ZDTP (2a), 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 17); in the case of ZDTP (2a) the plot

---

2* Control experiments showed that triphenyl phosphate did not hydrolyse under the kinetic conditions.

3* $T_1$ values were obtained usingn the inversion-recovery method and calculated from a least squares logarithmic plot of the data using a JEOL FX90Q program (see Chapter 5).

## Figure 18.

**Variation of pH vs. time during hydrolysis of diethyl ZDTP (2a)**

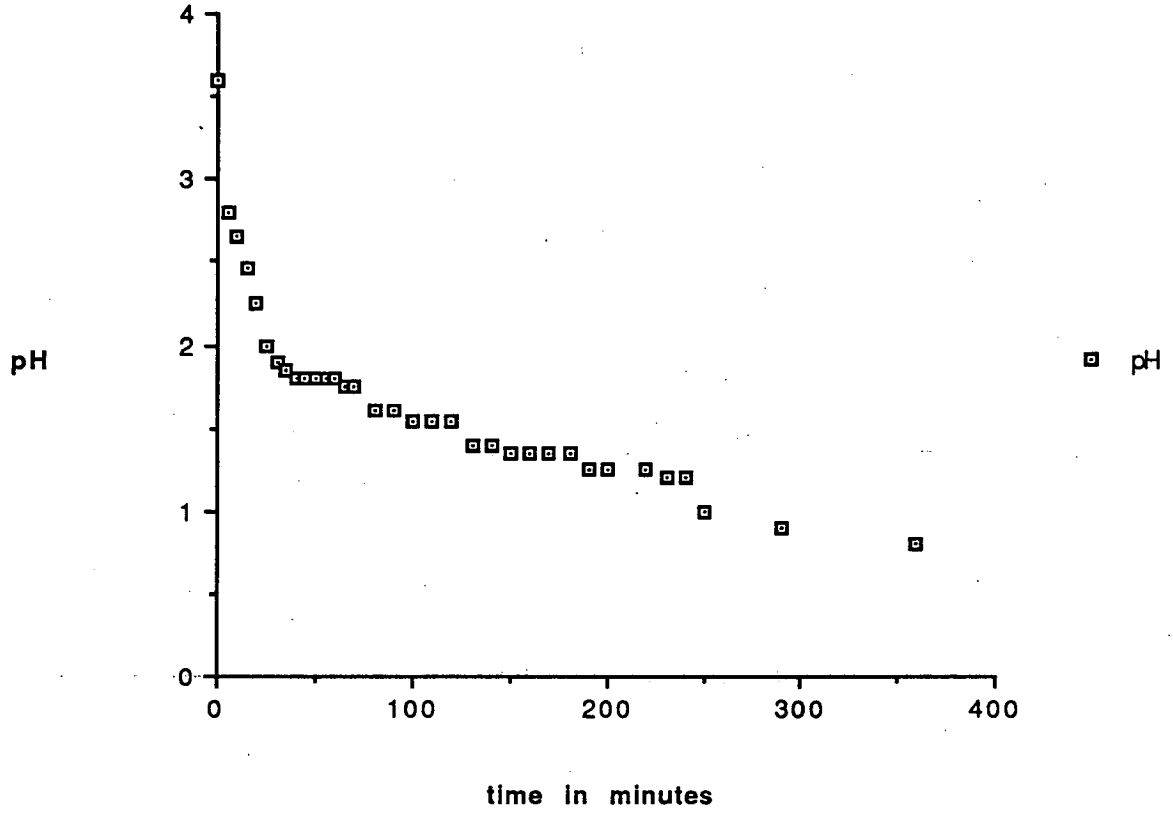
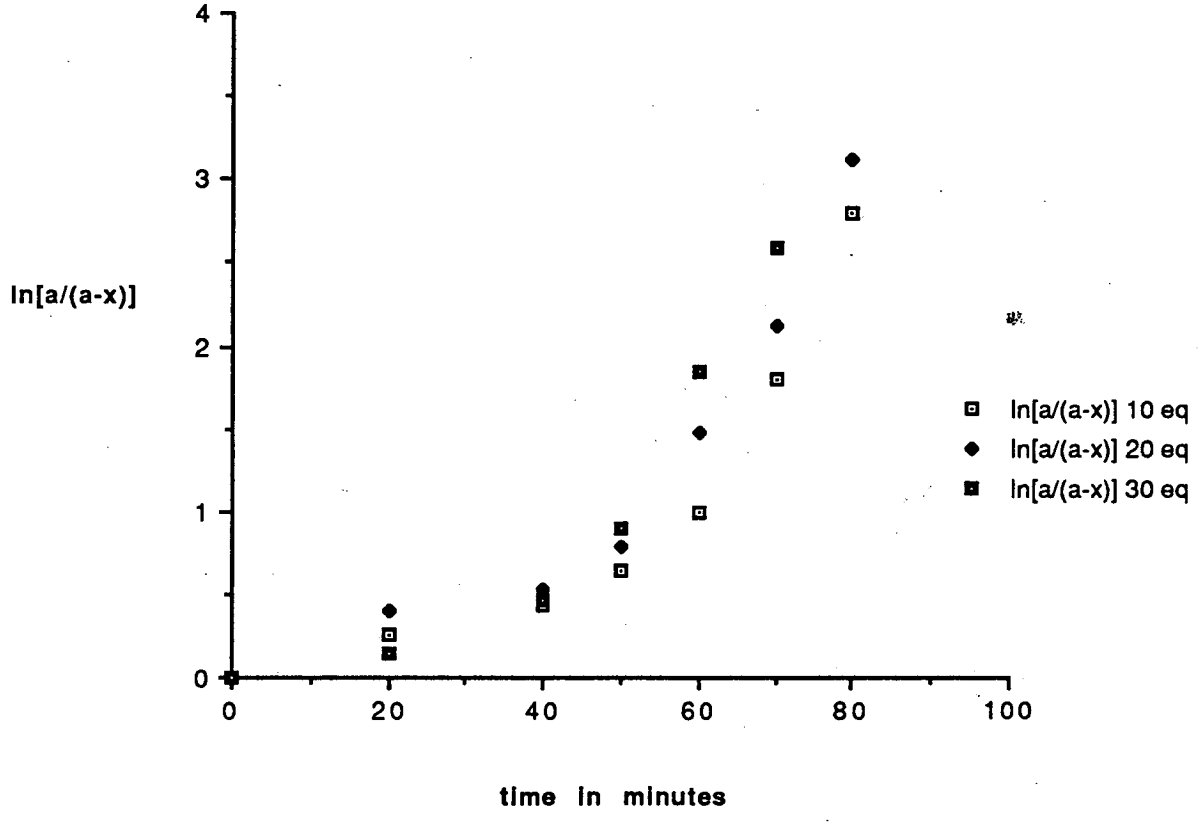


**Figure 19. Kinetic plots of hydrolysis of (2a) with 10, 20 and 30 eq of water.**



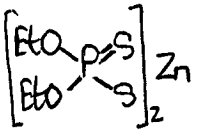
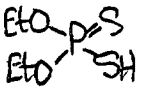
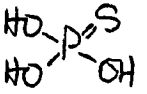
| Compound | $k_{obs}$ / x10 $^{-4}s^{-1}$ |
|---|---|
|  (2a) | 2.35 |
|  (18) | 135.0 |
|  (31) | 0.078 |

**Table 1. Rate constants (k) for the hydrolysis of (2a), (18) and (31) under pseudo-first order conditions.**

was linear for only ca two half-lives of the disppearance of substrate. During this period the only products to be observed were the dithio-acid (18) and thiophosphoric acid (31) ie - before the formation of ethyl thiophosphoric acid (32), diethyl thiophosphoric acid (23) and ethyl phosphoric acid (26); a separate identical hydrolysis when monitored showed that the pH of the hydrolysis mixture decreased from 4.5 to 1.0 (Figure 18). Thereafter the plot for the hydrolysis of (2a) showed an exponential increase presumably due to acid catalysis. This supposition was supported by the fact that NO CHANGE occurred in the rate profile, even in the presence of large excesses of water (the hydrolysis was repeated with twenty- and thirty equivs of water, see Figure 19).

The calculated pseudo-first-order rate constants ($k_{obs}$) for each species [(2a), (18) and (31)] are presented in Table 1, and more generally establish that the rate of hydrolysis of thiophosphoric acid (31) was VERY SLOW compared to that of its precursor diethyl dithiophosphoric acid (18) which in turn was hydrolysed at a FASTER rate than ZDTP (2a) itself.

The effect of these changes in the hydrolysis mixture was to lead to a build-up in the concentration of thiophosphoric acid (31) (Figure 16). Thereafter it would seem that (31)

either decomposed to phosphoric acid (27) or was transformed into ethyl thiophosphoric acid (32) or both processes occurred. It appeared reasonable to suggest that if both these processes occurred, they would in effect compete against each other for substrate. Thus, if the reaction conditions favoured phosphoric acid formation (ie-hydrolysis) one might expect the formation of (32) to be disfavoured. The latter process, effectively a transalkylation, would be expected to be more facile than hydrolysis given that the relative rate of hydrolysis of thiophosphoric acid (31) is SO SLOW.

Evidence for these ideas was gleaned from the stack plots of spectra of ZDTP hydrolyses with ten ,twenty and thirty equivs of water (see Figures 20-22). In considering the proposed transalkylation reactions, the alkylating agent is most probably diethyl dithiophosphoric acid (18) because ZDTP (2a) and ethanol (hydrolysis by-product) are more inert. Due to the fact that the initial kinetic studies were carried out before the mechanism was known fully, ten equivs of water was considered large enough excess. However, once the mechanism was better understood (Scheme 14), it became

Figure 20. $^{31}P$ NMR stack plot for the hydrolysis of ZDTP (2a), in aqueous DME, with 10 eq. water, at 85°C.

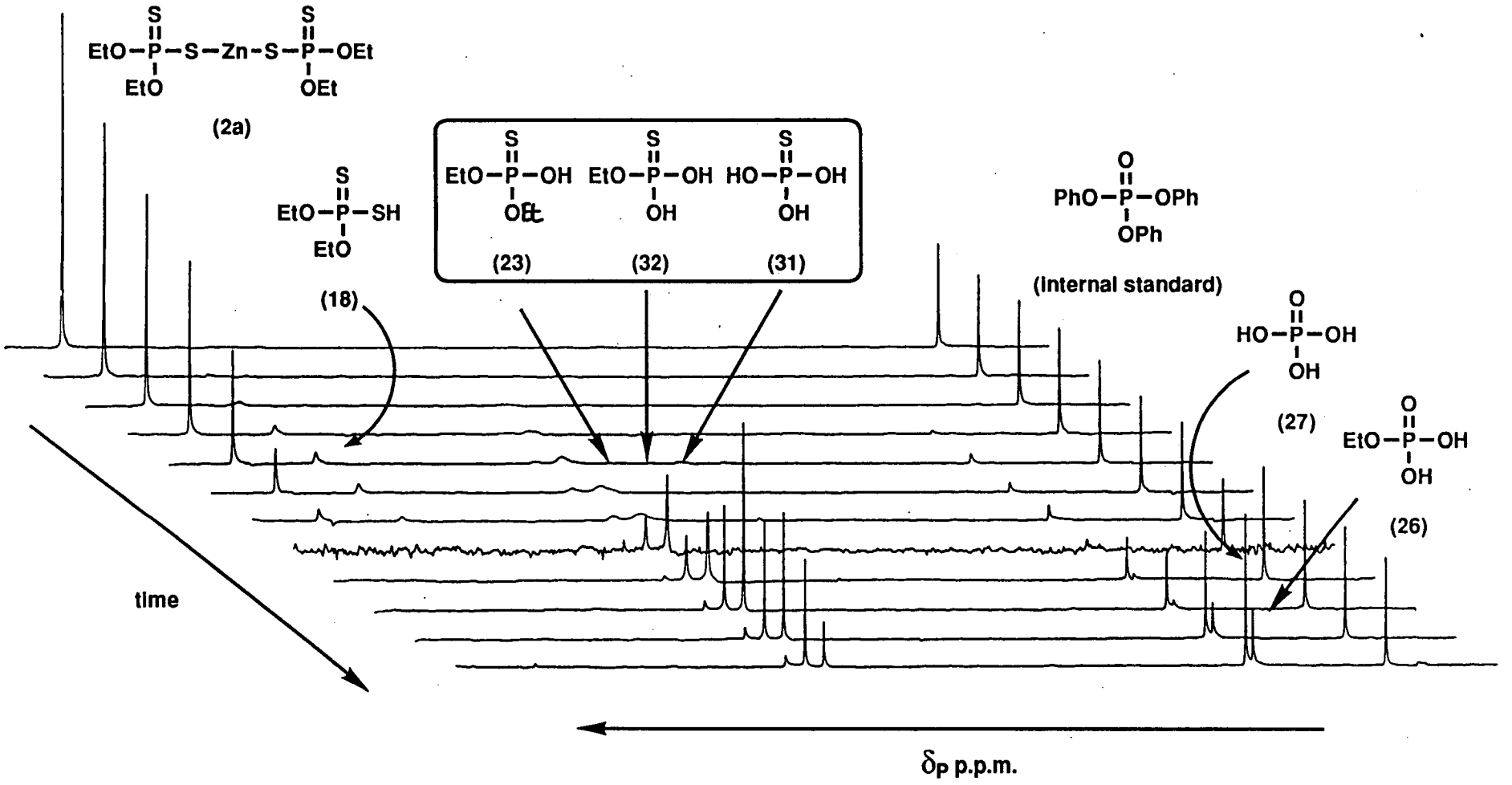


Figure 21. $^{31}P$ NMR stack plot for the hydrolysis of ZDTP (2a), in aqueous DME, with 20 eq. water, at 85°C.

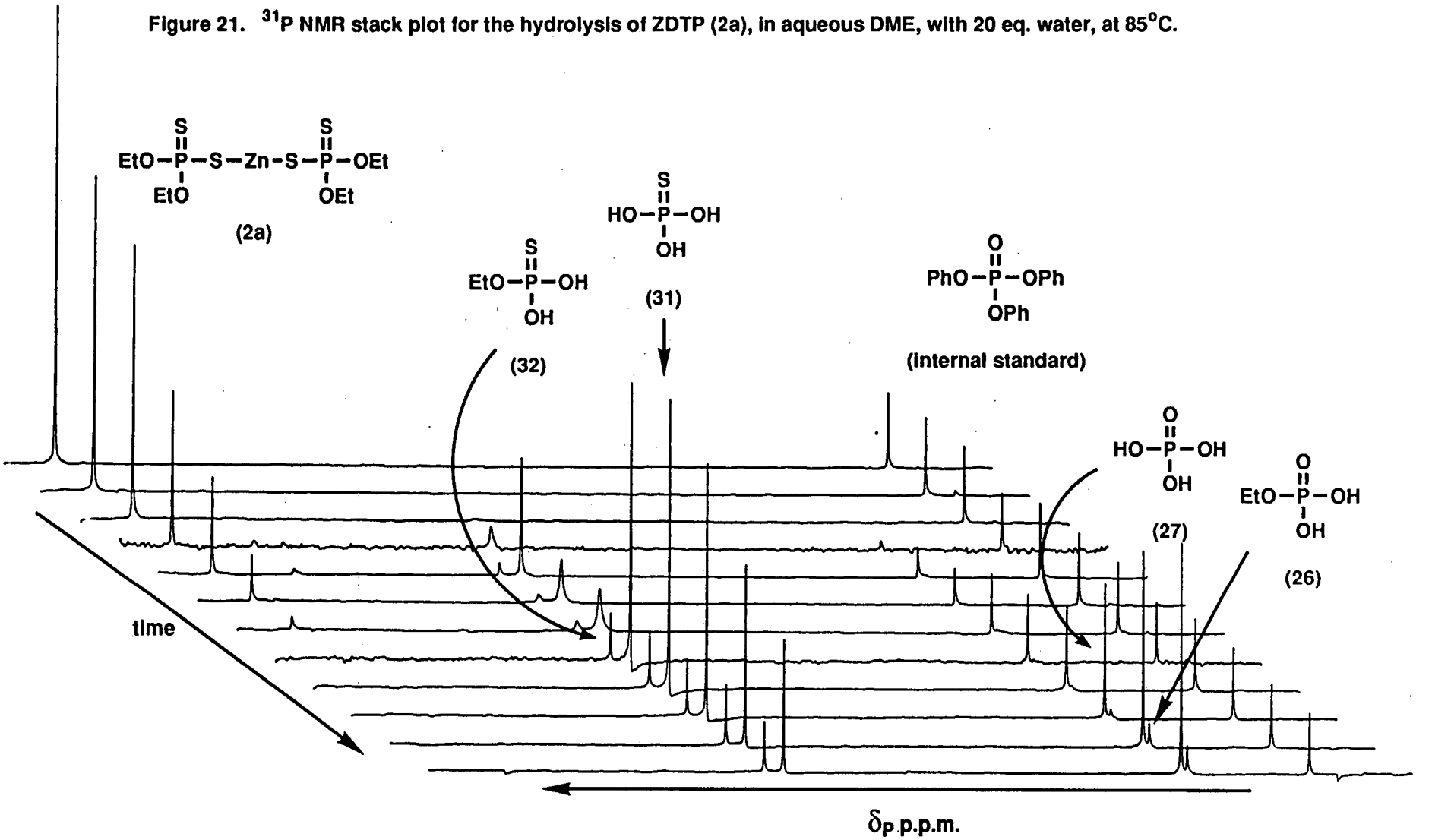
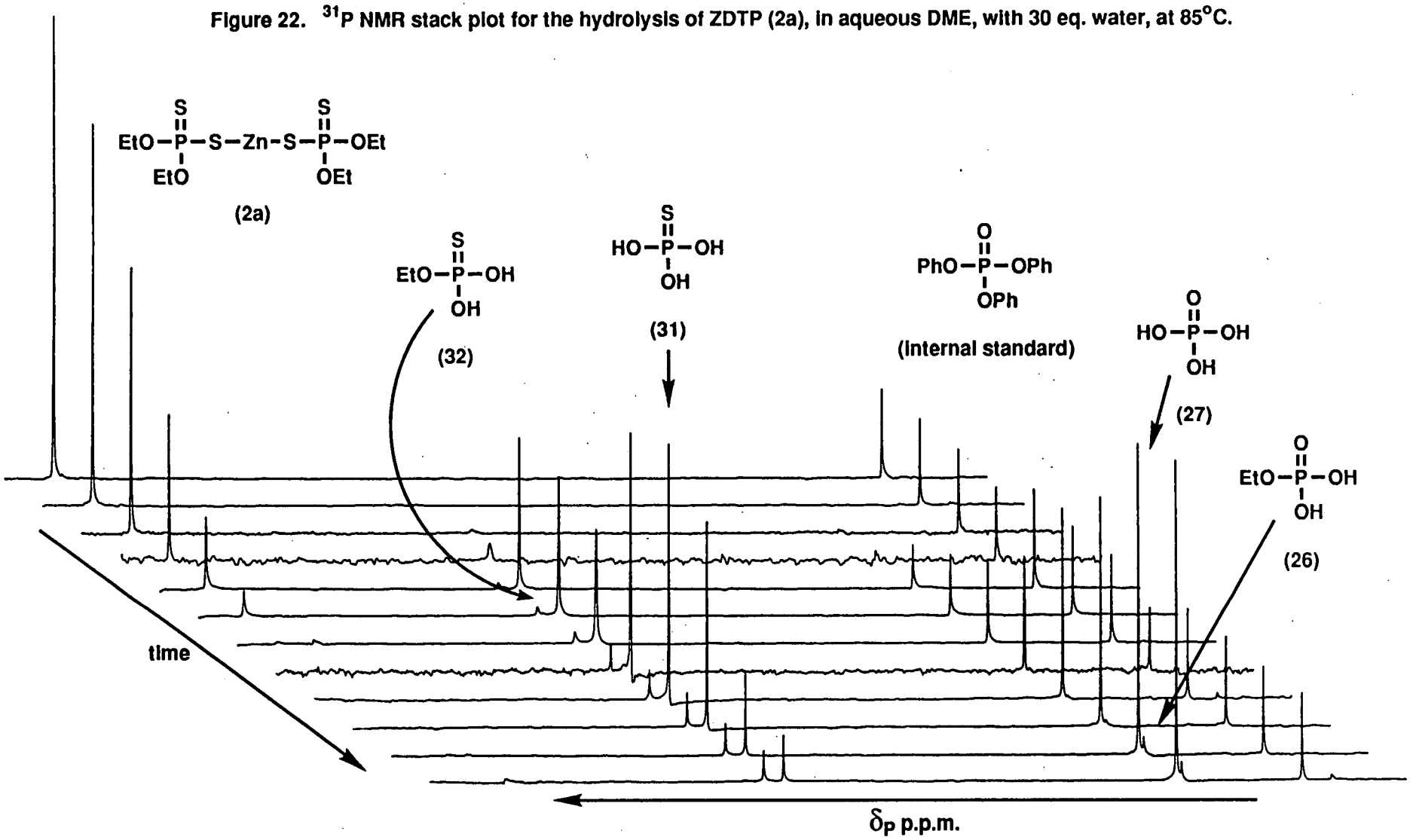
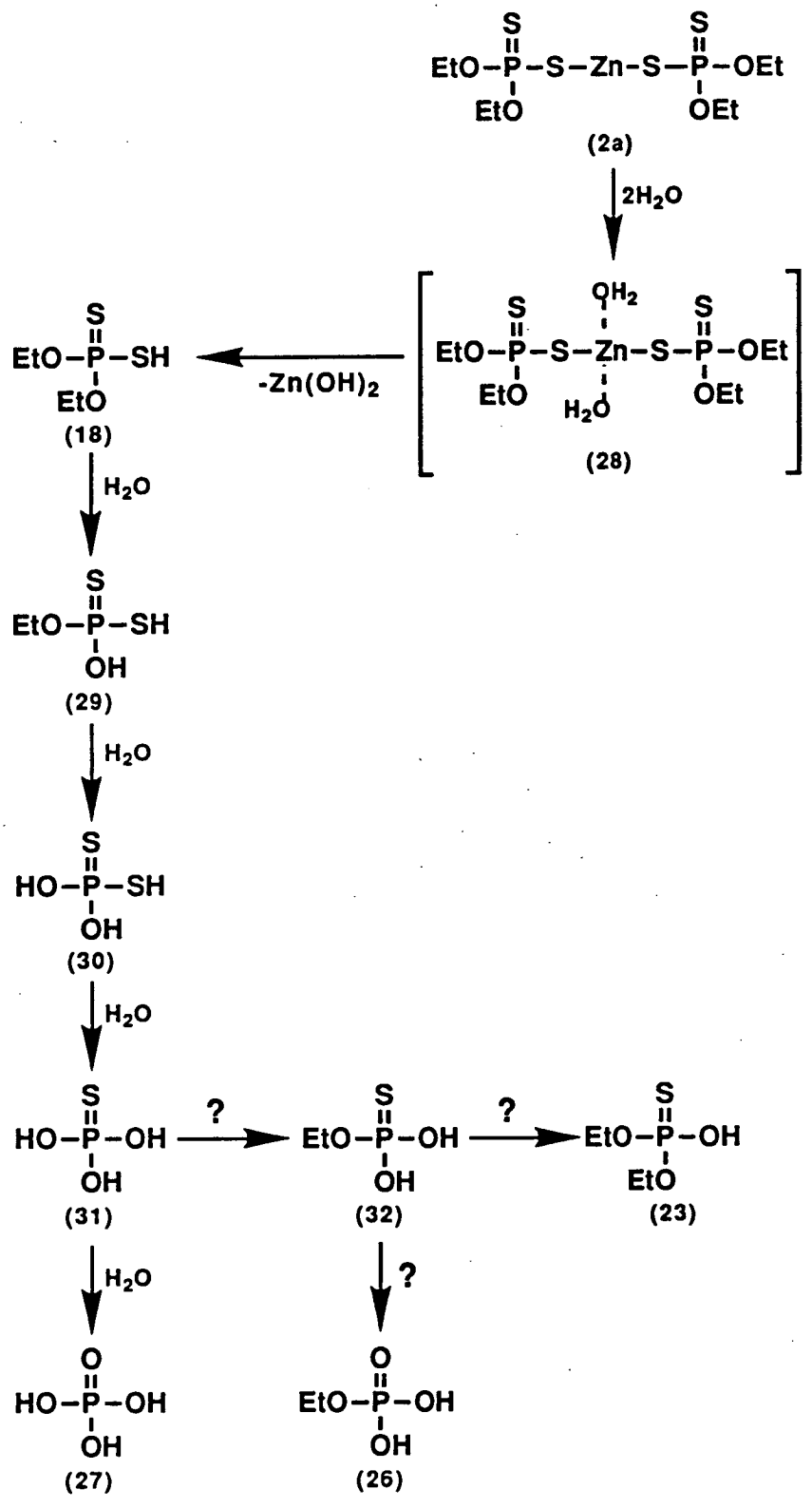


Figure 22. $^{31}P$ NMR stack plot for the hydrolysis of ZDTP (2a), in aqueous DME, with 30 eq. water, at 85°C.






SCHEME 15

clear that ten equivs of water was not a large enough excess, at least five (probably more) equivs of water is already known to be consumed in rapid succession. Primarily because of this, the repeat hydrolyses with twenty and thirty equivs of water were performed (vide supra) (Figures 19-22).

As evidenced by the stack plots of spectra for the above mentioned hydrolyses the amounts of ethyl thiophosphoric acid (32) and diethyl thiophosphoric acid (23) formed were greatly reduced (the latter compound (23) was inhibited) when the water content of the hydrolysis mixture was increased to twenty then thirty equivs. This concurred with the proposed mechanism shown in Scheme 15; for if ten equivs of water was insufficient to affect the hydrolysis of thiophosphoric acid (31) at its 'optimum' rate, thus allowing its concentration to build-up and thereby to initiate 'side-reactions', THEN the increased water content of the hydrolysis mixture would have allowed faster degradation of (31) to phosphoric acid (27), and by doing so would have reduced the amount of (31) available for the formation of by-products such as (32) and (23). The changes in the amount of ethyl phosphoric acid (26) formed from (32) (as suggested by Scheme 15) are also in agreement with the above hypothesis. As there was progressively less (32) formed (on going from ten equivs. of water to thirty equivs.), there was

| REACTANTS / REACTION | DIETHYL DITHIO-PHOSPHORIC ACID (18) | THIOPHOSPHORIC ACID (31) | DISTILLED WATER | ETHANOL | PHOSPHORIC ACID (27) | REACTION TIME IN 0.4 $CM^{-3}$ DME AT 85±2°C. |
|---|---|---|---|---|---|---|
| (a) | 0.0011 mole | 0.0005 mole | — | — | — | 15 minutes |
| (b) | 0.0011 mole | 0.0005 mole | 0.0044 mole | — | — | 15 minutes |
| (c) | — | 0.0005 mole | — | 0.0010 mole | — | 3 days |
| (d) | — | — | — | 0.0022 mole | 0.0011 mole | 3 days |
| (e) | 0.00028 mole | — | 0.0032 mole | 0.0005 mole | — | 5 minutes |
| (f) | 0.00026 mole | — | 0.0028 mole | — | — | 5 minutes |

**TABLE 2. Summary of transalkylation studies.**

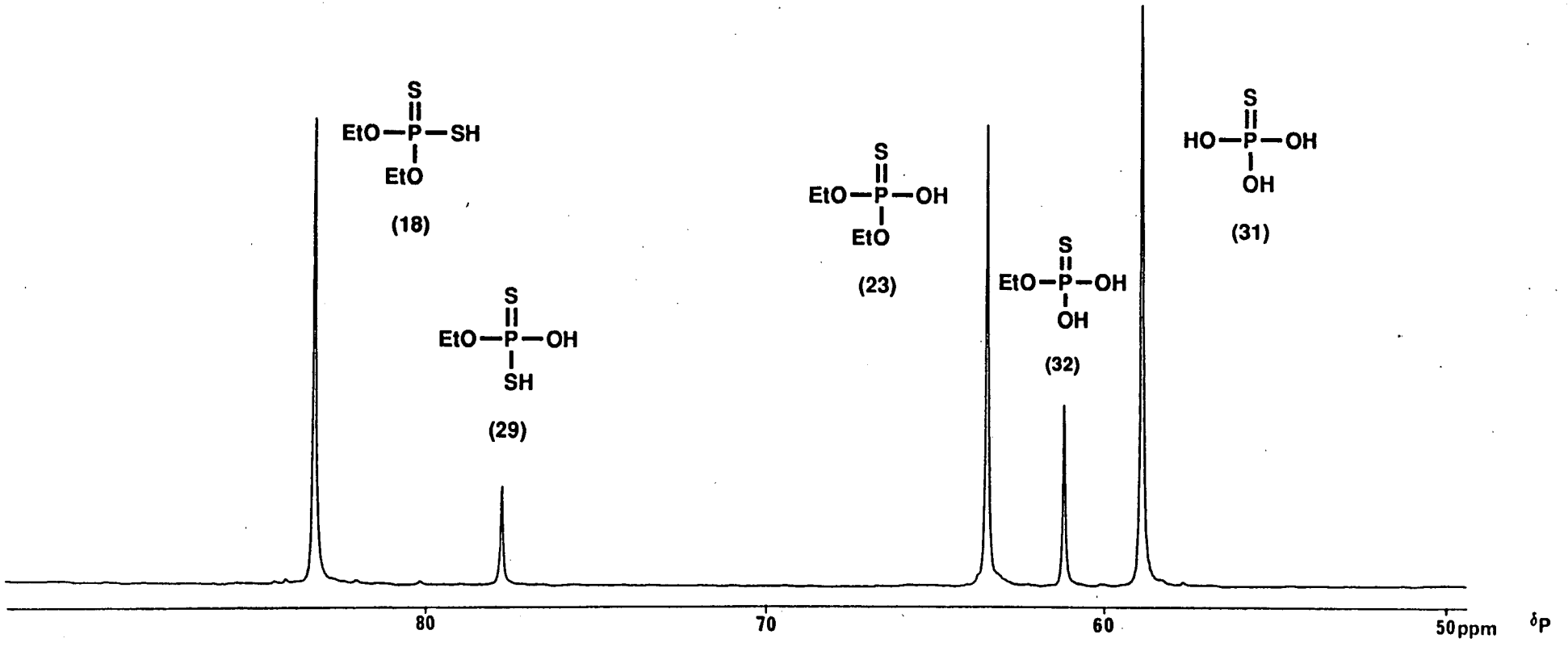
less of its subsequent hydrolysis product (26) observed (Figure 22). [The authenticity of ethyl phosphoric acid in the hydrolysis mixture was reconfirmed by independent synthesis[104] and checking by peak enhancement, as was that of the signal ascribed to phosphoric acid.]

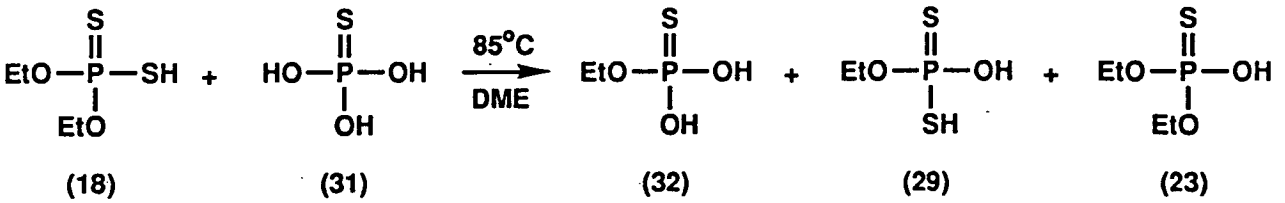
## 3.7 Transalkylation and secondary reactions

At this stage of the investigation the mechanism of ZDTP hydrolysis as regards the sequence of formation of the soluble products was quite well understood. The inevitable next course of action was to verify and probe the nature of the titled side-reactions. Consequently a series of reactions were carried out in which the major possibilities involving diethyl dithiophosphoric acid (18) and thiophosphoric acid (31) were examined (Table 2). The results of these experiments after $^{31}P$ NMR analysis are shown in Figures 23-28.

In reactions (a) and (b), the transalkylation between diethyl dithiophosphoric acid (18) and thiophosphoric acid (31) was verified and its rôlé (w.r.t. the hydrolysis) in the overall mechanism ascertained. In the absence of water (reaction (a)), the reaction was found to produce ethyl thiophosphoric acid (32) and diethyl thiophosphoric acid (23)

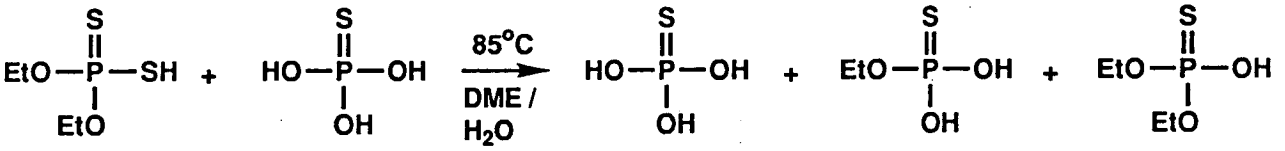
Figure 23. $^{31}P$ NMR $^{1}H$-decoupled spectrum of the reaction between thiophosphoric acid (31) and diethyl dithiophosphoric acid (18) in anhydrous DME at 85°C after 15 minutes.






(18) (31) (32) (29) (23)

Reaction (a)




(18) (31) (31) (32) (23)

major minor trace

Reaction (b)

## SCHEME 16

together with the transesterification by-product, ethyl dithiophosphoric acid (29) (Figure 23) and (Scheme 16). In the presence of water (reaction (b)), the hydrolysis predominated and the degradation of (18) to (31) occurred in preference to the formation of (32), (Figure 24) but not exclusively. As to the mechanism of the conversion of (31) into (32) and (23), it was noted that in none of these reactions were any S-ethyl species observed among the products. This implied that the conversion of thiophosphoric acid (31) into ethyl thiophosphoric acid (32) and subsequently diethyl thiophosphoric acid (23), involved transfer of an ethoxy group rather than direct ethyl group transfer, which would have led to some S-ethylation.

In reactions (c) and (d), the esterification of thiophosphoric acid (31) and phosphoric acid (27) respectively with ethanol was tried. In reaction (d) monitored periodically by $^{31}P$ NMR, no change was observed in the $^{31}P$ NMR spectrum even after 3 days, Figure 25. Over this same period of time, in reaction (c) the formation of (32) was detected by $^{31}P$ NMR BUT its rate of formation was found to be much slower and even after 3 days most of (31) remained unconverted (Figure 26).

In reactions (e) and (f), the rôlé of ethanol in the

Figure 24. $^{31}P$ NMR $^{1}H$-decoupled spectrum of the reaction between thiophosphoric acid (31) and diethyl dithiophosphoric acid (18) in aqueous DME at 85°C after 15 minutes.

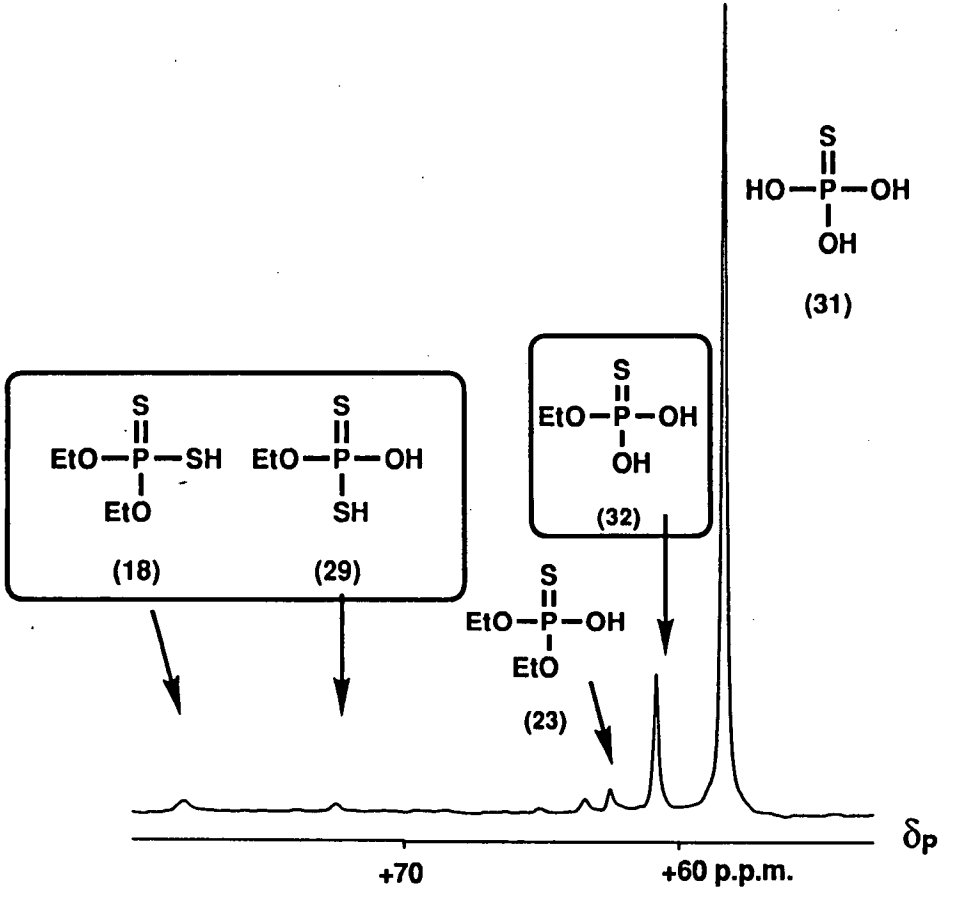


Figure 25. $^{31}P$ NMR $^{1}H$-decoupled spectrum of the attempted esterification of phosphoric acid (27) with EtOH after 3 days.

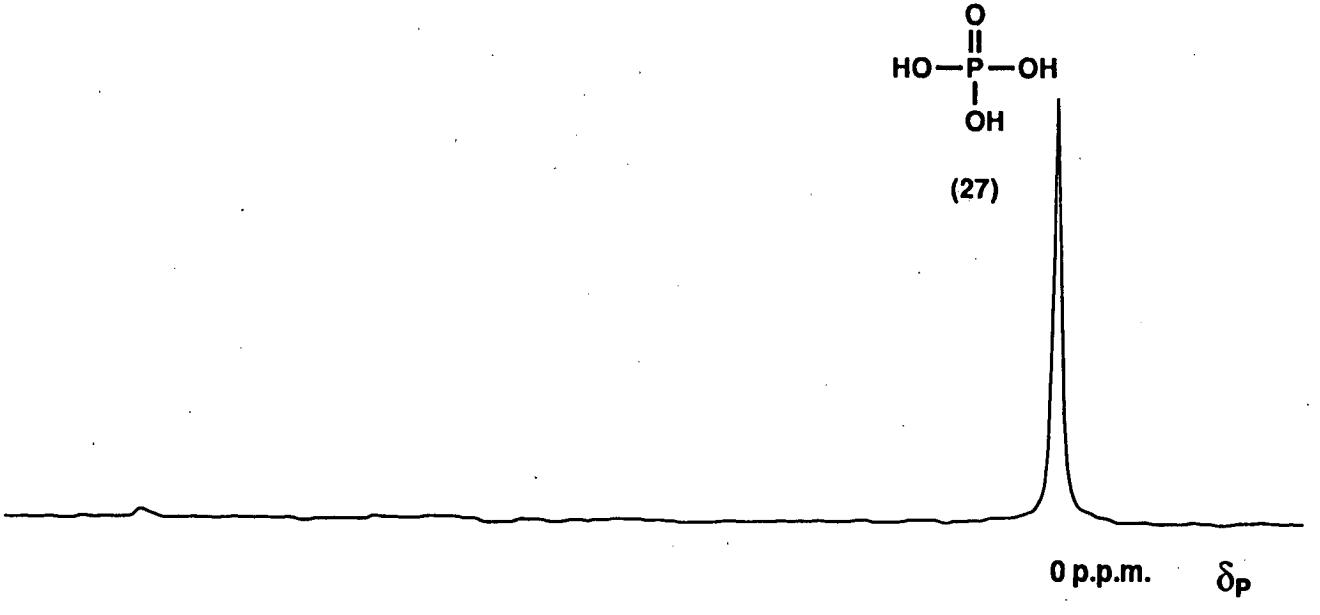
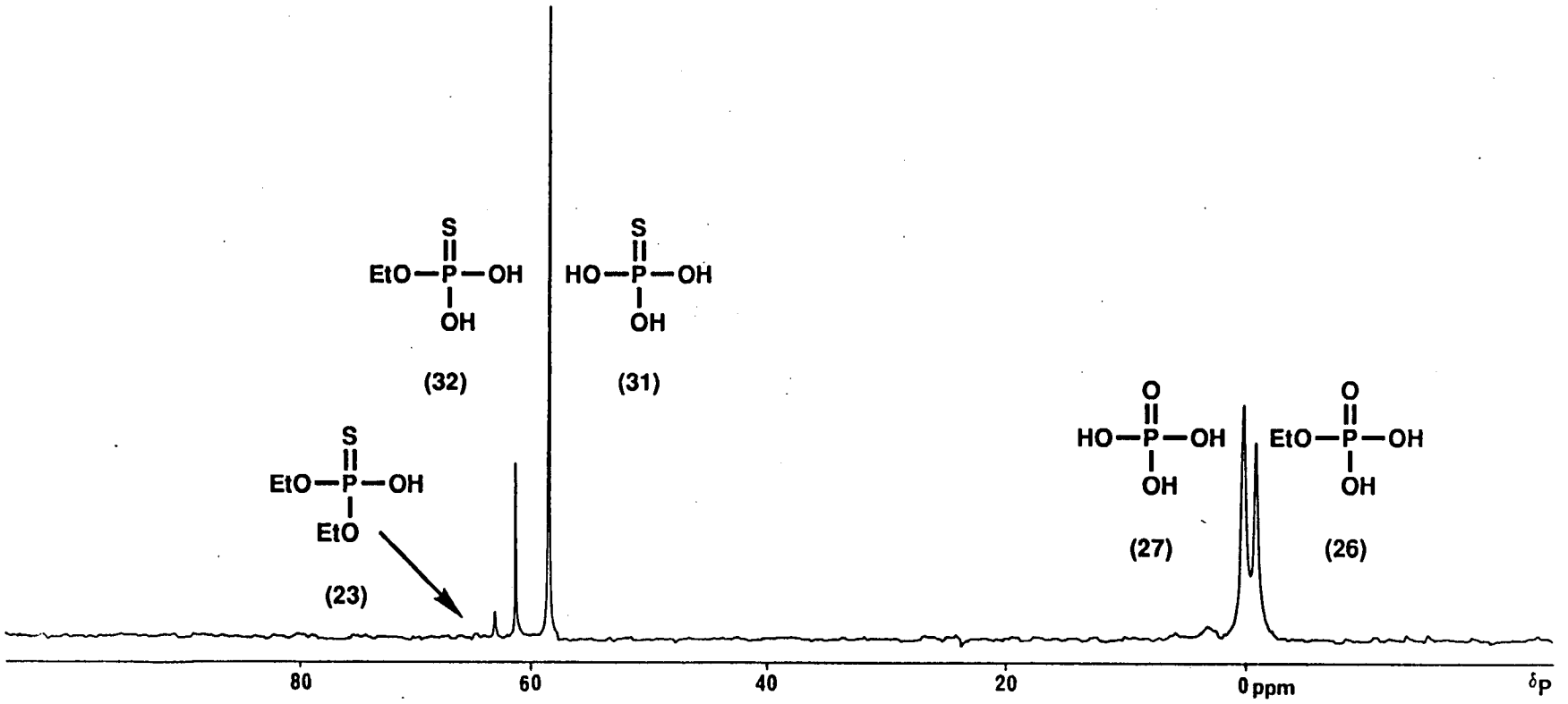


Figure 26. $^{31}P$ NMR $^{1}H$-decoupled spectrum of the reaction of thiophosphoric acid (31) with EtOH in anhydrous DME at 85°C after 3 days.



hydrolysis/transesterification mechanism was examined, (Figure 27-28). It was found that in the presence of added ethanol, the hydrolysis of diethyl dithiophosphoric acid (18) was inhibited, albeit very slightly. A greater concentration of the intermediates, ethyl dithiophosphoric acid (29) and dithiophosphoric acid (30), was observed in reaction (e) along with a lesser amount of ethyl thiophosphoric acid (32) being formed. Since ethanol is a by-product of the hydrolysis [(18)-->(31)], this observation was not totally unexpected.

As a result of the kinetic studies (section 3.6) and the preceeding work on the transalkylation reactions, it can be concluded that the rate of esterification of (31) to (32) is much faster than its hydrolysis to (27) and that the subsequent hydrolysis of (32) gave rise to the formation of ethyl phosphoric acid (26). Scheme 17 (which superceeds Scheme 15) summarises the overall breakdown of ZDTP (2a). Similar $^{31}P$ NMR analysis of the hydrolysis of isopropyl ZDTP (2b) showed that a comparable degradation took place.

Figure 27. $^{31}P$ NMR $^{1}H$-decoupled spectrum of the hydrolysis of diethyl dithiophosphoric acid (18) with added EtOH.

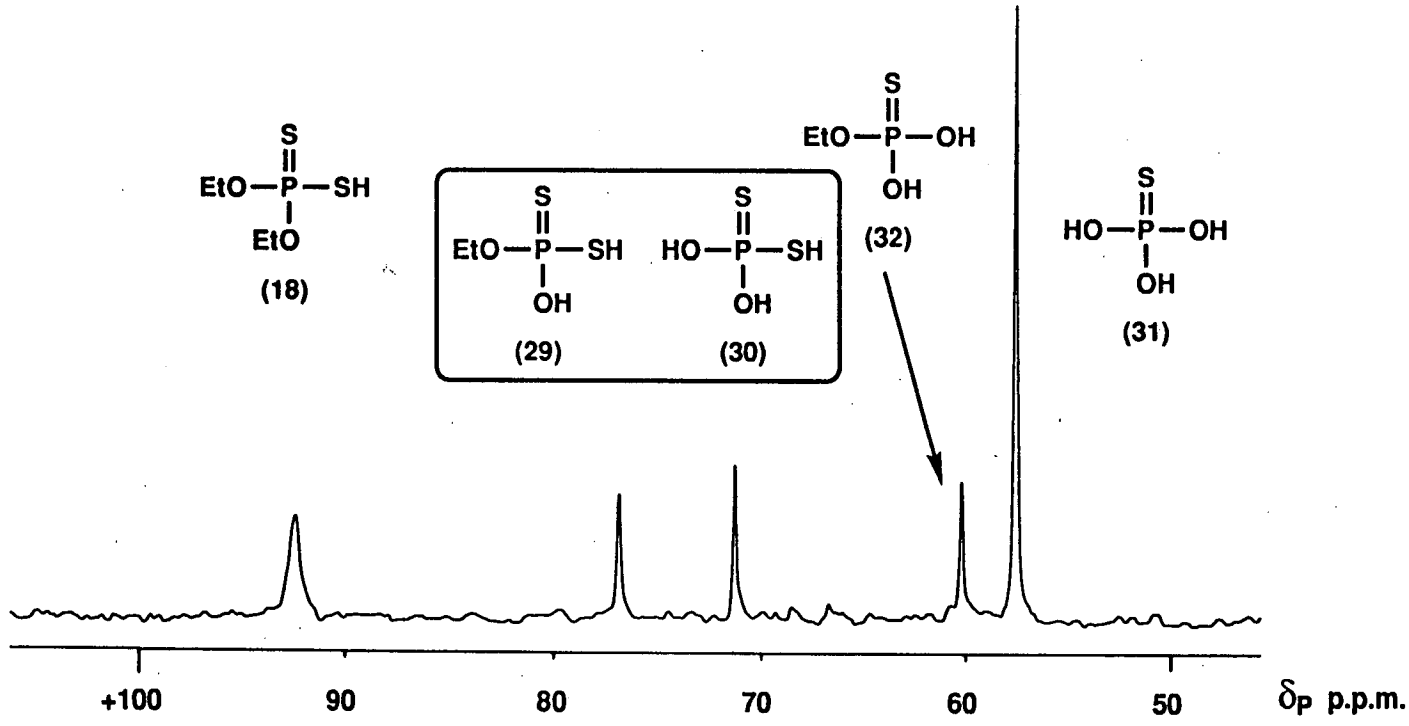
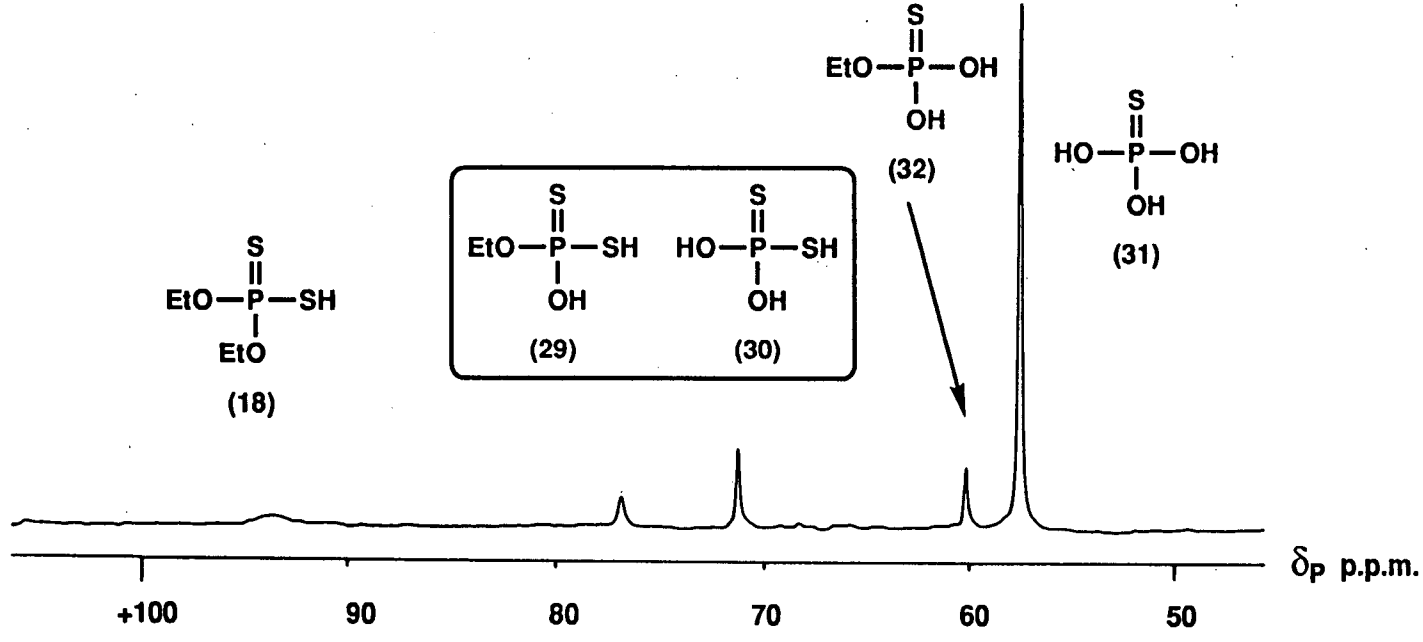
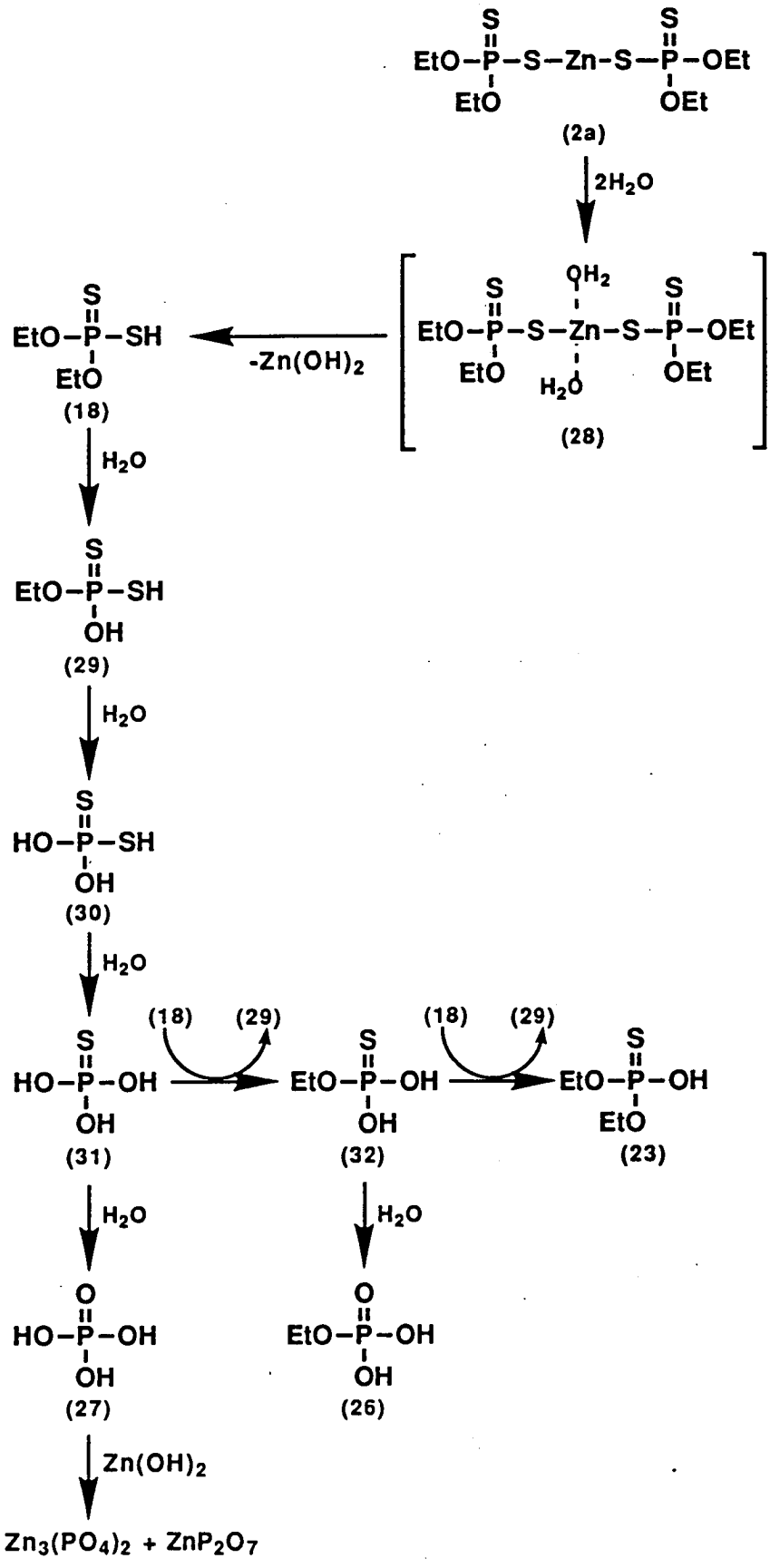


Figure 28. $^{31}P$ NMR $^{1}H$-decoupled spectrum of the hydrolysis of diethyl dithlophosphoric acid (18) without added EtOH.




(2a)
2H2O
(28)
-Zn(OH)2
(18)
H2O
(29)
H2O
(30)
H2O
(18)
(29)
(18)
(29)
(31)
(32)
(23)
H2O
H2O
(27)
(26)
Zn(OH)2
Zn3(PO4)2 + ZnP2O7

SCHEME 17

## 3.8 Identification of precipitates from ZDTP hydrolyses

Finally, turning to the ultimate fate of the zinc in (2a), it had been noted (Section 3.3) that hydrolysis was accompanied by the gradual formation of a colourless precipitate. It was assumed that the initially formed zinc complex (28) was transformed into insoluble zinc hydroxide, but the yield of precipitate[95] 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 was supported by the elemental analysis of a typical precipitate (Table 3) which shows that its composition is probably best formulated as a mixture of zinc hydroxide, zinc oxide, zinc sulphide, and zinc phosphates. Indeed, treatment[95] 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 2M aqueous sodium hydroxide showed signals at $\delta$ +6.3 p.p.m. and 4.1 p.p.m. which are identical to 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

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

**Table 3. Elemental analysis of a precipitate from the hydrolysis of ZDTP (2a).**

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 (2a) in the precipitate was almost quantitative (96.25±0.05%) regardless of its composition. This fact further reinforced the mechanism shown in Scheme 17 wherein attack of water occurred at the zinc centre, and in consequence did not give rise to any metal-containing soluble products.

## 3.9 Summary

In conclusion, $^{31}P$ n.m.r. spectroscopy was found to be an extremely useful aid in the determination of the exact mechanism of hydrolysis of the ZDTP's. The key to the mechanism was the identification of thiophosphoric acid (31) and the determination of its relative rate of hydrolysis. The final mechanism is shown in Scheme 17. Although the definite identity of the proposed complex (28) preceeding the formation of O,O'diethyl dithiophosphoric acid (18) remains somewhat sketchy, the rest of the mechanistic pathway is without doubt. Since the initial attack of water occurs at the zinc atom of the ZDTP (2a) to produce the dialkyl dithiophosphoric acid (18), the rest of the hydrolytic degradation follows down the thermodynamic gradient until

phosphoric acid (27) is reached; the acid then reacts with the liberated zinc moities to give a complex mixture of salts. If there is insufficient water to effect the immediate hydrolysis of the phosphorus containing species then transalkylation reactions begin to take over and a multitude of other products are seen [e.g. O-ethyl thiophosphoric acid (32)].

It is interesting to note (though it should not be too surprising) that the hydrolysis of (18) results in the removal of the alkoxy groups prior to desulphurisation of the compound (c.f. hard and soft acids and bases theory).

What is perhaps more interesting to investigate further is the fact that in the transalkylation reactions, no S-alkylated species were observed by $^{31}P$ n.m.r.

Future work in this area should look at heterogeneous systems in which the ZDTP will only be hydrolysed at the phase boundary of the two solvent systems and whether apart from the obvious slower rate of hydrolysis that will be seen, the amount of transalkylated products increase; whether S-alkylated species will begin to be seen, etc. Comparisons between commercially manufactured ZDTP's and analytically pure compounds should also be carried out, both in

homogeneous and heterogeneous systems AND at higher temperatures (ca. 150°C).

## CHAPTER 4

INHIBITION OF HYDROLYSIS OF 'NORMAL' ZINC (II) O,O'-DIISOPROPYL DITHIOPHOSPHATE BY ITS 'BASIC' FORM


| | | |
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| 4.3 | Hydrolysis of 'normal' ZDTP **(2b)** in the presence of its 'basic' form **(3b)**. | 121 |
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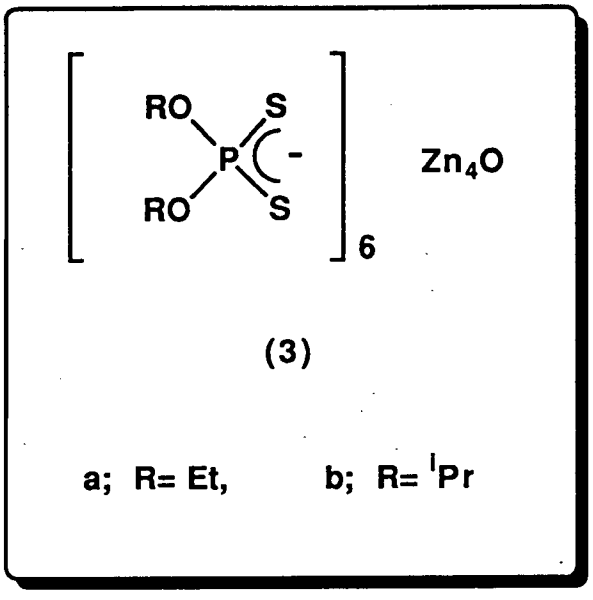
*'The Road goes ever on and on*
*Down from the door where it began.*
*Now far ahead the Road has gone,*
*And I must follow, if I can,*

*Pursuing it with weary feet,*
*Until it joins some larger way,*
*Where many paths and errands meet.*
*And whither then ? I cannot say.'*

*from The Fellowship of the Ring,*
*J.R.R. Tolkien*




(3)

a; R= Et, b; R= $^{i}$Pr

# CHAPTER 4

# INHIBITION OF HYDROLYSIS OF 'NORMAL' ZINC (II) O, O' - DIISOPROPYL DITHIOPHOSPHATE BY ITS 'BASIC' FORM.

## 4.1 Introduction

As mentioned earlier (section 1.2) 'basic' ZDTPs (3) of composition $Zn_4[S_2P(OR)_2]_6O$ [105] are by-products of the commercial manufacture of normal ZDTPs (2), and are present in the oil additive package to varying extents. They are reported [64] to be inactive as anti-oxidants and anti-wear agents and are thus, unwanted. In this chapter, the fate of analytically pure basic ZDTP, $Zn_4[S_2P(OPr^i)_2]_6O$ (3b) under aqueous conditions in DME solution at 85°C is reported in the light of earlier findings on the hydrolytic breakdown of its normal counterpart (2) [106].

These basic salts were first obtained by Wystrach and co-workers[91] in 1956 as a by-product of the reaction between zinc (II) chloride and sodium O, O' - di-n-butyl dithiophosphate in aqueous solution during the preparation of the corresponding normal salt. Later, Bacon and Bork[107] isolated other examples of the same series of compounds using

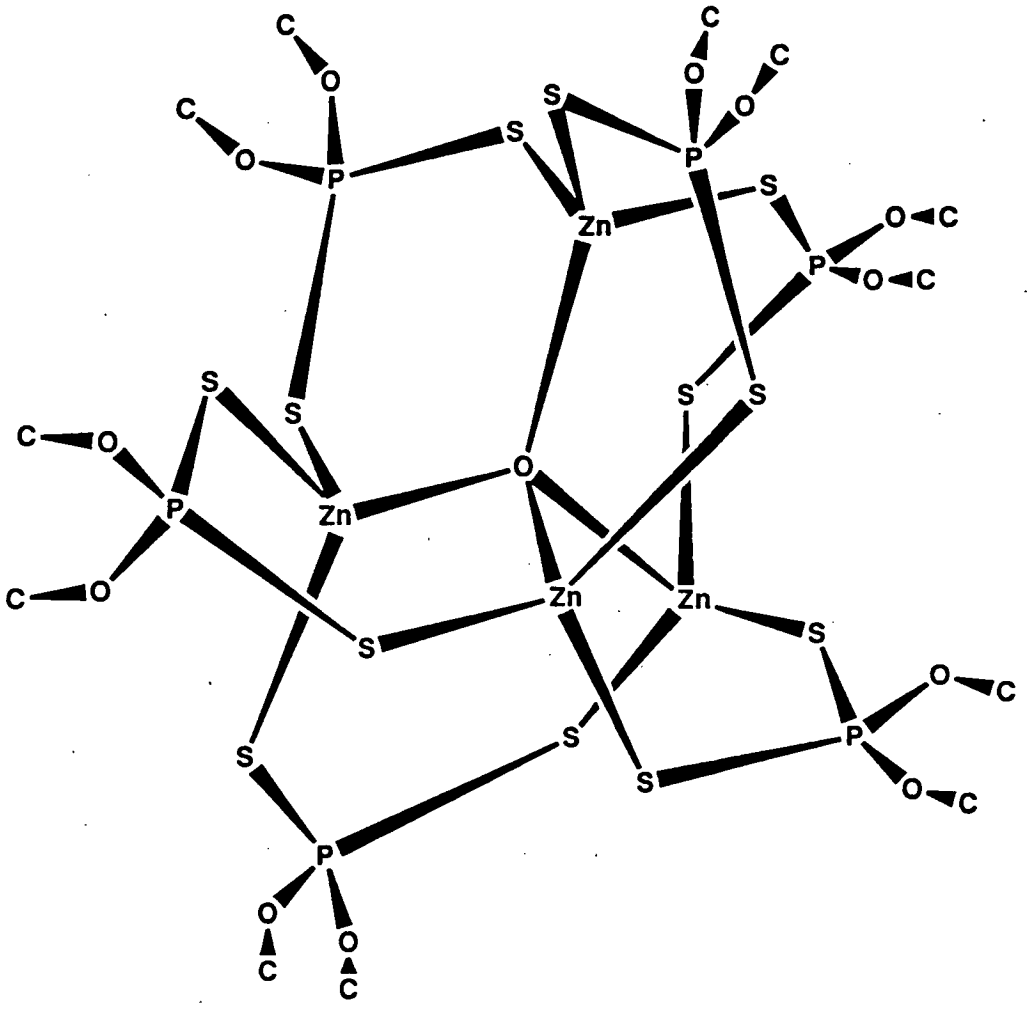



Figure 29

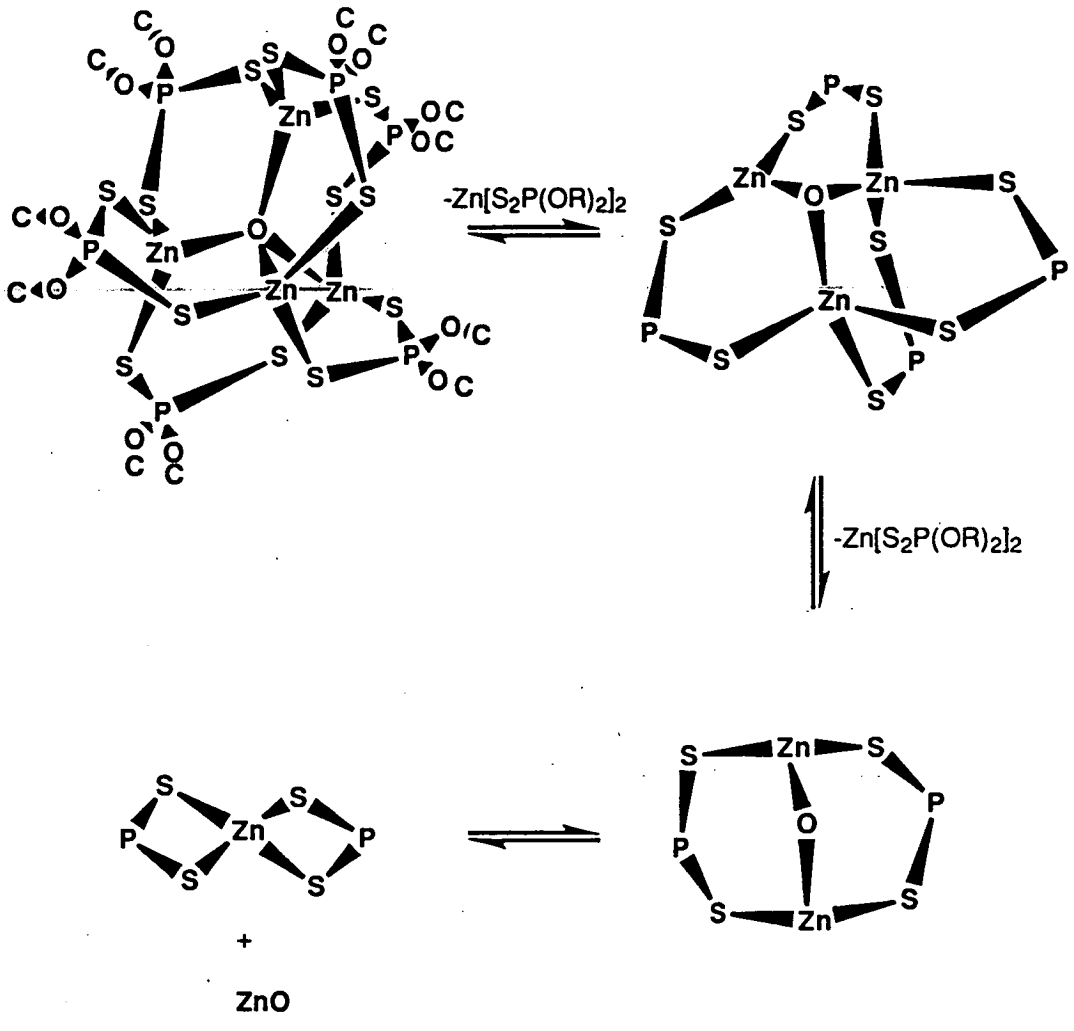
zinc (II) oxide and O, O' - dialkyl hydrogen dithiophosphates. The same basic salts could also be prepared by oxidizing the normal salts with hydroperoxides[42] (equation 9, section 1.3).

In 1965, Burn and Smith[105] obtained the structure for the isopropyl basic salt (3b) by a partial X-ray crystal analysis, (Figure 29). It was shown to consist of a cage structure formed by six $[S_2P(OPr^i)_2]$ moieties associated with four zinc atoms which are tetrahedrally coordinated around a central oxygen atom. Recently, extended X-ray absorption fine structure studies (EXAFS) have confirmed this finding.[108]

Recent studies[63, 64] have looked at the reactions of the normal (2b) and basic salt (3b) with nitrogen donors (as models for dispersant additives and their degradation products). Whilst they have shed some light on the properties of basic salts in general, little attention[65] has been paid to their behaviour in solution, especially in aqueous media.

$$Zn_4[S_2P(O^iPr)_2]_6O \rightleftharpoons 3Zn[S_2P(O^iPr)_2]_2 + ZnO \qquad 20.$$

(3b) (2b)




**SCHEME 18**

## 4.2 Factors influencing the basic : normal equilibrium

Recent investigations into the solution behaviour of the basic salt[65], have described the facile equilibrium (equation 20) in terms of stepwise breakdown of the $Zn_4[S_2P(OPr^i)_2]_6O$ cage involving successive elimination of normal $Zn[S_2P(OPr^i)_2]_2$ molecules as the temperature was increased to 80°C in toluene (Scheme 18). Upon standing at room temperature the dissociation was reversed. Other workers[21] have also noted that the basic salt (3) was transformed into the normal form (2) and zinc (II) oxide on heating at temperatures in excess of 95°C.

While investigating the influence of different solvents on the fracture of the basic cage (Scheme 18), it was observed that polar media favoured the formation of the normal salt (Figure 30). Thus, in a variety of anhydrous solvents (0.4 $cm^{-3}$) (xylene, toluene, diethyl ether, chloroform, 1,2-dimethoxyethane, acetone, dimethyl formamide and dimethyl sulphoxide) portions of the basic salt (3b) (6.7 x $10^{-5}$mole) were dissolved, transferred to NMR tubes and monitored (within half-an-hour) continuously by $^{31}P$ NMR at room temperature for several hours. It was observed that as the dielectric constant ($\epsilon$) of the solvent increased from

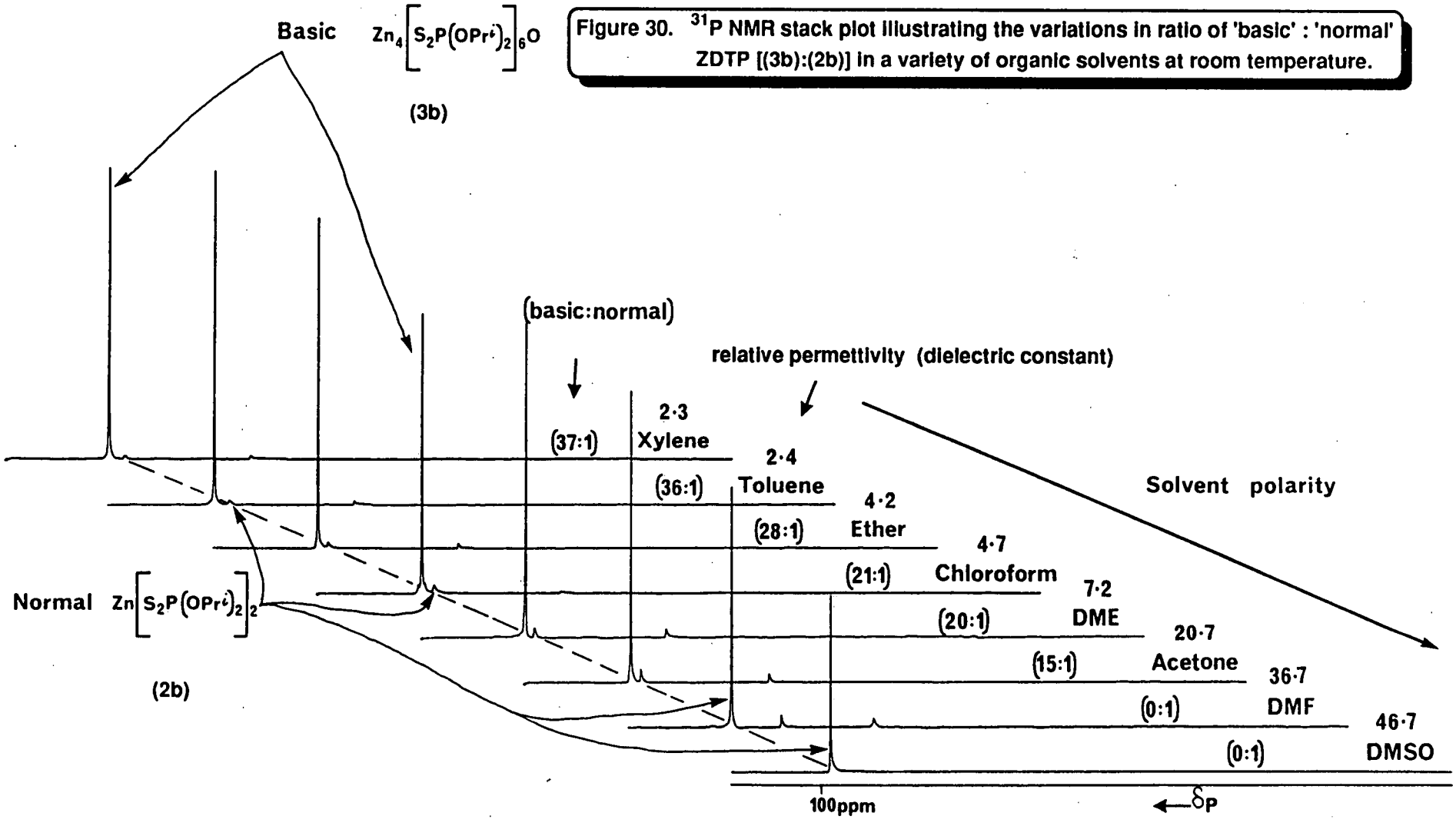
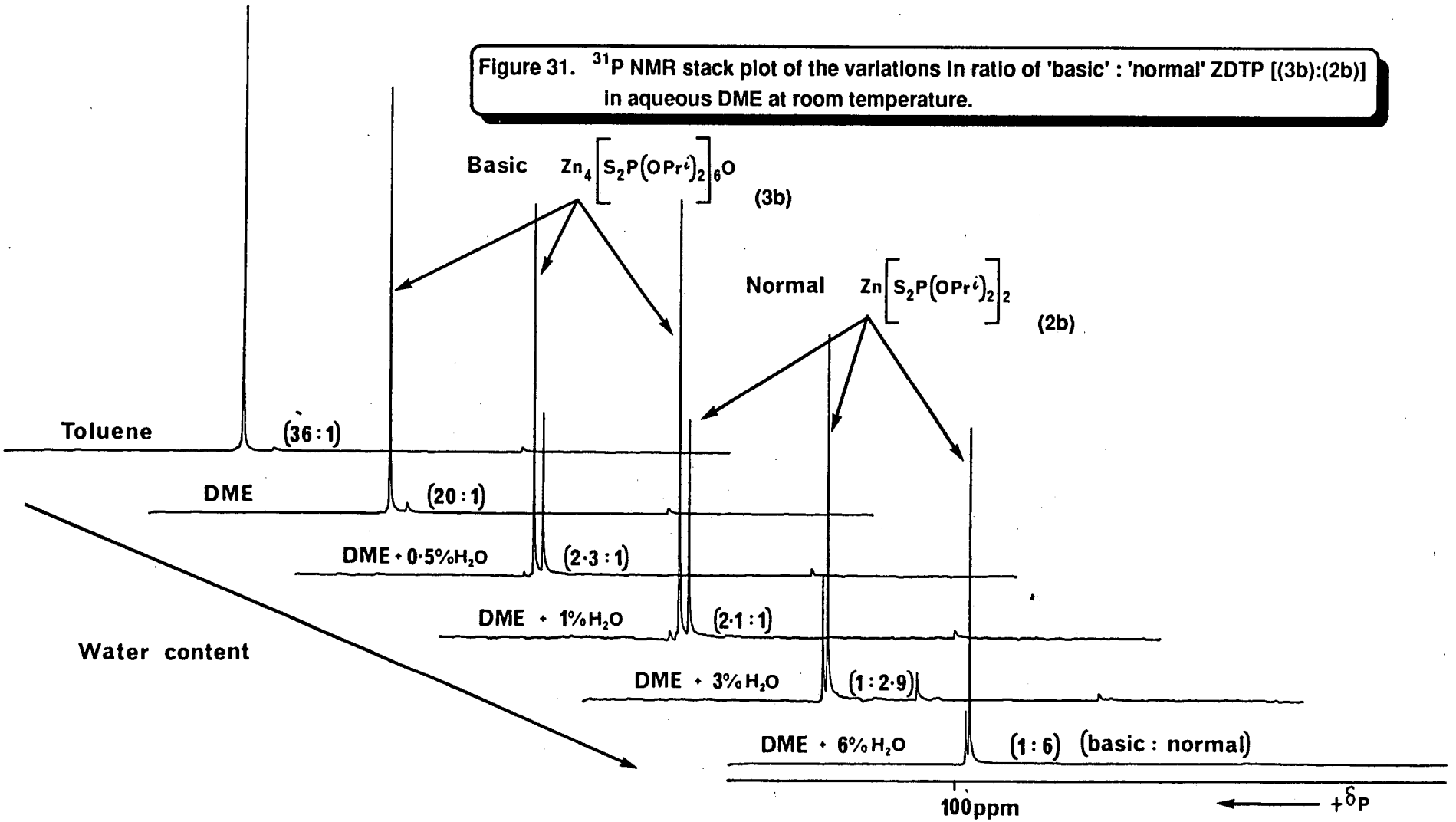



Figure 30. $^{31}P$ NMR stack plot illustrating the variations in ratio of 'basic' : 'normal' ZDTP [(3b):(2b)] in a variety of organic solvents at room temperature.

Figure 31. $^{31}P$ NMR stack plot of the variations in ratio of 'basic' : 'normal' ZDTP [(3b):(2b)] in aqueous DME at room temperature.



2.3 in xylene to 7.2 in DME and 46.7 in dimethyl sulphoxide (DMSO), the ratio of basic ZDTP (**3b**) to normal ZDTP (**2b**) changed from 37.1 : 1 to 20.5 : 1 to the normal salt entirely.

The influence of water on the facile equilibrium (equation 20) was also examined and in aqueous DME solution at room temperature it was found that increasing the water content favoured the dissociation of the basic salt (**3b**) into the normal salt (**2b**) and zinc (II) oxide (Figure 31). Portions of the basic salt (**3b**) ($6.7 \times 10^{-5}$ mole) were dissolved in anhydrous toluene, anhydrous DME, and aqueous DME (0.5%), (1%), (3%) and (6% water) and after being transferred to NMR tubes they were monitored by $^{31}P$ NMR spectroscopy as described in the preceeding experiment. The ratios of basic to normal salt ranged from 20:1 in anhydrous DME to 2:1 in 1% aqueous DME to 1:6 in 6% aqueous DME. This trend was in keeping with the changes in the polarity of the solution as the water content was increased (vide supra). Significantly, a reduction in the percentage water content by dilution with anhydrous DME did not reverse the trend, although removal of the solvent in vacuo at room temperature resulted in the recovery of pure basic salt as verified by $^{31}P$ NMR analysis.

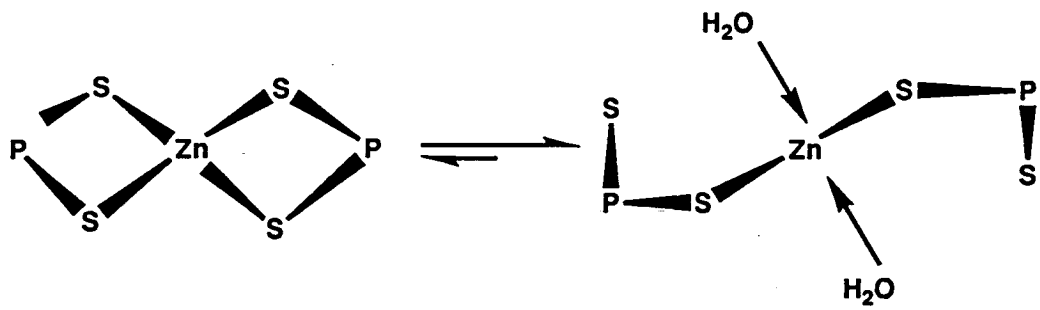



Figure 32

This suggested that the dissociation of the basic salt (3b) into its normal form in aqueous DME solution was not the result of hydrolysis. An explanation for the observed trend in the 'dilution' experiment could be that the water molecules coordinate to the central zinc atom of normal ZDTP (2b) thereby preventing its recombination with zinc (II) oxide to form the basic salt (3b) under these conditions. Evidence in support of this hypothesis was obtained from $^{31}P$ chemical shift data for the normal salt (2b) which increased in magnitude from $\delta$ +94.3 ppm to +97.8 ppm on going from anhydrous to aqueous conditions in DME solution. This change was consistent with Harrison's[65] conclusion that in these and related complexes the variation in the $^{31}P$ chemical shift is controlled largely by the change in the $S\hat{P}S$ bond angle. A change in the mode of attachment of the two dithiophosphate groups to zinc would occur (changing from bidentate to monodentate) as a result of the coordination of two water molecules to the zinc atom (Figure 32); this would be accompanied by an increase in the $S\hat{P}S$ bond angle.

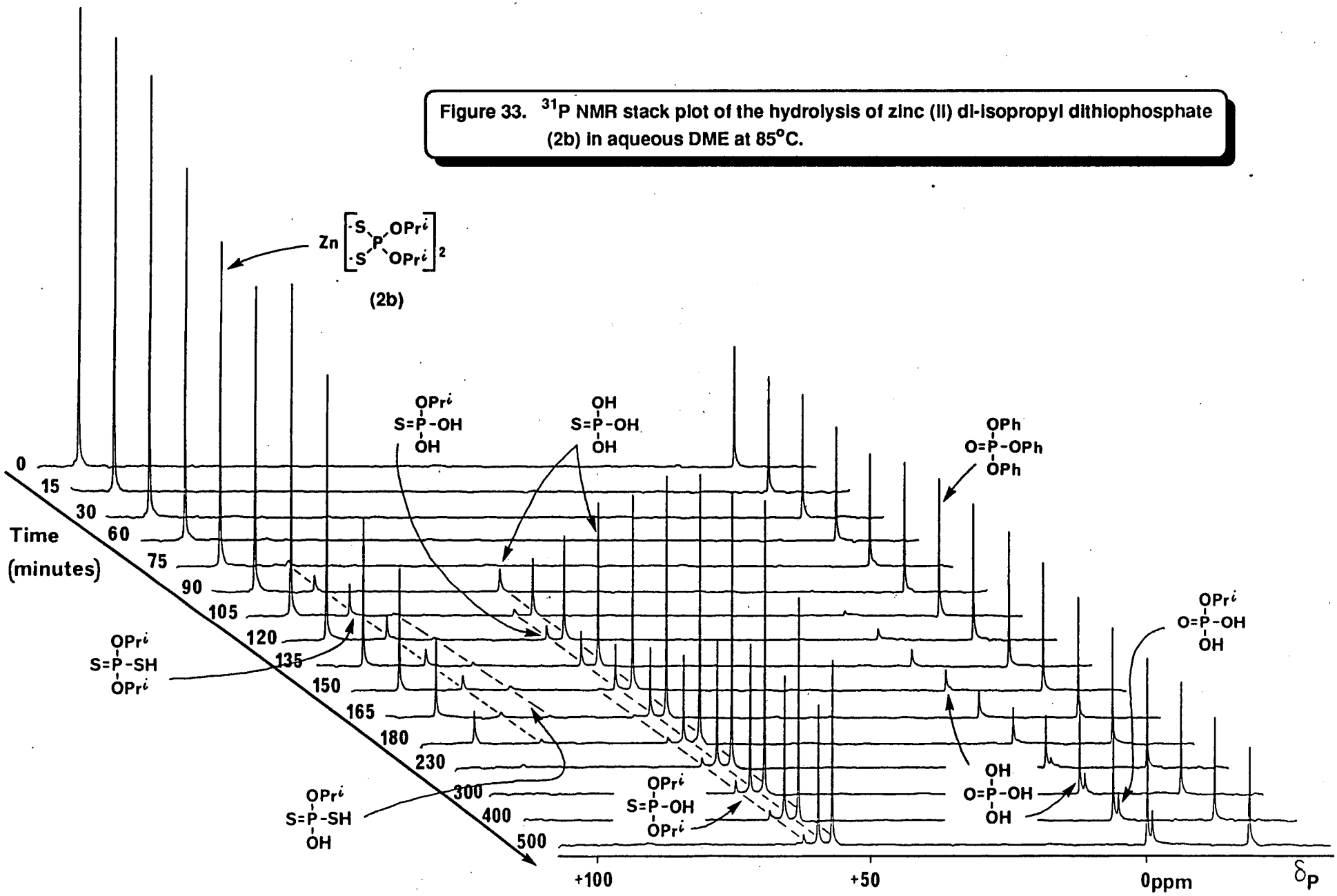
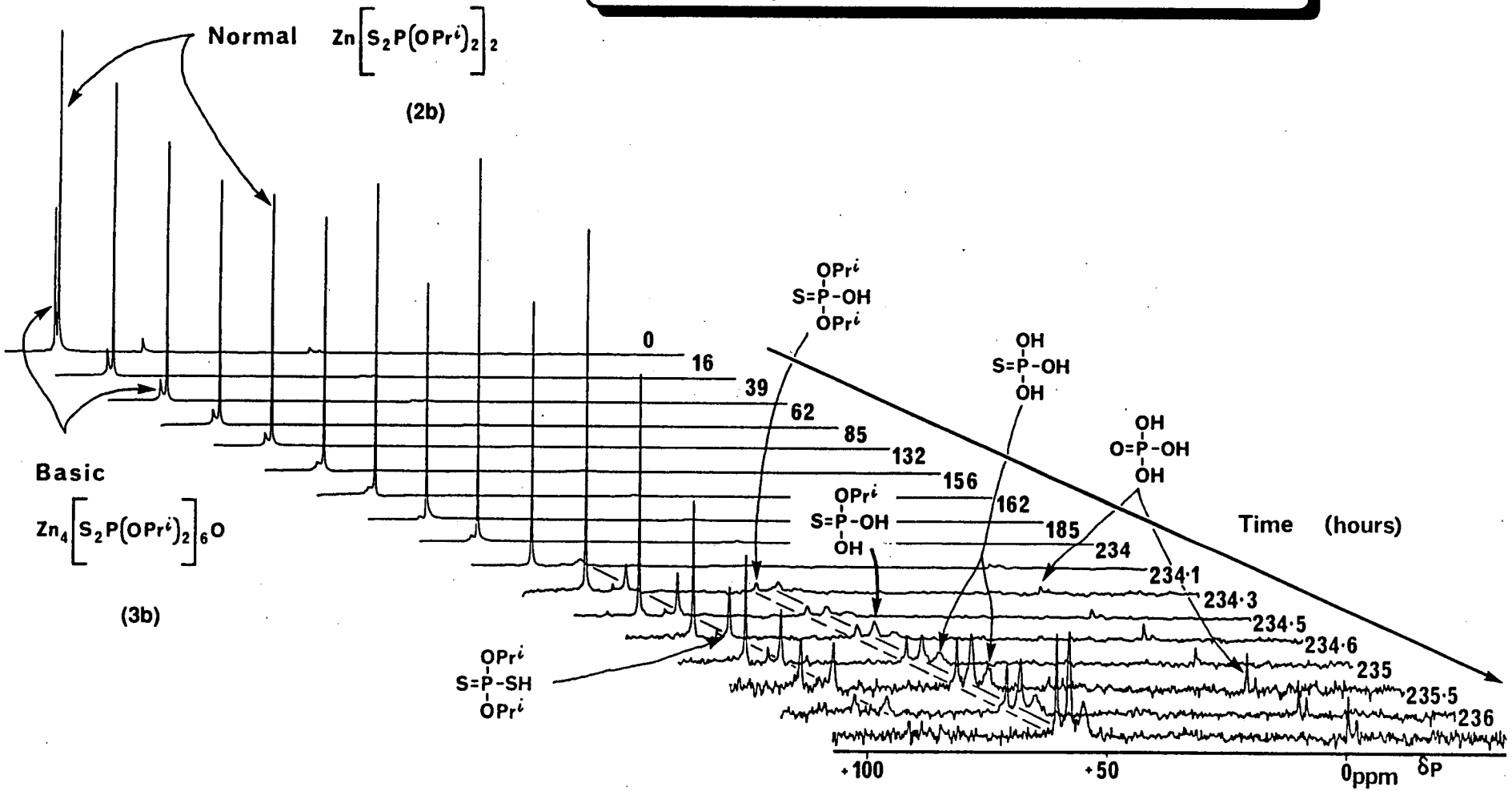


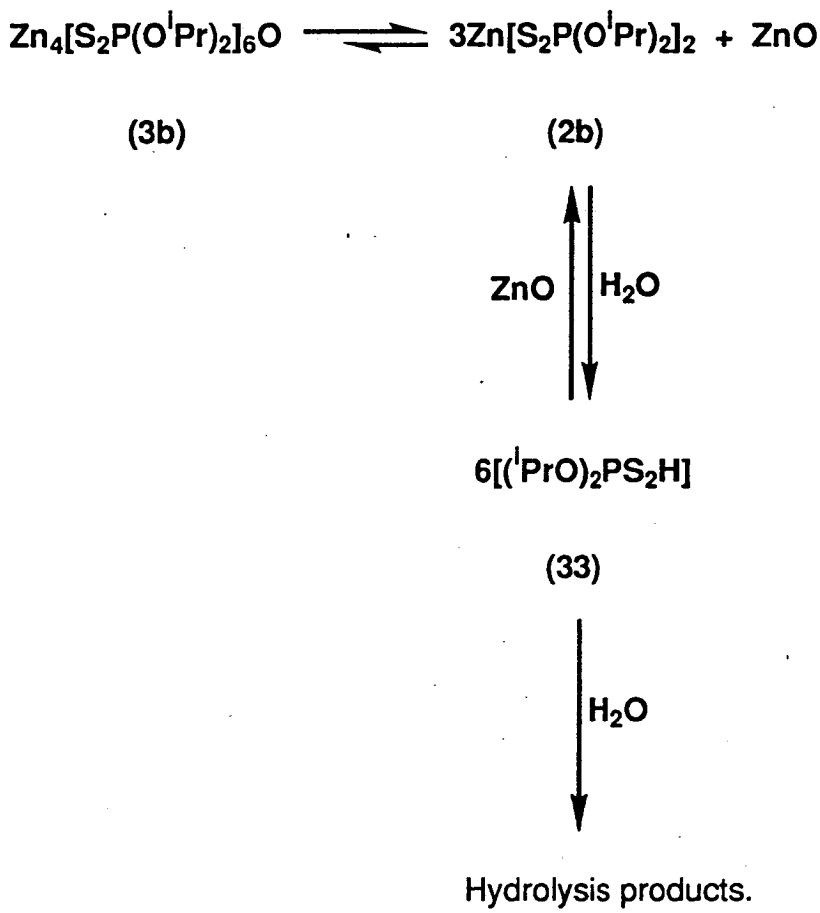

**Figure 33.** $^{31}P$ NMR stack plot of the hydrolysis of zinc (II) di-isopropyl dithiophosphate (2b) in aqueous DME at 85°C.

## 4.3 Hydrolysis of normal ZDTP (2b) in the presence of its basic form (3b)

Whereas the effect of water on the basic salt (3b) at room temperature was reversible, irrevocable breakdown occurred on raising the temperature to 85°C. This could be rationalised in terms of hydrolytic breakdown of the normal salt (2b). As in the case of its diethyl analogue (2a)[106] in aqueous DME solution (10 equivs $H_2O$) at 85°C, the normal isopropyl derivative (2b) underwent complete hydrolysis within ca 9 hours (Figure 33). (2b) (0.0033 mole) was dissolved in aqueous DME (10$cm^{-3}$) containing ten equivs of water and was heated at 85°C; aliquots (0.4 $cm^{-3}$) were removed for monitoring by $^{31}P$ NMR analysis at periodic intervals after quenching in an ice-bath. Under the same conditions, the corresponding basic salt (3b) (0.0033 mole) initially was found to convert gradually into its normal counterpart (2b) (Figure 34). This change coincided with the observation of a colourless precipitate, previously identified as zinc (II) oxide[95]. Subsequently, contrary to expectations, the normal salt (2b) so formed failed to undergo any hydrolysis until all the basic salt (3b) had disappeared. This required 9-10 days after which hydrolysis of the normal salt (2b) occurred as usual to give the same

Figure 34. $^{31}P$ NMR stack plot of the behaviour of 'basic' ZDTP (3b) in aqueous DME at 85°C.




Zn4[S2P(OiPr)2]6O
3Zn[S2P(OiPr)2]2 + ZnO
(3b)
(2b)
ZnO
H2O
6[(iPrO)2PS2H]
(33)
H2O
Hydrolysis products.

**SCHEME 19**

products in comparable distribution (c.f.- preceeding experiment).

Keeping in mind the stoichiometry of the solution equilibrium between the basic and normal forms of ZDTP, it would be reasonable to argue that there was insufficient water present in the reaction. Consequently, in a separate experiment, the basic salt (**3b**) (0.0033 mole) was dissolved in a solution of aqueous DME ($10cm^{-3}$) containing twice as much water (20 equivs $H_2O$). Heating at 85°C as before also resulted in hydrolytic breakdown of the normal salt (**2b**) after the complete disappearance of its basic form (**3b**), albeit in the shorter period of 7-8 days. Even in the presence of a large excess of water (30 equivs) hydrolysis of the resultant normal form (**2b**) was still very slow and required 3-4 days for completion.

This unexpected inhibition of the hydrolytic breakdown of the normal salt (**2b**) in the presence of its basic form (**3b**) could be rationalised in terms of the reactions outline in Scheme 19. In keeping with the hydrolytic breakdown of other simple ZDTPs[95, 106] the primary hydrolysis product of normal ZDTP (2b) is O, O' - diisopropyl dithiophosphoric acid (33), which is known to react with zinc (II) oxide[107] at ambient temperatures to generate the normal salt (**2b**). As

a result consumption of the zinc (II) oxide by the diisopropyl dithiophosphoric acid (33) gradually drives the equilibrium from the basic salt (3b) to its normal form (2b) until all the zinc (II) oxide is consumed, where upon the normal salt (2b) undergoes hydrolysis as usual. This was shown to be the case by a series of control experiments.

## 4.4 Rôlé of zinc (II) oxide in the solution equilibrium and hydrolysis

Thus, when an equilibrium of the basic salt (3b) (0.00013 mole) (containing ca 5% normal form (2b) in anhydrous DME (0.4 $cm^{-3}$) was treated with one molar equivalent of diisopropyl dithiophosphoric acid (33) at room temperature, it was found that the basic salt (3b) was completely converted into its normal form (2b) within a few minutes; this was accompanied by the disappearance of the precipitate of zinc (II) oxide.

In another experiment, it was also noted that addition of one molar equivalent of phosphoric acid, $H_3PO_4$ (27) to a similar solution of basic ZDTP (3b) in anhydrous DME catalysed its transformation to the normal counterpart (2b) with the concomitant disappearance of the zinc (II) oxide presumably by its conversion into zinc (II) phosphate.

Further support for these proposals was obtained from a control experiment in which the hydrolysis of normal ZDTP (**2b**) (0.0033 mole) was observed to be inhibited by the presence of added zinc (II) oxide. Thus, when (**2b**) and zinc (II) oxide were mixed in a 3:1 molar ratio in aqueous DME ($10cm^{-3}$) (20 equivs water) and heated at 85°C, no hydrolysis occurred until after an 'induction period' of ca 179 hours ($\sim$ 7.5 days). This pattern of behaviour was akin to that observed in the treatment of the basic salt (**3b**) in aqueous DME (20 equivs water) at 85°C (vide supra) and differred markedly from the usual hydrolysis of the normal salt as described earlier. It is pertinent to note that none of the basic salt (**3b**) was formed under these conditions by reversing the equilibrium depicted in Scheme 19.

In a separate experiment the normal salt (**2b**) (0.0033 mole) and zinc (II) oxide were mixed in a 3:1 molar ratio, but stirred in anhydrous DME solution ($10cm^{-3}$) at ambient temperature. Under these conditions, the formation of a small amount of the basic salt (**3b**) was observed by $^{31}P$ NMR spectroscopy, indicating that the dissociation of (**3b**) into (**2b**) and zinc (II) oxide was reversible in some circumstances.

## 4.5 Summary

It can be concluded that the hydrolysis of normal ZDTP $Zn[S_2P(OPr^i)_2]_2$ (**2b**) was inhibited by the presence of its basic form $Zn_4[S_2P(OPr^i)_2]_6O$ (**3b**) owing to the latter's dissociation in solution to produce zinc (II) oxide which reacted with the primary hydrolysis product 0, 0' - diisopropyl dithiophosphoric acid (**33**) to reform the normal salt (**2b**). The periods of inhibition were inversely proportional to the water content in the reaction solution and could be rationalised in terms of the relative rates of hydrolysis of (**2b**). As the water content was increased, this resulted in a faster rate of hydrolysis, which in turn led to faster consumption of the zinc (II) oxide by the resultant dithiophosphoric acid (**33**). This coincided with shorter inhibition times due to the ensuing faster rate at which the basic salt (**3b**) was being converted into its normal form (**2b**).

*'Once you've got all these chemicals together in the brew...*

*....what's left is sheer cookery....'*

*Prof. Stuart Trippett, University of Leicester, 1986.*

## CHAPTER 5

### Experimental Details (Part A)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# CHAPTER 5

# EXPERIMENTAL DETAILS (PART A)

## 5.1 Instrumentation

Melting points were determined on a Gallenkamp m.p. apparatus and are uncorrected. Combustion analyses were carried out on Perkin Elmer 240 or Carlo Elba 1106 elemental analysers. $^{1}H$ 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 coaxial $C_6D_6$ capillary lock. Mass spectra were recorded with a Kratos Ms50 instrument.

## 5.2 $^{31}P$ NMR parameters

$^{31}P$ chemical shifts expressed in ppm are quoted with reference to 85% $H_3PO_4$; shifts to high frequency are +ve in sign. The spectral window for kinetic measurements was 5200 Hz with 8K data giving a digital resolution of 0.635 Hz per point. A pw of 4 μs (20°) was used with 0.787s acquisition time and a pulse delay of 5s; and accumulations over 100 scans per spectrum gave a typical signal : noise ratio $\geq$10 : 1 with solution strengths of

ca. 0.33 mol $dm^{-3}$. For qualitative spectra the spectrometer was operated in both the proton-decoupled (COMP) and proton-coupled (NON) modes. For quantitative work the COMP mode was used exclusively.

## 5.3 Other NMR parameters

Chemical shifts expressed in ppm are quoted relative to internal tetramethylsilane (TMS) for $^{1}H$ and $^{13}C$ NMR spectra. The main NMR solvents employed were $CDCl_3$ or DME (for $^{31}P$ NMR) but other solvents when used are indicated.

## 5.4 $^{31}P$ NMR 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.[84] The 90° and 180° pulse times were 20.5 and 41 μs; T was 60s; and typical values of $\tau$ were 20ms, 80 ms, 0.5s, 1s, 2s, 3s, 4s, 5s, 7s, 15s, 20s. The $T_1$'s were calculated with the JEOL $T_1$ program which uses a least squares fit to the equation:

$$(M_0 - M_z)/2M_0 = \exp(-\tau/T_1).$$

Duplicate measurements suggest a precision of ±10%. The results are summarised in Table 4.

| Compound | $T_1$ / s |
|---|---|
| Triphenyl phosphate | 18.2 |
| (2a) | 7.1 |
| (18) | 10.2 |
| (29) | 13.4 |
| (30) | 15.6 |
| (31) | 6.1 |
| (27) | 2.4 |
| (32) | 16.9 |
| (23) | 14.2 |
| (26) | 3.5 |

**Table 4. Phosphorus - 31 spin-lattice ( $T_1$ ) relaxation times for the compounds observed in the ZDTP hydrolysis studies.**

## 5.5 Solvents

All solvents used were Analar grade and were normally dried before use, e.g. diethyl ether (ether) and 1.2-dimethoxyethane (DME) were dried and stored over sodium wire. Water used in the hydrolyses was deionised distilled water.

## 5.6 pH Measurement

Measurement of the variation in solution pH of the ZDTP hydrolysis mixture over the course of the reaction was carried out with a BDH Gelplas combination electrode and an EIL 7015 meter calibrated at pH 7.0 with phosphate buffer and at 4.0 with acetate buffer. Values are accurate to within $\pm$ 0.2.

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The synthesis of the starting materials, intermediates and products are arranged in the general order in which they appear in the discussion (Chapters 3 and 4); where higher homologues (i.e. - $Pr^i$) were also prepared the general method with the lowest member is given.

## 5.7 Preparation of 0,0'-dialkyl dithiophosphoric acids

0,0'-Diethyl dithiophosphoric acid

(18)[91] - Ethanol (46g, 1 mol) was added dropwise to a well stirred slurry of phosphorus pentasulphide (55.57g, 0.25 mol) in toluene[1*] (500 ml) 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 cooling to room temperature a viscous layer was deposited, the brown solution was decanted and solvent removed in vacuo to yield (18) (77.7g, 83%), which was further purified by distillation, b.p. 54-55°C at 0.5 mmHg (lit.,[109] 65°C at 0.75mmHg); (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 (6H, dt, $^4J_{PH}$ < 1Hz, $CH_3$), 3.37 (1H, s, SH), and 4.17 (4H, dq, $^3J_{PH}$ 10.3Hz, $CH_2$); $\delta_P$ (DME) 84.7, (neat) 84.6 (lit.,[71] ($CDCl_3$) 84.5).

0,0'-Diisopropyl dithiophosphoric acid (33) - $\delta_P$ ($Pr^iOH$) 80.5 ($^3J_{PH}$ 12.7Hz).

## 5.8 Potassium salts of 0,0'-dialkyl dithiophosphoric acids

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1* With isopropyl alcohol and higher homologues, best results are achieved with no solvent.

Potassium O,O'- diethyl dithiophosphate. - (18) (96.3g, 0.52 mol) was neutralised with saturated aqueous $KHCO_3$ solution till pH 6-7 and the solution was extracted with ether (3 x 50ml). Removal of water from the aqueous layer after separation yielded the potassium salt (80.4g, 72%) which was dried in vacuo over phosphorus pentoxide overnight and recrystallised from acetone/ether, m.p. 194-195°C (lit.,[110] 152-153°C(ether/ethanol)); (Found: C,20.8; H, 4.5. Calc. for $C_4H_{10}O_2PS_2K$: C,21.4; H, 4.5%); $\delta P$ ($D_2O$) 110.6, (lit.,[71] 110,5).

Potassium O,O'- diisopropyl dithiophosphate. - M.p. 203°C (lit.,[111] 193°C); $\delta P(D_2O)$107.1, (lit.,[71] 107.4).

## 5.9 'Normal' zinc (II) O,O' - dialkyl dithiophosphates

'Normal' zinc (II) O,O'- diethyl dithiophosphate (2a). - Potassium O,O'-diethyl dithiophosphate was mixed with zinc (II) sulphate in a 2:1 molar 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 (2a) (90%) which was recrystallised from n-heptane, m.p. 79-80°C (lit.,[61] 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 (12H, dt, $^4J_{PH}$ < 1Hz, $3J_H$ 7.1 Hz, $CH_3$), 4.23 (8H, dq, $^3J_{PH}$ 9.7Hz, $CH_2$);

**Table 5. N.m.r. data for 'normal' $Zn[S_2P(O^iPr)_2]_2$ (2b) and 'basic' $Zn_4[S_2P(O^iPr)_2]_6O$ (3b).**

| | $Zn[S_2P(O^iPr)_2]_2$ | $Zn_4[S_2P(O^iPr)_2]_6O$[a] |
|---|---|---|
| $^1H$ n.m.r. ($CDCl_3$) | | |
| $\delta(CH_3)$[b]/p.p.m. | 1.35 (2) | 1.2 (2) |
| $\delta(CH)$[b]/p.p.m. | 4.85[c] | 4.9[c] |
| $^3J$ ($^1H$-$^1H$) / Hz | 6.3 | 6.2 |
| $^{13}C$ n.m.r. ($CDCl_3$) | | |
| $\delta(CH_3)$[b]/p.p.m. | 23.3 (2) | 22.7 (2) |
| $\delta(CH)$[b]/p.p.m. | 73.7 (2) | 72.4 (2) |
| $^2J$ ($^{13}C$-$^{31}P$) / Hz | 6.8 | 8.3 |
| $^3J$ ($^{13}C$-$^{31}P$) / Hz | 4.2 | 4.1 |
| $^{31}P$ n.m.r. | | |
| $\delta_P$/p.p.m. ($^1H$-decoupled) | 94.8[d] | 99.6[d] |
| | 94.3[e] | 98.7[e] |
| | 94.7[f] | 100.6[f] |
| $^3J$ ($^{31}P$-$^1H$) / Hz | 12.7 | 12.7 |

a Spectrum also contains resonances due to $Zn[S_2P(^iPr)_2]_2$.
b Multiplicities in parentheses.
c Pseudo-nonet.
d In $CDCl_3$.
e In DME.
f In toluene-$d_8$.

$\delta_C$ ($CDCl_3$)15.66 (d, $^3J_{PC}$ 8.3 Hz, $CH_3$), 64.47 (d, $^2J_{PC}$ 6.7 Hz, $CH_2$); $\delta_P$ (DME) 101.5, ($CDCl_3$) 96.5.

'Normal' zinc (II) O,O' - diisopropyl dithiophosphate (2b). - The yield was 85% and recrystallisation from n-heptane gave m.p. 144-145°C (lit.,[43] 144.5); (Found: C, 29.2; H, 5.8. Calc. for $C_{12}H_{28}O_4P_2S_4Zn$: C,29.3; H, 5.7%); see Table 5 for NMR data.

5.10

Dithiophosphoric acid (30) - 2-Methyl-2-propanol (t-butyl alcohol) (14.8g/0.199 mol) was added dropwise to a vigorously stirred mixture of phosphorus pentasulphide (4g, 0.018 mol) in DME (15ml) under nitrogen at 45±1°C for 5 h. The resultant O, O'-di-t-butyl dithiophosphoric acid[112] (ca. 80%) [$\delta_P$ (DME) + 64.2] was neutralised with saturated aqueous $KHCO_3$ solution and dried in vacuo. The dried potassium salt [$\delta_P$ ($D_2O$) + 91.3, (DME) + 93.8] was treated with aqueous lead (II) acetate solution (5.5g in 25ml $H_2O$) to yield the lead (II) salt (8.9g, 72.6%) which was dried and recrystallised from di-isopropyl ether, m.p. 88-92°C (decomp.) (lit.,[112] 109°C (decomp.)); (Found: C, 27.6; H, 5.2. Calc. for $C_{16}H_{36}O_4P_2S_4Pb$: C, 27.9; H, 5.3%); $\delta_H$($CDCl_3$) 1.75 (36H, bs); $\delta_C$($CDCl_3$) 30.48 (d, $^3J_{PC}$ 4.2

Hz, $CH_3$), 86.1 (d, $^2J_{Pc}$ 11.98 Hz, -$\underline{C}(CH_3)_3$); $\delta$ P($CDCl_3$) + 76.5. The free acid (30) was obtained by treating either the crude O,O'-di-t-butyl dithiophosphoric acid or the potassium salt, in DME, with three equivalents of trifluoroacetic acid (TFA) at room temperature. This reaction gave (30) (ca. 10%) and several other by-products as observed by $^{31}P$ NMR spectroscopy.

**5.11**

Thiophosphoric acid (31)[99] - Distilled water (100 ml) was added dropwise to a vigorously stirred slurry of phosphorus pentasulphide (111.1g, 0.5mol) in acetone (200ml) cooled to 0°C. The reaction temperature was maintained at below 10°C and after completion of the addition the mixture was stirred for 1.5h 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 (31) (95g, 83%) which was then stored in dry methanol at below -20°C. The di-anilinium salt of (31) decomposed at 124-126°C without melting, (methanol/ether)(unreported): $\delta$ H($(CD_3)_2SO$) 5.65 (7H, s, $HN_3^+/H^+$) 6.25 (6H, m, -$(CH)_3$-), 6.75 (4H, m, -$(CH)_2$-C-N); $\delta$ C($(CD_3)_2SO$) 116.37 (s, -$\underline{C}H)_2$-C-N), 118.89 (s, -$\underline{C}H$)-$(CH)_2$-C-N), 129.23 (s, $\underline{C}H$)-(CH)-C-N), 144.77 (s, -C-N);

$\delta_P$ ($(CD_3)_2SO$) 57.48, ($CD_3OD$) 47.59, ($CH_3OD$) 47.99; 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.

**5.12**

O-Ethyl thiophosphoric acid(**32**)[101] - Ethyl dichlorothiophosphate (10g, 0.056 mol) was added dropwise to a vigorously stirred solution of aqueous sodium hydroxide (100ml, 10%) and dioxan (15ml) kept at 90°C. Stirring was continued for 30 minutes after the mixture became homogeneous and it was then cooled and neutralised with hydrochloric acid. After removing the solvent the residue was extracted with hot methanol (3 x 20 ml) and the extracts were concentrated to ca. 10ml. On addition of acetone, the disodium salt (7.75g, 90%) crystallised out, 240-242°C (decomp.); $\delta_{H(D_2O)}$ 1.35 (3H, t, $^3J_H$ 7.2Hz, $CH_3$), 4.00 (2H, dq, $^3J_{PH}$ 6.8Hz, $CH_2$); $\delta_{P(MeOH)}$ 51.5, ($D_2O$) 42.8 (Lit.,[102] ($D_2O$) 42.02); m/z 187 (($M^+ + 1$), 50%) FAB. (**32**) 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 (3H, t, $^3J_H$ 7.2Hz, $CH_3$), 3.85 (2H, dq, $^3J_{PH}$ 9.2 Hz, $CH_2$), 4.65 (1H, s, OH); $\delta_P$ (DME) 61.3.

**5.13**

O,O'-Diethyl thiophosphoric acid(23)[103] - Prepared by the acidification of N,N,N-triethyl ammonium O,O'- diethyl thiophosphate, made by boiling a mixture of diethyl phosphite (14.8g, 0.107 mol), sulphur (3.4g, 0.106 mol) and triethylamine (10.3g, 0.102 mol) in ether (40ml) for 3.5 h. $\delta_H$ ($CDCl_3$) 1.25 (1H, s, NH), 1.45 (15H, dt, $^3J_H$ 7.2Hz, $CH_3$), 3.25 (6H, q, $NCH_2$), 4.10 (4H, dq, $^3J_{PH}$ 8.3Hz, $OCH_2$); $\delta_P$ ($CDCl_3$) 57.2, (DME) 56.5. Treatment with hydrochloric acid and extraction with ether gave (23) (14.8g, 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 (6H, t, $^3J_H$ 7.2Hz, $CH_3$), 4.30 (4H, dq, $^3J_{PH}$ 9.3Hz, $CH_2$) 7.80 (1H, s, OH); $\delta_P$ ($CDCl_3$) 57.5, (DME) 63.5 (lit., [113] (neat) 58.1).

**5.14**

O-Ethyl phosphoric acid **(26)**[104] - Phosphorous acid (0.88g, 0.011 mol) was boiled under reflux at 87°C for 15 min with vigorous stirring in the presence of mercury (II) chloride (2.72g, 0.010 mol), ethanol (15ml) and triethylamine (5ml, 0.036 mol). The reaction mixture was filtered twice and solvent removed to yield (26) (1.08g, 80%), derivatised as the dicyclohexyl ammonium salt, m.p. 205-206°C (ethanol) (lit.,[114] 205-206°C (aq. $Me_2CO$));

(Found: C, 51.5; H, 10.4; N, 8.3. Calc. for $C_{14}H_{33}O_4N_2P$: C, 51.8; H, 10.3; N, 8.6%); $\delta_H$ ($D_2O$) 1.1 (2H, s, $NH^+$), 1.25 (12H, s, $-(CH_2)_3-$), 1.35 (3H, t, $^3J_H$ 7.2Hz, $CH_3$), 1.85 (12H, m, $-(CH_2)_2$ $-C-NH_2$) 3.2 (2H, m, -CH-N), 3.85 (2H, dq, $^3J_{PH}$ 7.7Hz, $-CH_2O-$); $\delta_P(D_2O)$ 3.8; free acid (DME) -0.6.

**5.15**

'Basic' zinc (II) O,O'-dialkyl dithiophosphates or hexakis-[O,O'-dialkyl dithiophosphate]-$_4$-tetraoxozinc (3)[42].

'Normal' zinc (II) O,O'-diisopropyl dithiophosphate (**2b**) (19.3g/0.039 mole) was dissolved in light petroleum (80-100°C) (200 $cm^{-3}$), to which was added t-butyl hydroperoxide (0.88g/0.0098 mole) and the resultant solution was stirred overnight at room temperature. A white precipitate (**3b**) was filtered off, washed with light petroleum and dried in vacuo (yield 10.7g, 70%), m.p. 203-205°C (lit.,[91] 204-206°C); (Found: C, 27.8; H, 5.5. Calc. for $C_{36}H_{84}O_{13}P_6S_{12}Zn_4$: C, 27.8; H, 5.4%); see Table 5 for NMR data.

**EXPERIMENTAL DETAILS (PART B)**

**5.16**

Hydrolysis of 'normal' zinc (II) O,O' diethyl dithiophosphate (2a). - (2a) (1.55g, 3.55 mmol) was mixed with triphenyl phosphate (0.546g, 1.67 mmol) and distilled water (0.642g, 35.6 mmol) in DME (10ml). 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 ± 10%.

Hydrolysis experiments were repeated with twenty and thirty equivs. of water at 85°C (see sections 3.3 and 3.6 for further details).

**5.17**

Hydrolysis of O,O'-diethyl dithiophosphoric acid (18). - (18) (0.656g, 3.52 mmol) was mixed with triphenyl phosphate (0.553g, 1.69 mmol) and distilled water (0.661g, 36.7 mmol) in DME (10ml). Hydrolysis and kinetic

measurements were carried out as previously described for the hydrolysis of ZDTP.

Hydrolyses of (18) on a smaller scale (ca. 0.3 mmole) were also carried out (in NMR tubes). Moreover, experiments involving hydrolysis with ten equivs. of water at ROOM TEMPERATURE and with two equivs. of water at 85°C were also conducted (see sections 3.3 to 3.6 for further details).

**5.18**

Hydrolysis of thiophosphoric acid (31). - Triphenyl phosphate (0.554g, 1.70 mmol) was mixed with (31) (0.438g, 3.84 mmol) and distilled water (0.694g, 38.5 mmol) in DME (10 ml). Hydrolysis and kinetic measurements were carried out as described for the hydrolysis of ZDTP.

**5.19**

Reactions of thiophosphoric acid (31). - (a) with O,O'-diethyl dithiophosphoric acid (18). - (18) (0.21g, 1.1 mmol) was mixed with (31) (0.06g, 0.5 mmol) and triphenyl phosphate (0.18g, 0.55 mmol) in anhydrous DME (0.4 $cm^{-3}$).

| REACTANTS / REACTION | DIETHYL DITHIO-PHOSPHORIC ACID (18) | THIOPHOSPHORIC ACID (31) | DISTILLED WATER | ETHANOL | PHOSPHORIC ACID (27) | REACTION TIME IN 0.4 $CM^{-3}$ DME AT 85±2°C. |
|---|---|---|---|---|---|---|
| (a) | 0.0011 mole | 0.0005 mole | — | — | — | 15 minutes |
| (b) | 0.0011 mole | 0.0005 mole | 0.0044 mole | — | — | 15 minutes |
| (c) | — | 0.0005 mole | — | 0.0010 mole | — | 3 days |
| (d) | — | — | — | 0.0022 mole | 0.0011 mole | 3 days |
| (e) | 0.00028 mole | — | 0.0032 mole | 0.0005 mole | — | 5 minutes |
| (f) | 0.00026 mole | — | 0.0028 mole | — | — | 5 minutes |

**TABLE 2. Summary of transalkylation studies.**

(c) with ethanol. - (31) (0.06g, 0.5 mmol) was mixed with ethanol (0.05g, 0.001 mmol) and triphenyl phosphate (0.08g, 0.25 mmol) in anhydrous DME (0.4 $cm^{-3}$).

Both reactions were monitored as described in the hydrolysis of ZDTP.

(See Table 2 section 3.7 for further details on reaction conditions). (Table 2 is repeated on the facing page for simplicity's sake).

**5.20** Other transalkylation investigations.

Reaction (b) was a control for reaction (a) as was reaction (f) for reaction (e). Table 2 (from Section 3.7) summarises the reactions and reaction conditions. All the reactions were monitored by $^{31}P$ NMR as described earlier.

**5.21** $^{31}P$ NMR spectroscopy studies on the dissociation of 'basic' ZDTP (3b) in solution. - (a) (3b) (0.105g, 6.7 x $10^{-5}$ mole) was dissolved in anhydrous solvent, S, (0.4 ml) (S = xylene, toluene, diethyl ether, chloroform, 1,2-dimethoxyethane, acetone, dimethyl formamide and dimethyl sulphoxide). The resultant solutions were transferred to

NMR tubes and monitored continuously by $^{31}P$ NMR spectroscopy at room temperature for several hours. The ratios of 'basic' salt (**3b**) to its 'normal' counterpart (**2b**) were observed.

(b) (**3b**) (0.105g, 6.7 x $10^{-5}$ mole) was dissolved in solvent, X, (0.4 ml) [X = anhydrous toluene, anhydrous DME, aqueous DME (0.5%), (1%), (3%) and (6% water)]. The resultant solutions were transferred to NMR tubes and monitored continuously by $^{31}P$ NMR spectroscopy as described above.

(c) (**3b**) (0.105g, 6.7 x $10^{-5}$ mole) was dissolved in aqueous DME (6% water) (0.4 ml) in an NMR tube. A $^{31}P$ NMR spectrum was obtained after which the solution was diluted by half with anhydrous DME (0.4 ml) to 3% water. Another $^{31}P$ NMR spectrum was obtained and the solution was diluted again by half with anhydrous DME (0.8 ml) to 1.5% water. The solution was then monitored continuously by $^{31}P$ NMR spectroscopy at room temperature for several days.

**5.22** <u>Hydrolysis of 'normal' ZDTP (2b) in the presence of 'basic' ZDTP (3b)</u>. - (**3b**) (5.19g, 0.0033 mole) was dissolved in aqueous DME (10 ml) containing (a) ten equivalents water (0.6 ml), (b) twenty equivalents water (1.2 ml) and (c) thirty equivalents water (1.8ml). The resultant solutions were heated at 85 $\pm$ 1°C. At various time intervals samples (0.4 ml) were taken, transferred to

NMR tubes and quenched in an ice-bath. The reaction was monitored continuously by $^{31}P$ NMR spectroscopy at room temperature until completed.

5.23 Hydrolysis of 'normal' ZDTP (2b). - (a) (2b) (1.64g, 0.0033 mole) was dissolved in aqueous DME (10 ml) containing ten equivs. distilled water (0.6 ml) and triphenyl phosphate (0.539 g, 0.0017 mole).
(b) (2b) (1.64g, 0.0033 mole) was dissolved in aqueous DME (10 ml) containing twenty equivs. water (1.2 ml), triphenyl phosphate (0.543g, 0.0017 mole) and zinc (II) oxide (90mg, 0.0011 mole). The mixture was stirred continuously. The resultant solutions were heated at 85 $\pm$ 1°C and monitored continuously by $^{31}P$ NMR spectroscopy as described.

5.24 Reaction of 'normal' ZDTP (2b) with zinc (II) oxide. (2b) (1.64g, 0.0033 mole) was dissolved in anhydrous DME (10ml) containing triphenyl phosphate (0.543g, 0.0017 mole) and zinc (II) oxide (90mg, 0.0011 mole). The resultant mixture was stirred at room temperature and monitored continuously by $^{31}P$ NMR spectroscopy for several days.

5.25 Reaction of 'basic' ZDTP (3b) with 0,0'-diisopropyl

dithiophosphoric acid (33). - To (3b) (0.207g, 0.00013 mole) in anhydrous DME (0.4 ml) was added (33) (28 mg, 0.00013 mole) and the mixture monitored continuously by $^{31}P$ NMR spectroscopy at room temperature for several hours.

5.26 Reaction of 'basic' ZDTP (3b) with ortho-phosphoric acid, $H_3PO_4$. - To (3b) (0.208g, 0.00013 mole) in anhydrous DME (0.4 ml) was added $H_3PO_4$ (13 mg, 0.00013 mole) and the mixture monitored continuously by $^{31}P$ NMR spectroscopy at room temperature for several hours.

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# 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 ($^3J_{PH}$ = *ca.* 10 Hz).

* 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*).

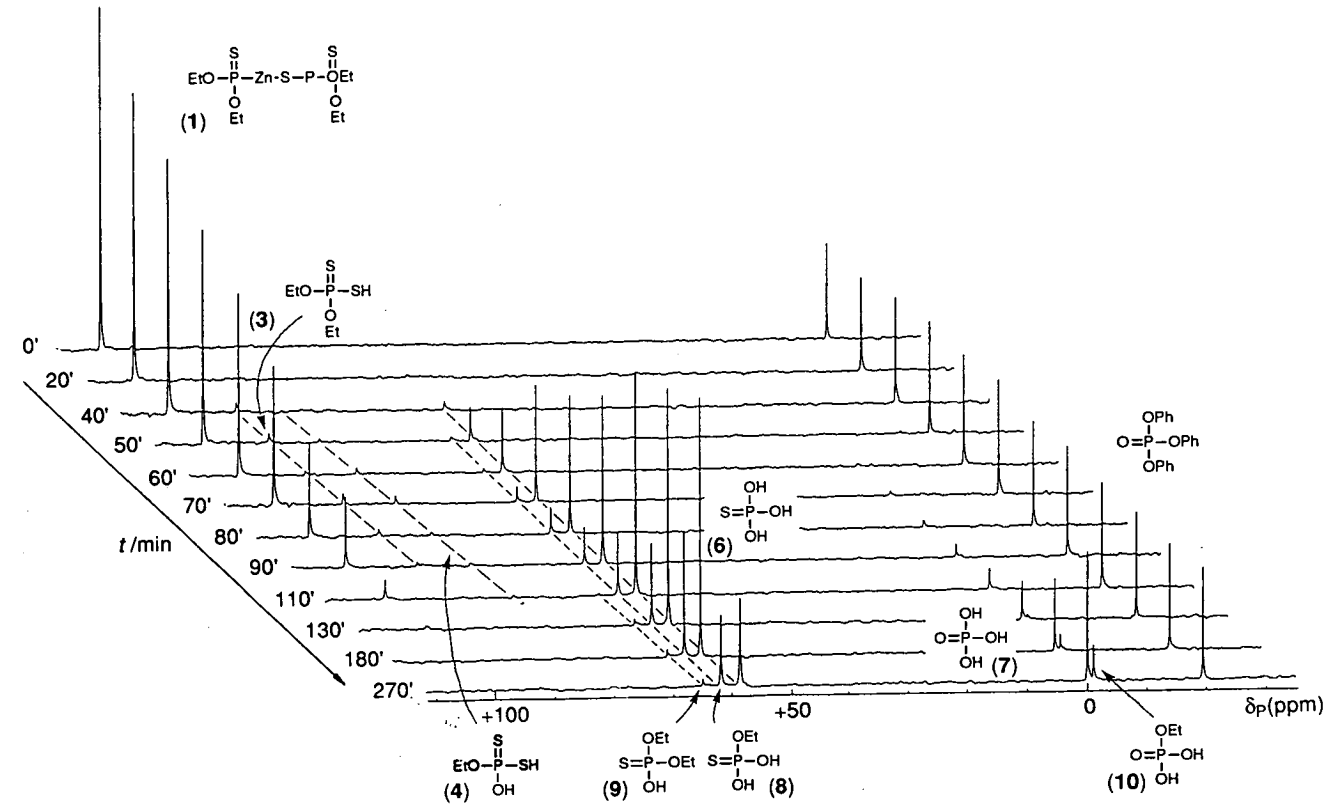
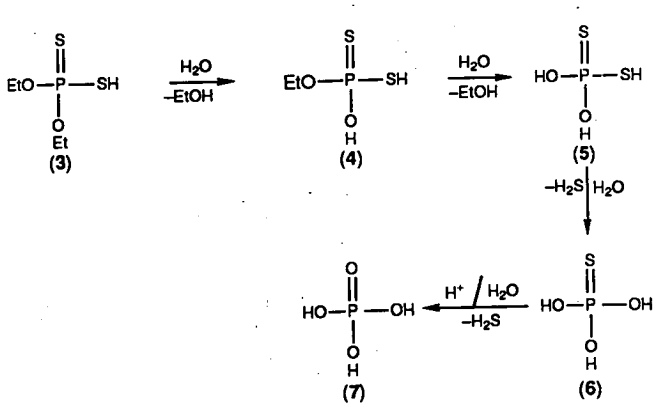



**Figure 1.** $^{31}$P NMR spectra of the hydrolysis of ZDTP (1) as a function of time in DME at 85 ± 1 °C with 10 equiv. of water.




**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

* 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).

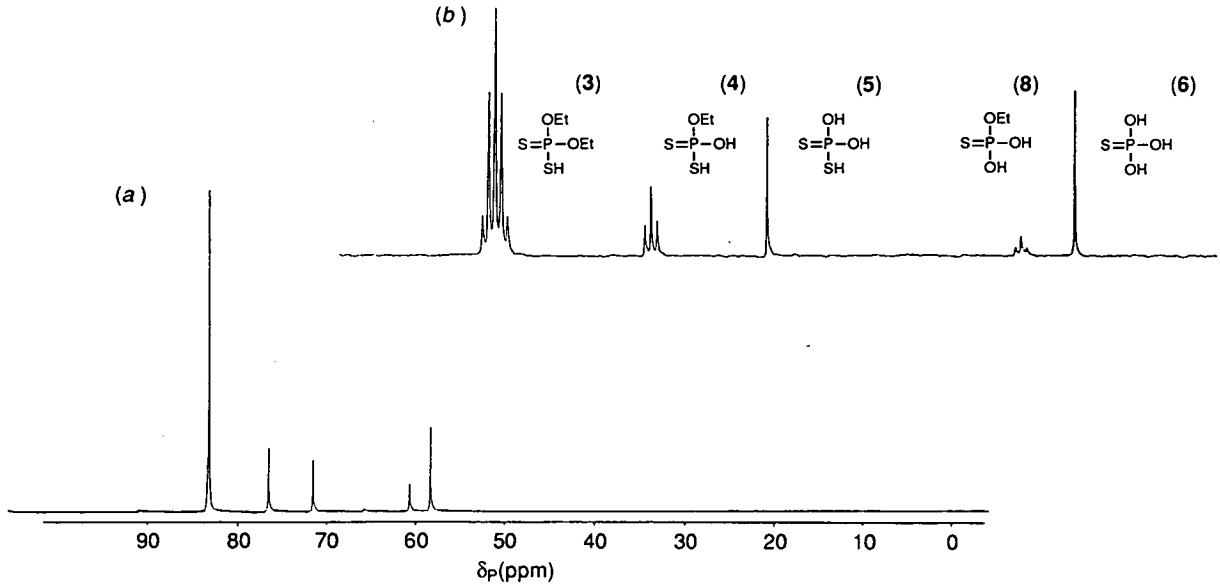



**Figure 2.** $^{31}P$ NMR spectra of the room temperature hydrolysis of *O,O*-diethyl *S*-hydrogen phosphorodithioate acid (**3**) in DME with 10 equiv. of water: (*a*) $^{1}H$-decoupled; (*b*) $^{1}H$-coupled.

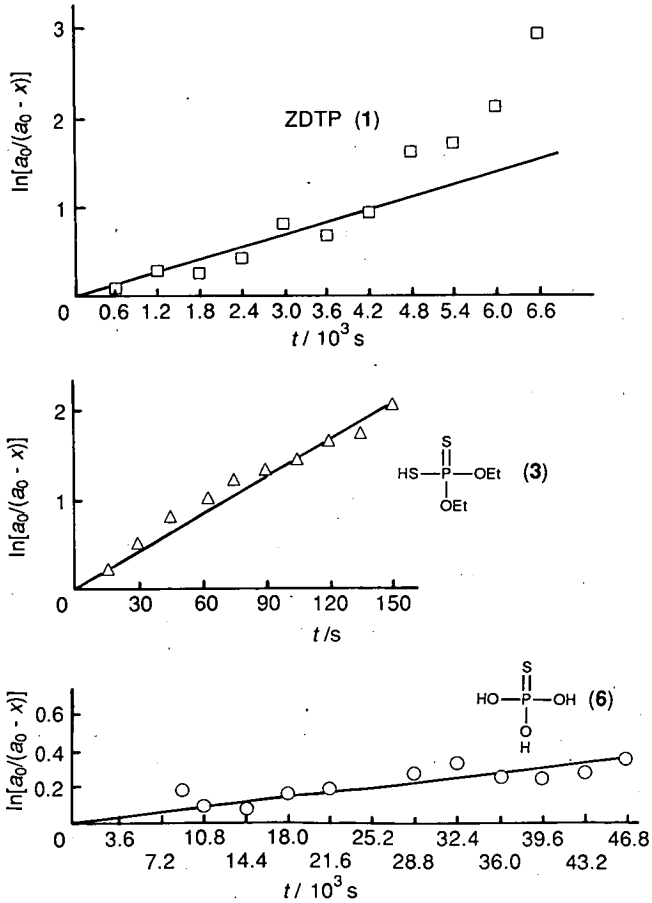



**Figure 3.** Plots of pseudo-first-order decay of (**1**), (**3**), and (**6**) at 85 ± 1 °C in DME with 10 equiv. of water.

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

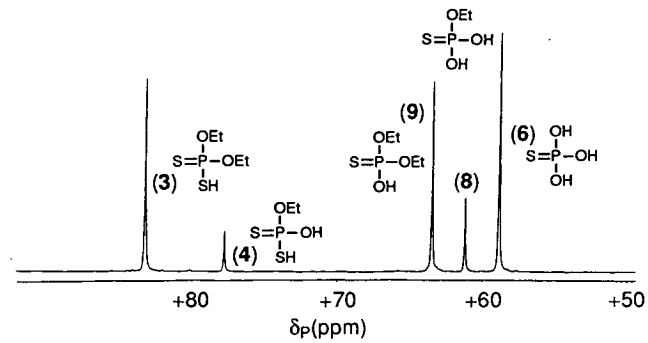



**Figure 4.** $^{31}P$ NMR H-decoupled spectrum of the reaction between phosphorothioic *O,O,O*-acid (**6**) and (**3**) in anhydrous DME at 85 ± 1 °C after 15 min.

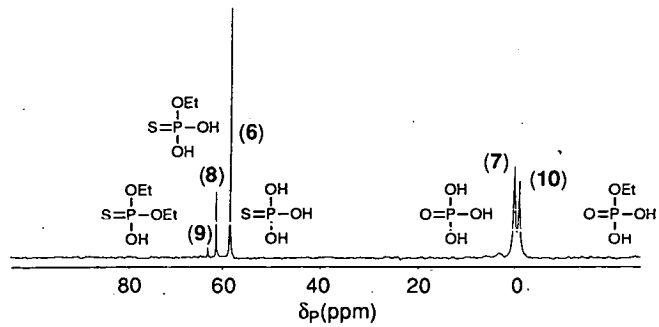
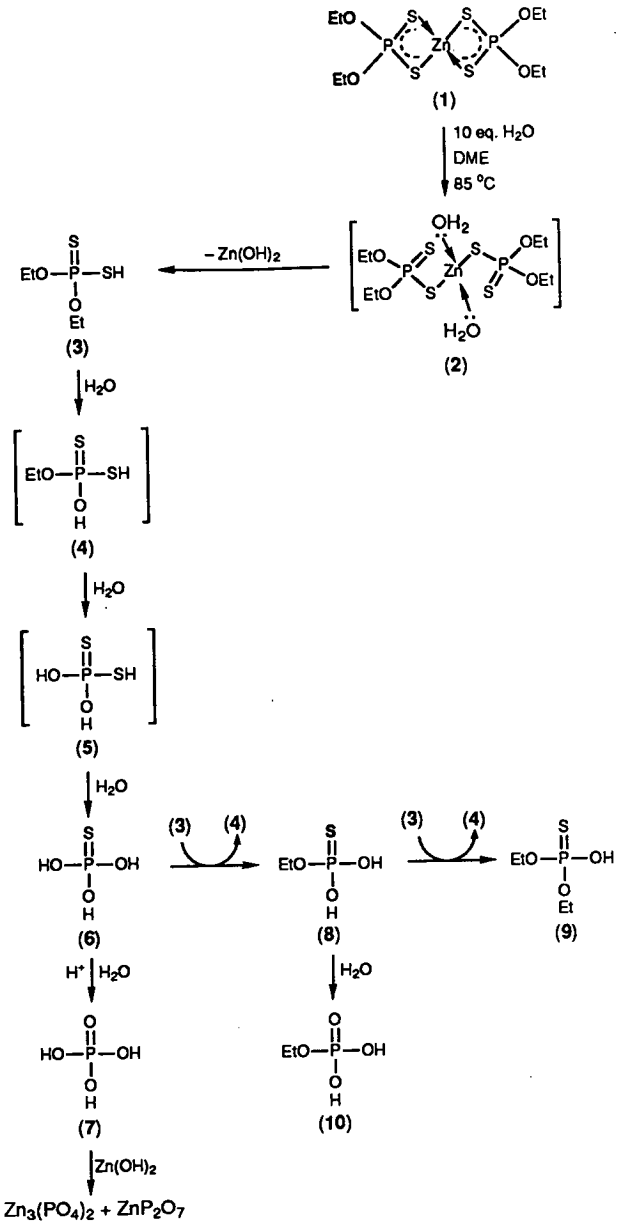



**Figure 5.** $^{31}P$ NMR H-decoupled spectrum of the reaction of (**6**) with ethanol in anhydrous DME at 85 ± 1 °C after 3 days.

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




**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 ≥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

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

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, $CH_2$); $\delta_P$(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] $\delta_P$ 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, $CH_2$); $\delta_P$(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, $-(CH)_2-C-N$], 118.89 [s, $-(CH)-(CH)_2-C-N$], 129.23 [s, $(CH)-(CH)-C-N$], 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, $CH_2$); $\delta_P$(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); $\delta_P$(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] $\delta_P$(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%) [$\delta_P$(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 ±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.

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