Inhibition of Hydrolysis of 'Normal' Zinc(II) *O,O'*-Di-isopropyl Dithiophosphate by the 'Basic' Form

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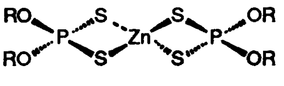
'Basic' zinc(II) *O,O'*-di-isopropyl dithiophosphate dissociates in a variety of organic solvents (including xylene, toluene, diethyl ether, chloroform, 1,2-dimethoxyethane, acetone, dimethylformamide, and dimethyl sulphoxide) *via* a facile equilibrium into its 'normal' salt and zinc(II) oxide. The dissociation is promoted by an increase in temperature and solvent polarity and by an increase in the water content in aqueous 1,2-dimethoxyethane. This equilibrium in favour of the 'normal' salt and zinc(II) oxide is also acid-catalysed. The zinc(II) oxide which arises from the dissociation of the 'basic' form is found to inhibit the hydrolysis of 'normal' zinc(II) *O,O'*-di-isopropyl dithiophosphate by reaction with its primary hydrolysis product, *O,O*-di-isopropyl *S*-hydrogen phosphorodithioate. Eventual hydrolysis occurs after all the zinc(II) oxide has been consumed.

In a previous paper,[1] we described the mechanism and kinetics of the homogeneous phase hydrolysis of zinc(II) bis(*O,O'*-diethyl dithiophosphate), $Zn[S_2P(OEt)_2]_2$ (**1a**) in 1,2-dimethoxyethane (DME) at 85 °C as observed by ^{31}P NMR spectroscopy. As a general class of compounds, zinc dialkyl dithiophosphates† (ZDTPs) form an integral part of additive packages in lubricating oils, having been used for over four decades, because of their pronounced anti-oxidant and anti-wear properties. The so-called 'normal' ZDTPs (**1**) are known to exist in equilibrium with zinc(II) oxide and a 'basic' form of composition $Zn_4[S_2P(OR)_2]_6O$.[2] These 'basic' salts are present in the oil additive package through the manufacturing process and are reported[3] to be inactive as anti-oxidants and anti-wear agents and are, thus, unwanted. In this paper, we report on the fate of analytically pure 'basic' ZDTP, $Zn_4[S_2P(OPr^i)_2]_6O$ (**2**), under aqueous conditions in DME solution at 85 °C in the light of our earlier findings on the hydrolytic breakdown of its 'normal' counterpart.[1] ^{31}P NMR spectroscopy was used extensively to unravel the complexities of the reactions involved. Recent studies[3,4] have looked at the reactions of the 'normal' (**1b**) and 'basic' salt (**2**) 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[5] has been paid to their behaviour in solution, especially in aqueous media.



(**1**) **a**; R = Et
b; R = Pr^i

Results and Discussion

Factors Influencing the 'Basic' $\rightleftharpoons$ 'Normal' Equilibrium (**2**) $\rightleftharpoons$ (**1b**).—The solid-state structure of 'basic' ZDTP, $Zn_4[S_2P(OPr^i)_2]_6O$ (**2**) has been determined[2,6] and shown to consist of a cage structure formed by six $[S_2P(OPr^i)_2]$ moieties associated with four zinc atoms tetrahedrally co-ordinated around a central oxygen atom (Figure 1). Recent investigations into the solution behaviour of the 'basic' salt,[5] have described the facile equilibrium [equation (1)] in terms of a 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 is increased to 80 °C in toluene (Figure 2). When the reaction is allowed to stand at room temperature the dissociation is reversed. Other workers[7] have also noted that the 'basic' salt (**2**) is transformed into the 'normal' form (**1b**) and zinc(II) oxide on being heated at temperatures in excess of 95 °C.

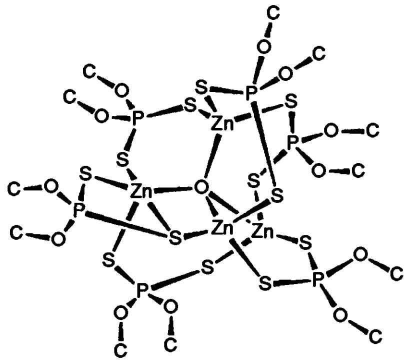


Figure 1. Structure of 'basic' $Zn_4[S_2P(OPr^i)_2]_6O$ (**2**).

$$\underset{(\mathbf{2})}{Zn_4[S_2P(OPr^i)_2]_6O} \rightleftharpoons \underset{(\mathbf{1b})}{3Zn[S_2P(OPr^i)_2]_2} + ZnO \quad (1)$$

The investigation of the influence of different solvents on the fracture of the 'basic' cage (Figure 2), revealed that polar media favoured the formation of the 'normal' salt (Figure 3). Thus, as the relative permettivity (ε) of the solvent increased from 2.3 in xylene to 7.2 in DME and 46.7 in dimethyl sulphoxide (DMSO), the ratio of 'basic' ZDTP to 'normal' ZDTP changed immediately from 37.1:1 to 20.5:1 to the 'normal' salt entirely.

The influence of water on the facile equilibrium [equation (1)]

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† These compounds are also known as 'zinc bis(dialkyl dithiophosphoridates)' and 'zinc bis(dialkyl phosphorodithioates).'

was also examined and in aqueous DME solution at room temperature it was found that an increase in the water content favoured the instant dissociation of the 'basic' salt (**2**) into the 'normal' salt (**1b**) and zinc(II) oxide (Figure 4). The ratio 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 is in keeping with the changes in the polarity of the solution as the water content is increased (see above). Significantly, a reduction in the 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 spectroscopy. This suggested that the dissociation of the 'basic' salt (**2**) 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 (**1b**), thereby preventing its recombination with zinc(II) oxide to form the 'basic' salt (**2**) under these conditions. Evidence in support of this hypothesis is obtained from ^{31}P chemical shift data for the 'normal' salt (**1b**) which increased in magnitude from 94.3 to 97.8 ppm on going from anhydrous to aqueous conditions in DME solution. This change is consistent with Harrison's[5] conclusion that in these and related complexes the variation in the ^{31}P chemical shift is controlled largely by the change in the SPS bond angle. A change in the mode of attachment of the two dithiophosphate groups to zinc occurs (changing from bidentate to monodentate) as a result of the co-ordination of two water molecules to the zinc atom (Figure 5); this is accompanied by an increase in the SPS bond angle.

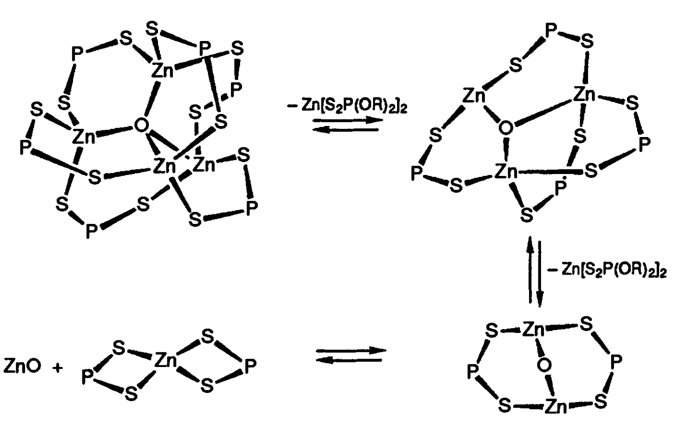


Figure 2. Schematic representation of the breakdown of the 'basic' $Zn_4[S_2P(OR)_2]_6O$ cage; the alkoxy groups attached to phosphorus have been omitted (from ref. 5).

Hydrolysis of 'Normal' ZDTP, Zinc(II) *Bis*(O,O'*-di-isopropyl dithiophosphate*) (**1b**) *in the Presence of its 'Basic' Form* (**2**).—Whereas the effect of water on the 'basic' salt (**2**) at room temperature is reversible, irrevocable breakdown occurred when the temperature was raised to 85 °C. This can be rationalised in terms of hydrolytic breakdown of the 'normal' salt (**1b**). As in the case of its diethyl analogue (**1a**)[1] in aqueous DME solution (10 equiv. H_2O) at 85 °C, the 'normal' isopropyl derivative (**1b**) undergoes complete hydrolysis within *ca.* 9 h (Figure 6). Under the same conditions, the corresponding 'basic' salt (**2**) was found to be converted into its 'normal' counterpart (**1b**), albeit not completely (Figure 7). This change coincided with the observation of a colourless precipitate, identified as zinc(II) oxide.[8] Contrary to expectations, the 'normal' salt (**1b**) so formed failed to undergo any hydrolysis until all the 'basic' salt (**2**) had disappeared. This required 9–10 days after which hydrolysis of the 'normal' salt (**1b**) occurred as usual to give the same products in comparable distribution.

In a separate experiment, the 'basic' salt (**2**) was dissolved in a solution of aqueous DME containing twice as much water (20 equivalents H_2O). Heating of the reaction at 85 °C as before, also resulted in hydrolytic breakdown of the 'normal' salt (**1b**) after the complete disappearance of its 'basic' form (**2**), albeit over a shorter period of 7–8 days. Even in the presence of a large excess of water (30 equiv.) hydrolysis of the 'normal' form (**1b**) was still very slow and required 3–4 days for completion.

This unexpected inhibition of the hydrolytic breakdown of the 'normal' salt (**1b**) in the presence of its 'basic' form (**2**) can be rationalised in terms of the reactions outlined in Scheme 1. In keeping with the hydrolytic breakdown of other simple

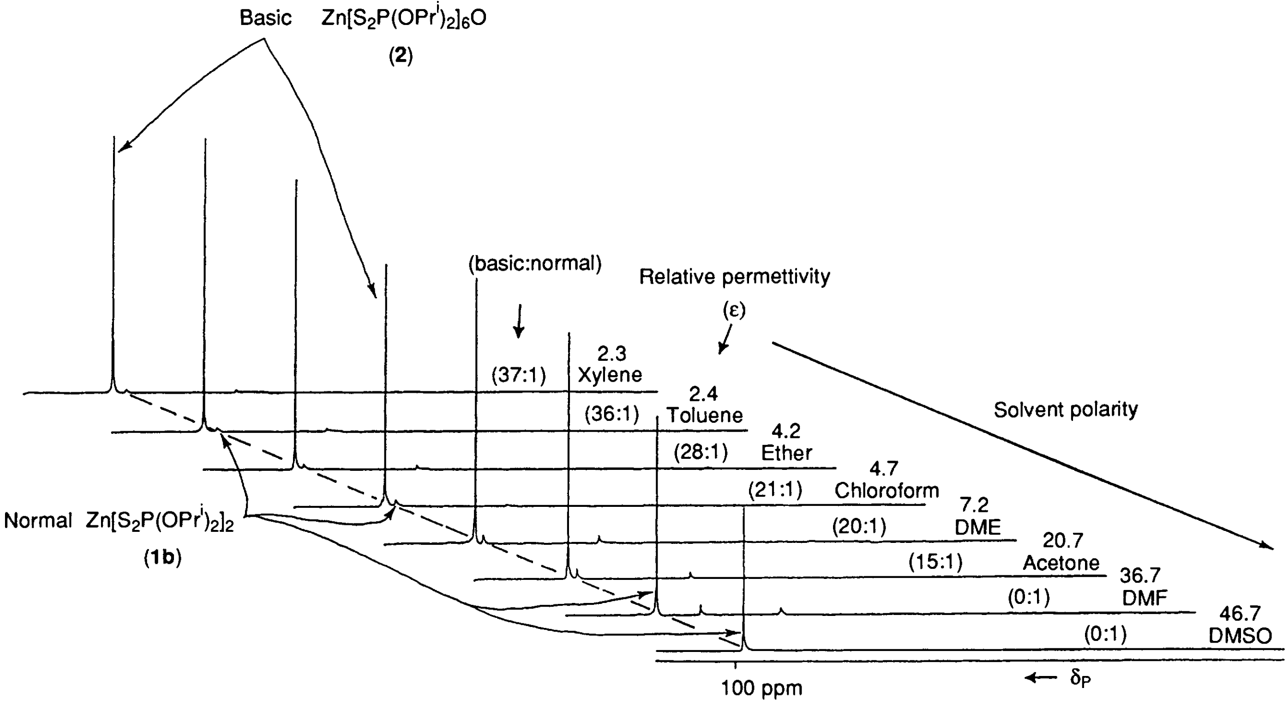


Figure 3. ^{31}P NMR spectrum of 'basic' $Zn_4[S_2P(OPr^i)_2]_6O$ (**2**) (0.166 mol dm^{-3}) in a variety of solvents.

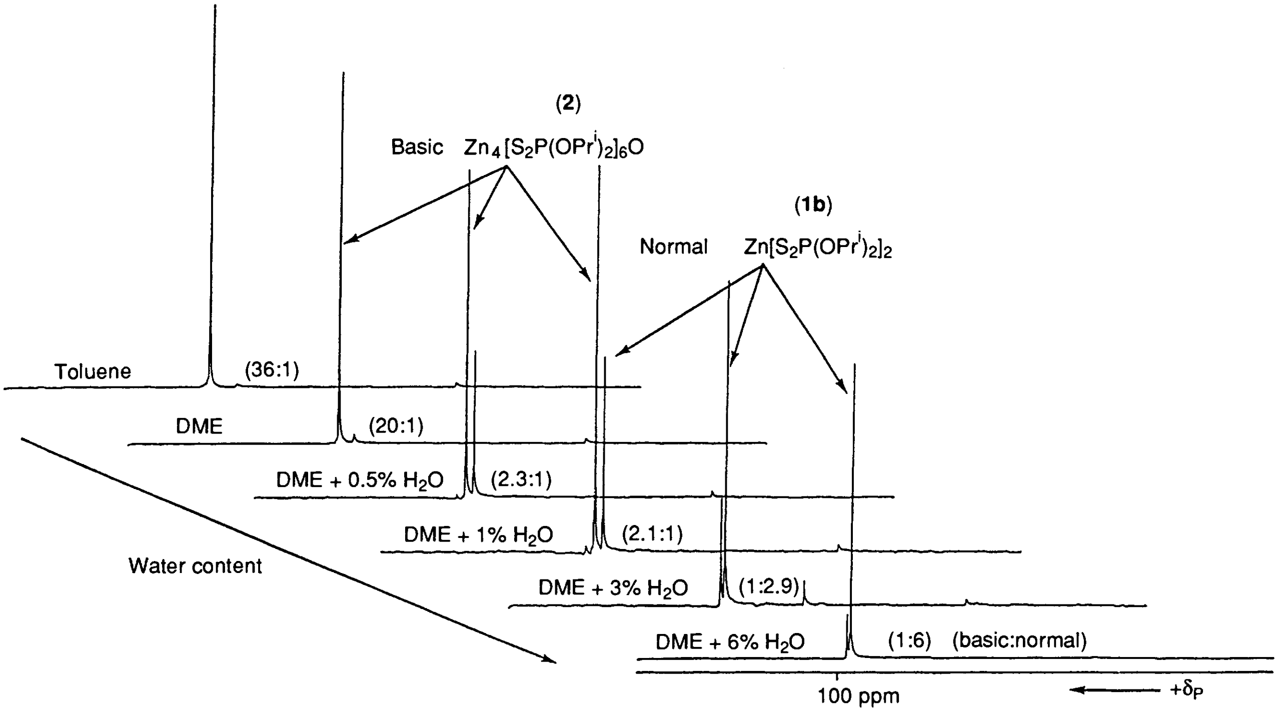


Figure 4. ^{31}P NMR spectrum of 'basic' $Zn_4[S_2P(OPr^i)_2]_6O$ (**2**) in toluene and aqueous DME.

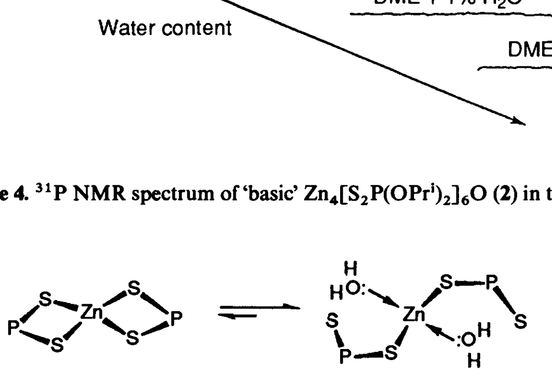
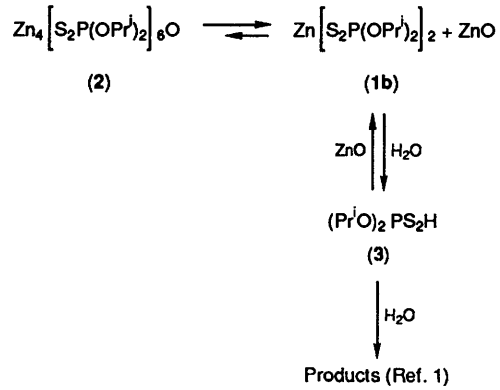


Figure 5. Schematic representation of the co-ordination of water to 'normal' $Zn[S_2P(OPr^i)_2]_2$; alkoxy groups attached to phosphorus have been omitted.

Table 1. Physical data for 'normal' $Zn[S_2P(OPr^i)_2]_2$ (**1b**) and 'basic' $Zn_4[S_2P(OPr^i)_2]_6O$ (**2**).

Compound (Formula)	Yield (%)	M.p./°C (lit.)	Found (%) (calculated) C	H
(**1b**)	85	144–145	29.2	5.8
($C_{12}H_{28}O_4P_2S_4Zn$)		(144.5)[11]	(29.3)	(5.7)
(**2**)	70	203–205	27.8	5.5
($C_{36}H_{84}O_{13}P_6S_{12}Zn_4$)		(204–206)[12]	(27.8)	(5.4)

ZDTPs,[8] the primary hydrolysis product of 'normal' ZDTP (**1b**) is di-isopropyl hydrogen phosphorodithioate (**3**), which is known to react with zinc(II) oxide[9] at ambient temperatures to generate the 'normal' salt (**1b**). As a result, consumption of the zinc(II) oxide by (**3**) gradually drives the equilibrium from the 'basic' salt (**2**) to its 'normal' form (**1b**) until all the zinc(II) oxide is consumed, whereupon the 'normal' salt (**1b**) undergoes hydrolysis as usual. This was shown to be the case by a series of control experiments. Thus, when an equilibrium solution of the 'basic' salt (**2**) [containing *ca.* 5% 'normal' form (**1b**)] in anhydrous DME was treated with 1 mol equiv. of (**3**) at room temperature, it was found that the 'basic' salt (**2**) was completely converted into its 'normal' form (**1b**) within a few minutes; this was accompanied by the disappearance of the precipitate of zinc(II) oxide.



Scheme 1.

In another experiment, it was also noted that addition of 1 mol equiv. of phosphoric acid, H_3PO_4, to a similar solution of 'basic' ZDTP (**2**) in anhydrous DME catalysed its immediate transformation into the 'normal' counterpart (**1b**) with the concomitant disappearance of the zinc(II) oxide, presumably by conversion into zinc(II) phosphate.

Further support for these proposals was obtained from a control experiment in which the hydrolysis of 'normal' ZDTP (**1b**) was observed to be inhibited by the presence of added zinc(II) oxide. Thus, when 'normal' ZDTP (**1b**) and zinc(II) oxide were mixed in a 3:1 mole ratio in aqueous DME (20 equiv. H_2O) and heated at 85 °C, no hydrolysis occurred until after an 'induction period' of *ca.* 179 h (*ca.* 7.5 days). This pattern of behaviour is akin to that observed in the treatment of the 'basic' salt (**2**) in aqueous DME (20 equiv. H_2O) at 85 °C (see above) and differs markedly from the usual hydrolysis of the 'normal' salt as described earlier. It is pertinent to note that none of the 'basic' salt (**2**) is formed under these conditions by a reversal of the equilibrium depicted in Scheme 1. In a separate experiment, the 'normal' salt (**1b**) and zinc(II) oxide were mixed in a 3:1 mole

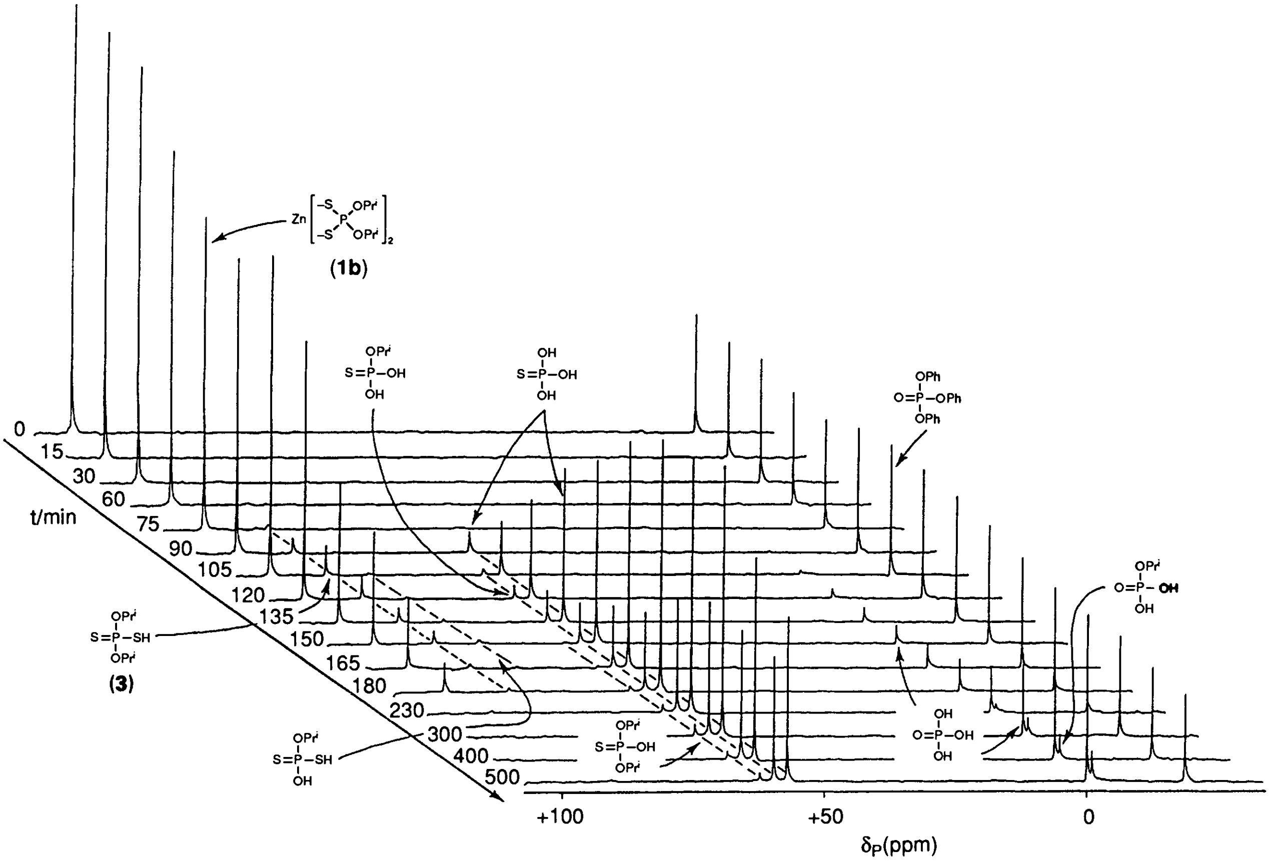


Figure 6. ^{31}P NMR spectrum of the hydrolysis of 'normal' $Zn[S_2P(OPr^i)_2]_2$ (**1b**) as a function of time in aqueous DME (10 equiv. H_2O) at 85 ± 1 °C.

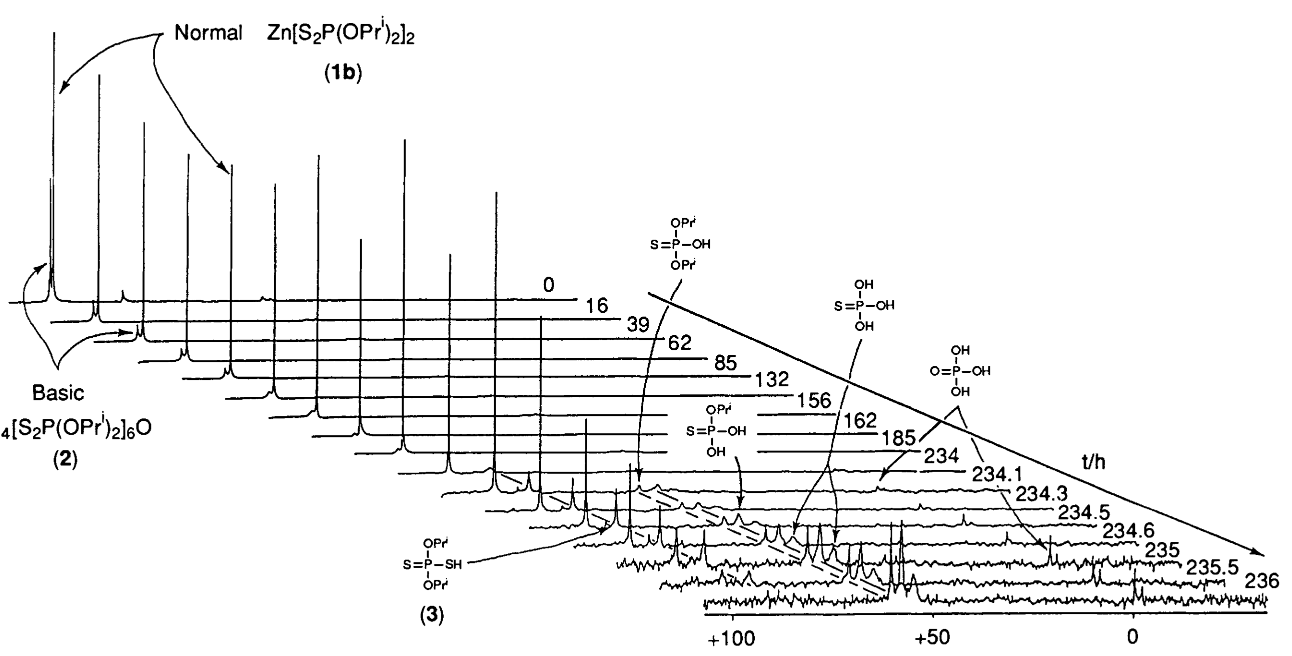


Figure 7. ^{31}P NMR spectrum of the hydrolysis of 'normal' $Zn[S_2P(OPR^i)_2]_2$ (**1b**) as a function of time, in the presence of its 'basic' form (**2**) and zinc(II) oxide in aqueous DME (10 equiv. H_2O) at 85 ± 1 °C.

ratio, but stirred in anhydrous DME solution at ambient temperature. Under these conditions, the formation of a small amount of the 'basic' salt (**2**) was observed by ^{31}P NMR spectroscopy, which indicates that the dissociation of (**2**) into (**1b**) and zinc(II) oxide is reversible in some circumstances.

We conclude that the hydrolysis of 'normal' $Zn[S_2P(OPr^i)_2]_2$

Table 2. NMR data for 'normal' $Zn[S_2P(OPr^i)_2]_2$ (**1b**) and 'basic' $Zn_4[S_2P(OPr^i)_2]_6O$ (**2**).

	$\delta_H(CDCl_3)$			$\delta_C(CDCl_3)$					
	CH_3[b]	CH[b]	$^3J_{H,H}$/Hz	CH_3[b]	CH[b]	$^2J_{C,P}$/Hz	$^3J_{C,P}$/Hz	$\delta_P(^1H$-decoupled)	$^3J_{P,H}$/Hz
$Zn[S_2P(OPr^i)_2]_2$	1.35(2)	4.85[c]	6.3	23.3(2)	73.7(2)	6.8	4.2	98.4[d] 94.3[e] 94.7[f]	12.7
$Zn_4[S_2P(OPr^i)_2]_6O$[a]	1.2(2)	4.9[c]	6.2	22.7(2)	72.4(2)	8.3	4.1	99.6[d] 98.7[e] 100.6[f]	12.7

[a] Spectrum also contains resonances due to $Zn[S_2P(OPr^i)_2]_2$.[5] [b] Multiplicities in parentheses. [c] Pseudo-nonet. [d] In $CDCl_3$. [e] In DME. [f] In $[^2H]_8$-toluene.

(**1b**) is inhibited by the presence of its 'basic' form $Zn_4[S_2P(OPr^i)_2]_6O$ (**2**) owing to the dissociation of the latter in solution to produce zinc(II) oxide which reacts with the primary hydrolysis product *O*,*O*-di-isopropyl *S*-hydrogen phosphorodithioate (**3**) to reform the 'normal' salt (**1b**). The periods of inhibition are inversely proportional to the water content in the reaction solution and can be rationalised in terms of the relative rates of hydrolysis of (**1b**). As the water content is increased, this results in a faster rate of hydrolysis, which in turn leads to faster consumption of the zinc(II) oxide by the resultant phosphorodithioate (**3**). This coincides with shorter inhibition times owing to the faster rate at which the 'basic' salt (**2**) is converted into its 'normal' form (**1b**).

Experimental

All solvents used were AnalaR grade. Zinc(II) bis(*O*,*O'*-di-isopropyl dithiophosphate) (**1b**) and hexakis[*O*,*O'*-di-isopropyl dithiophosphate]-μ_4-tetraoxozinc (**2**) were synthesized by literature methods.[1,3,4,10–12] The syntheses of their hydrolysis products have also been previously described.[1] The physical characteristics and NMR data of (**1b**) and (**2**) are shown in Tables 1 and 2. Instrumentation for NMR, elemental analyses, m.p.s and MS was as previously described.[1] Chemical shifts are quoted relative to internal tetramethylsilane (δ_H) or external 85% H_3PO_4 (δ_P; positive values at high frequency). The spectral window was 5 200 Hz with 8 K data giving a digital resolution of 0.635 Hz per point. A pulse width of 5 μs (25°) was used with 0.787 s acquisition time and a pulse delay of 0.5 s; accumulations over 80 scans per spectrum gave a typical signal-to-noise ratio $>10:1$ with solution strengths of *ca.* 0.33 mol dm^{-3}.

^{31}P NMR Spectroscopy Studies on the Dissociation of 'Basic' ZDTP (**2**) *in Solution.*—(*a*) Compound (**2**) (0.105 g, 6.7×10^{-5} mol) was dissolved in anhydrous solvent S (0.4 cm^3) (S = xylene, toluene, diethyl ether, chloroform, 1,2-dimethoxyethane, acetone, dimethylformamide 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 (**2**) to its 'normal' counterpart (**1b**) were observed.

(*b*) Compound (**2**) (0.105 g, 6.7×10^{-5} mol) was dissolved in solvent X (0.4 cm^3) [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*) Compound (**2**) (0.105 g, 6.7×10^{-5} mol) was dissolved in aqueous DME (6% water) (0.4 cm^3) in an NMR tube. A ^{31}P NMR spectrum was obtained after which the solution was diluted by half with anhydrous DME (0.4 cm^3) to 3% water. Another ^{31}P NMR spectrum was obtained and the solution was diluted again by half with anhydrous DME (0.8 cm^3) to 1.5% water. The solution was then monitored continuously by ^{31}P NMR spectroscopy at room temperature for several days.

Hydrolysis of 'Normal' ZDTP (**1b**) *in the Presence of 'Basic' ZDTP* (**2**).—(**2**) (5.19 g, 0.0033 mol) was dissolved in aqueous DME (10 cm^3) containing: (*a*) 10 equiv. water (0.6 cm^3), (*b*) 20 equiv. water (1.2 cm^3), and (*c*) 30 equiv. water (1.8 cm^3). The resultant solutions were heated at 85 ± 1 °C. At various time intervals samples (0.4 cm^3) 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 the hydrolysis of (**1b**) was complete.

Hydrolysis of 'Normal' ZDTP (**1b**).—(*a*) (**1b**) (1.64 g, 0.0033 mol) was dissolved in aqueous DME (10 cm^3) containing 10 equiv. distilled water (0.6 cm^3) and triphenyl phosphate (0.539 g, 0.0017 mol).

(*b*) Compound (**1b**) (1.64 g, 0.0033 mol) was dissolved in aqueous DME (10 cm^3) containing 20 equiv. water (1.2 cm^3), triphenyl phosphate (0.543 g, 0.0017 mol) and zinc(II) oxide (90 mg, 0.0011 mol). The mixture was stirred continuously. The resultant solutions were heated at 85 ± 1 °C and monitored continuously by ^{31}P NMR spectroscopy as described.

Reaction of 'Normal' ZDTP (**1b**) *with Zinc*(II) *Oxide.*—Compound (**1b**) (1.64 g, 0.0033 mol) was dissolved in anhydrous DME (10 cm^3) containing triphenyl phosphate (0.543 g, 0.0017 mol) and zinc(II) oxide (90 mg, 0.0011 mol). The resultant mixture was stirred at room temperature and monitored continuously by ^{31}P NMR spectroscopy for several days.

Reaction of 'Basic' ZDTP (**2**) *with* O,O-*Di-isopropyl* S-*Hydrogen Phosphorodithioate* (**3**).—To compound (**2**) (0.207 g, 0.000 13 mol) in anhydrous DME (0.4 cm^3) was added (**3**) (28 mg, 0.000 13 mol) and the mixture was monitored continuously by ^{31}P NMR spectroscopy at room temperature for several hours.

Reaction of 'Basic' ZDTP (**2**) *with Orthophosphoric Acid,* H_3PO_4.—To compound (**2**) (0.208 g, 0.000 13 mol) in anhydrous DME (0.4 cm^3) was added H_3PO_4 (13 mg, 0.000 13 mol) and the mixture was monitored continuously by ^{31}P NMR spectroscopy at room temperature for several hours.

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