Analysis of the Hydrolytic Stability of Zinc(II) *O,O*-Dialkyl Dithiophosphates as a Function of the Nature of the Alkyl Groups by ^{31}P NMR Spectroscopy

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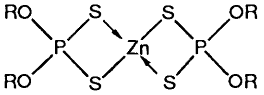
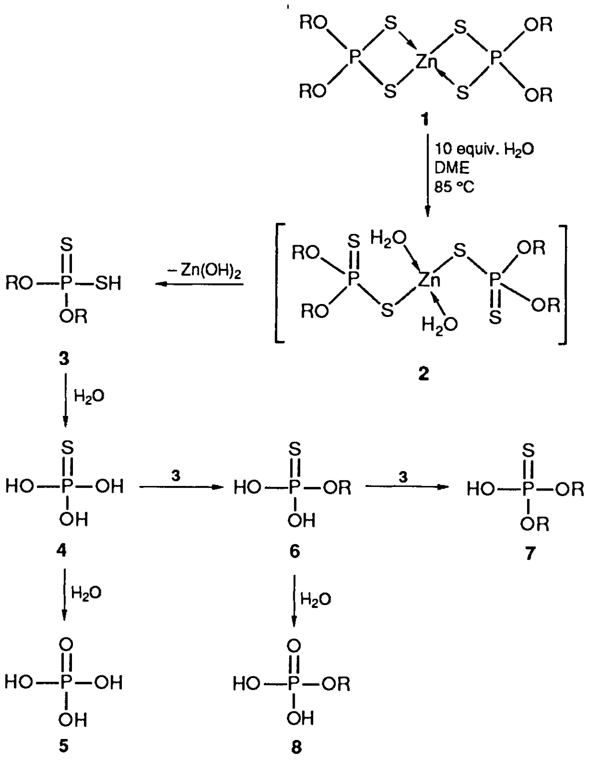
Zinc(II) bis(*O,O*-dialkyl dithiophosphates) $Zn[S_2P(OR)_2]_2$ **1** where R = ethyl **1a**, 2-propyl **1b**, 2-butyl **1c**, hexyl **1d**, 4-methyl-2-pentyl **1e**, and 2-ethylhexyl **1f**, are hydrolysed to phosphoric acid **5** and other by-products *O*-alkyl *O,O*-dihydrogen thiophosphate **6**, *O,O*-dialkyl *O*-hydrogen thiophosphate **7**, and alkyl dihydrogen phosphate **8** *via* the corresponding *O,O*-dialkyl *S*-hydrogen dithiophosphate **3** and thiophosphoric acid **4**. Contrary to expectation, the rates of hydrolysis of the zinc(II) *O,O*-dialkyl dithiophosphates are found to be independent of the alkyl substituent present and fall within the range $k_{obs} = (2.34–2.96) \times 10^{-4}\ s^{-1}$. The null effect of the alkyl groupings is attributed to hydrophobic interactions that leave the central zinc atom exposed to attack by water irrespective of their size.

'Normal' or 'neutral' zinc dialkyl dithiophosphates (ZDTPs) **1** have enjoyed widespread usage for the past forty years as anti-oxidants[1–4] and anti-wear agents[5–11] in lubricating oils. Based on extensive studies, it has become apparent that both of these properties are dependent upon the thermal stability of ZDTPs, which in turn, is governed by the nature of the substituent alkyl groups. In particular, Dickert and Rowe[9] have shown that the thermal stability of such complexes is directly related to the number of β-hydrogen atoms present on the alkyl groups, *i.e.* the lower the number of β-hydrogen atoms, the greater is the thermal stability. Thus, straight-chain alkyl groups give rise to ZDTPs of higher thermal stability than those derived from branched alkyl groups. Further studies[12,13] have shown that, in general, the lower the thermal stability of a ZDTP complex, the more effective an additive it is, owing to more efficient degradation to the 'active state' at operating temperatures. By comparison, relatively little is known about the effect of alkyl substituents upon ZDTP hydrolytic stability.



1a; CH_3CH_2
b; $(CH_3)_2CH$
c; $CH_3CH_2CH(CH_3)$
d; $CH_3(CH_2)_4CH_2$
e; $(CH_3)_2CHCH_2CH(CH_3)$
f; $CH_3(CH_2)_3CH(CH_2CH_3)CH$

In previous papers, we have described the mechanism and kinetics of the hydrolysis of zinc(II) bis(*O,O*-diethyl dithiophosphate), $Zn[S_2P(OEt)_2]_2$ **1a**,[14] together with the inhibiting effects of its 'basic' counterpart, $Zn_4[S_2P(OEt)_2]_6O$.[15] By using ^{31}P NMR spectroscopy to unravel the complexities of the reactions involved, it was found that diethyl ZDTP **1a** hydrolysed to phosphoric acid **5** *via* *O,O*-diethyl *S*-hydrogen dithiophosphate **3a** and thiophosphoric acid **4**, along with several by-products **6a**, **7a** and **8a** (Scheme 1). The simple ethyl analogue **1a** is not favoured in commercial oil packages, and in this paper, we have undertaken further kinetic studies into the initial stages of the hydrolysis of the more commonly used additives, 4-methyl-2-pentyl ZDTP **1e** and 2-ethylhexyl ZDTP **1f**, as well as other alkyl derivatives **1b–d** of varying chain-length in order to establish the effect, if any, of alkyl substituents in terms of size, shape, and nature (*i.e.* primary or secondary) upon their hydrolytic stability and product formation.



Scheme 1 Mechanism for the hydrolysis of zinc(II) bis(*O,O*-dialkyldithiophosphates) **1**

Results and Discussion

The hydrolytic studies were carried out using freshly prepared zinc dialkyl dithiophosphates and distilled water in a 1:10 molar ratio in 1,2-dimethoxyethane (DME) and the solutions heated at 85 °C until hydrolysis was complete. The ^{31}P NMR hydrogen-decoupled (broad band) spectra of the solutions were monitored for the disappearance of the ZDTP and the formation of the intermediates and products. For kinetic studies, an inert internal standard of triphenyl phosphate was used to compare peak intensities, and the ^1H-decoupled spectra obtained under conditions in which the longitudinal relaxation

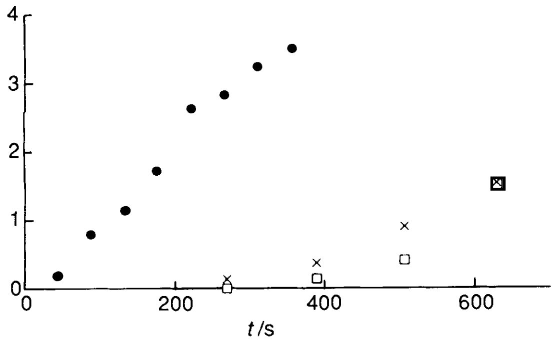


Fig. 1 Effect of acidic conditions upon the hydrolysis of 4-methyl-2-pentyl ZDTP **1e**. □, Hydrolysis is under normal ('neutral') conditions (pH = 3–6); ×, hydrolysis in acidified DME (pH = 1.0); ●, hydrolysis in acidified DME (pH < 0).

Table 1 Ratio of primary transesterification products (**6** + **8**) to secondary (**7**) formed in ZDTP hydrolysis studies[a]

ZDTP	(**6** + **8**):**7**	
Ethyl **1a**	10.7	1.0
2-Propyl **1b**	8.8	1.0
2-Butyl **1c**	2.7	1.0
n-Hexyl **1d**	3.9	1.0
4-Methyl-2-pentyl **1e**	3.8	1.0
2-Ethylhexyl **1f**	3.2	1.0

[a] Measured from peak intensities of the ^{1}H-decoupled ^{31}P NMR spectra in Figure 2.

Table 2 Rate constants (k_{obs}) for hydrolysis of zinc(II) *O,O*-dialkyl dithiophosphates **1a–f** under pseudo-first-order conditions (10 equiv. of water at 85 ± 1 °C in DME)

R	$k_{obs}/10^{-4}$ s^{-1} [a]
Ethyl **1a**	2.34[b]
2-Propyl **1b**	2.57
2-Butyl **1c**	2.96
n-Hexyl **1d**	2.64
4-Methyl-2-pentyl **1e**	2.74
2-Ethylhexyl **1f**	2.55

[a] All observed rate constants (k_{obs}) were reproducible to within ±10%. [b] From ref. 14.

times of the different species to be studied were taken into account so that their signal intensities were proportional to their concentrations. Precise relaxation times were not calculated for all the ZDTPs used as previous studies[14] had shown a 5 s pulse delay to be adequate.

Hydrolysis of Zinc(II) O,O-*Dialkyl Dithiophosphates*.—Hydrolysis was carried out on the following ZDTP derivatives: 2-propyl **1b**, 2-butyl **1c**, hexyl **1d**, 4-methyl-2-pentyl **1e** and 2-ethylhexyl **1f**. In each case, monitoring of the ^{31}P NMR spectra during hydrolysis showed peaks corresponding to the characteristic formation of intermediates and products in the same order of appearance as had been observed previously for the hydrolysis of the ethyl derivative **1a**.[14] The spectra verified that the mechanism of hydrolysis is the same irrespective of the alkyl group and follows the pathway outlined in Scheme 1. For the complexes, hexyl **1d**, 4-methyl-2-pentyl **1e**, and 2-ethylhexyl **1f**, a considerable induction period was observed before hydrolysis commenced. A similar phenomenon was observed during investigations into the hydrolysis of the ethyl analogue **1a**, but only on samples which were not freshly prepared and as a result had formed coatings of zinc(II) oxide. In the present context, an induction period occurred regardless of sample freshness and is ascribed once again to the presence of zinc(II) oxide whose origin may lie in the facile equilibrium (1) due to

$$Zn_4[S_2P(OR)_2]_6O \rightleftharpoons 3Zn[S_2P(OR)_2]_2 + ZnO \quad (1)$$

contamination by trace amounts of the 'basic' form. Alternatively, the zinc(II) oxide may result from the reaction of zinc sulfate with potassium hydrogen carbonate, traces of which may be present in the potassium salt of the dithiophosphoric acid owing to difficulties in purifying the latter by recrystallisation [eqn. (2)]. Significantly, those complexes that

$$ZnSO_4 + 2KHCO_3 \longrightarrow ZnO + K_2SO_4 + CO_2 + H_2O \quad (2)$$

showed this induction period were all isolated as viscous oils which could not be purified further, and in consequence, are likely to contain traces of impurities, whereas both the ethyl **1a** and 2-propyl **1b** complexes are crystalline compounds and easily obtained in analytically pure form by recrystallisation. This proposal was reinforced by hydrolytic studies carried out on the 4-methyl-2-pentyl complex **1e** under acidic conditions. Previous work had shown that during hydrolysis the acidity of the solution increased from pH 3.3 to pH 1.0, with a concomitant acceleration in the rate due to acid catalysis. It was found that for hydrolysis of **1e** in the presence of acid (pH = 1.0), the induction period could be reduced, and if sufficient acid was present (pH < 0), eradicated completely (Fig. 1), presumably owing to the conversion of zinc(II) oxide into zinc chloride by the acid. It was also noted that addition of acid changed the rate profile and increased the rate of hydrolysis, thus emphasising the acid-catalysed nature of the reaction.

Comparison of the ^{31}P NMR spectra for the complete hydrolytic consumption of each ZDTP studied showed that the concentrations of the final products varied even though the same reaction pathway was operating. In order to obtain more detailed information on the effect of change in alkyl substituents upon final product distribution, the ^{31}P NMR spectra of ZDTPs **1a–f** were recorded after their complete hydrolysis using a 15 s pulse delay in order that all peak intensities would be comparitive. *i.e.* fully relaxed (Fig. 2). From the measured ratios of products (Table 1), it is clear that the extent of primary transesterification of thiophosphoric *O,O,O*-acid **4** to give *O*-alkyl *O,O*-dihydrogen thiophosphate **6** (and consequently, its hydrolysis product, ethyl dihydrogen phosphate **8**) exceeds secondary transesterification of **6** to *O,O*-dialkyl *O*-hydrogen thiophosphate **7**, particularly for the ethyl and 2-propyl derivatives **1a** and **1b**, respectively. A valid explanation for the lack of secondary transesterification in the case of **1a** and **1b** is the relative ease of hydrolysis of the corresponding dithiophosphoric acids **3a** compared to the other longer-chain ones as previously reported by Cote and Bauer;[16] as a result less is available to induce transesterification.

Kinetic Studies.—Kinetic analyses of the hydrolyses of ZDTPs **1b–f** were carried out under identical conditions in DME solution at 85 °C with 10 mol equiv. of water, by monitoring their disappearance using ^{31}P NMR spectroscopy. In all cases, if the induction period was disregarded, the hydrolyses followed an initial period of pseudo-first-order kinetics followed by an exponential increase in rate due to acid catalysis (Fig. 3). The calculated relative rate constants (k_{obs}) for the linear region of each plot are presented in Table 2, and show that the rates of hydrolysis have little or no dependence upon either the size or the nature, *i.e.* linear or branched, of the alkyl substituents. In our previous study of the hydrolytic breakdown

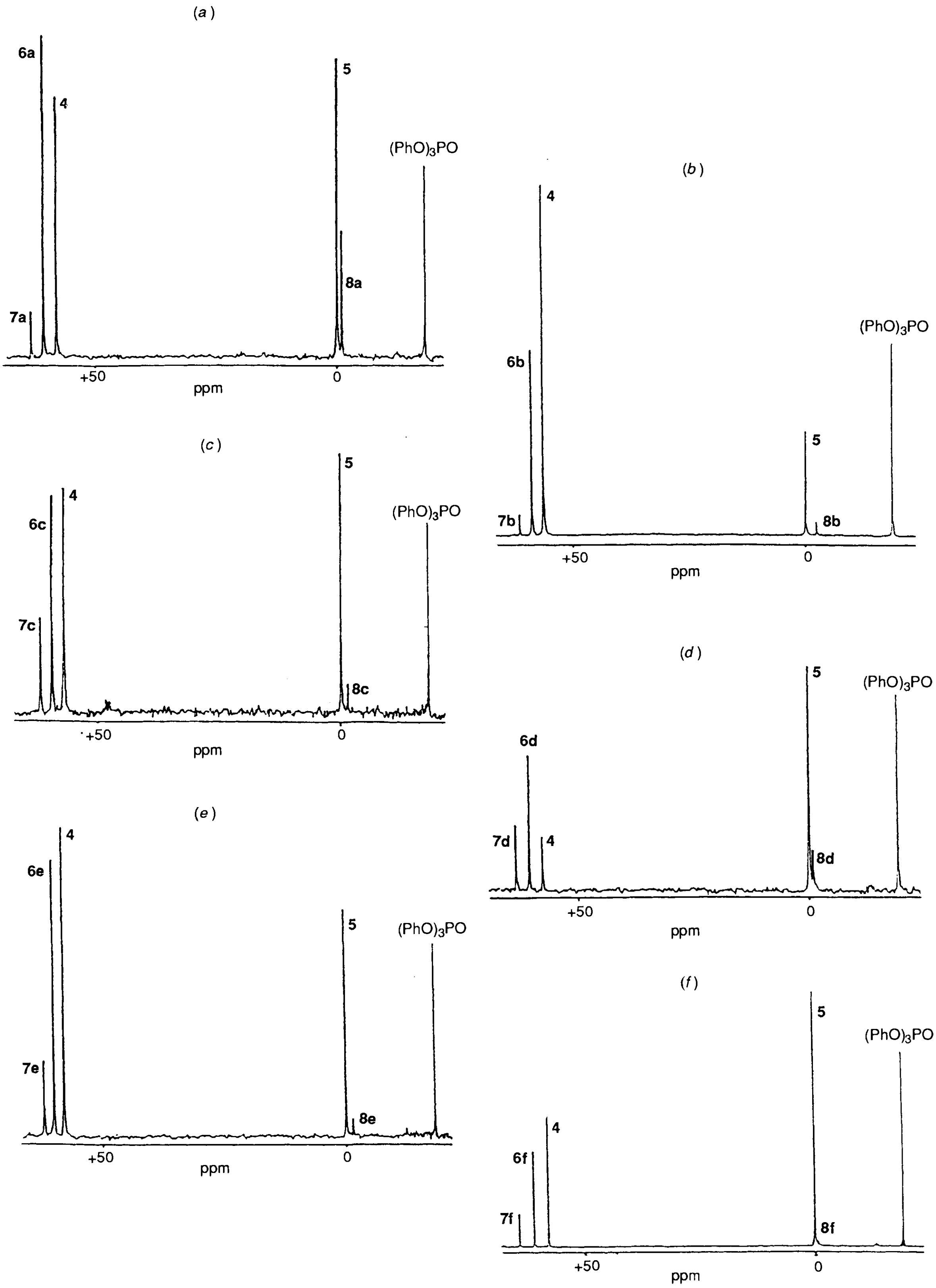


Fig. 2 Quantitative ^{31}P NMR H-decoupled spectra of the hydrolyses mixtures after complete disappearance of ZDTPs **1a**–**f** at 85 °C with 10 mol equiv. of water. (*a*) **1a**, t = 180 min; (*b*) **1b**, t = 180 min; (*c*) **1c**, t = 240 min; (*d*) **1d**, t = 360 min; (*e*) **1e**, t = 420 min; (*f*) **1f**, t = 480 min.

of the ethyl ZDTP **1a**, we proposed that the initial, and rate-determining, step for hydrolysis is attack by water at zinc with the likely formation of an intermediate, probably **2**, as evidenced by the subsequent appearance of the corresponding *O*,*O*-dialkyl dithiophosphoric acid **3**; R = Et (Scheme 1). The constancy in the observed rate constants, irrespective of the alkyl substituents in the ZDTP, provides further evidence for attack at the zinc centre rather than any other site in the molecule. Most surprisingly, the data reveal that for a given ZDTP, its structure represents no steric or hydrophobic hindrance to attack by water, presumably owing to the remoteness of the alkyl groups from the tetrahedral zinc atom. It is well

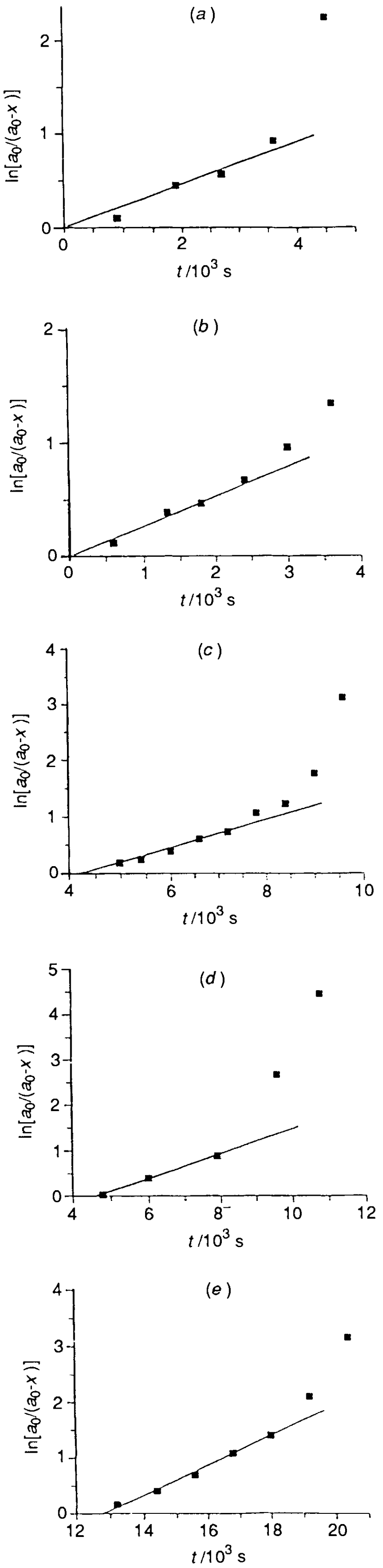


Fig. 3 Plot of pseudo-first-order decay of ZDTPs **1b–f** in DME at 85 °C with 10 mol equiv. of water. (*a*), **1b**; (*b*), **1c**; (*c*), **1d**; (*d*), **1e**; (*e*), **1f**.

established[17] that in solution ZDTPs exist as a chelated monomeric species in equilibrium with a dimeric form possessing a bridged structure (Fig. 4). In essence, association to the dimeric form is favoured by high ZDTP concentrations and polar solvents. For straight-chain alkyl ZDTPs, the dimer becomes more predominant as the alkyl group increases in size from ethyl to hexyl; thereafter, the monomer is favoured owing to increased steric requirements of the alkyl group. In the case of branched alkyl ZDTPs, the tendency to associate into dimers decreases as the size of the alkyl groups increases for similar reasons.

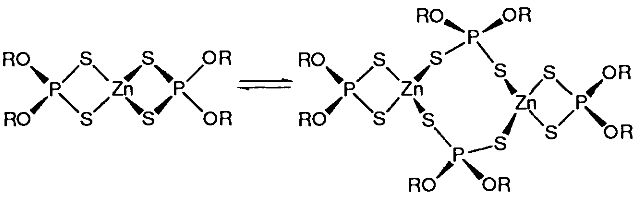


Fig. 4 Monomer–dimer equilibrium for ZDTPS

From the viewpoint of our investigations, given that high ZDTP concentrations (0.35 mol dm^{-3}) and a relatively polar solvent (relative permittivity = 7.20) are used, it is evident that the dimeric species predominate under these conditions, even for the larger, branched alkyl ZDTPs such as 4-methyl-2-pentyl ZDTP **1e** and 2-ethylhexyl ZDTP **1f**, especially when compared to their ethyl **1a** and isopropyl **1b** counterparts. Since only a single peak is observed in the ^{31}P NMR spectra for solutions of all the ZDTPs, the monomer $\rightleftharpoons$ dimer equilibrium is obviously rapid on the NMR time-scale and in view of the small variation in k_{obs}, it exerts little, if any, influence on the rate of hydrolysis.

Whether attack by water occurs preferentially on the monomer or dimer is unclear, but given the negligible change in the geometry at zinc [or for the chelating and bridging $S_2P(OR)_2$ ligands] on going from one form to the other, little difference in rate seems likely. Irrespective of which species is attacked, the lack of influence by the alkyl groups on the rate of hydrolysis points to their remoteness from the zinc centre. Such an inability of the longer alkyl groups to provide a protective shield can probably be ascribed to hydrophobic interactions (often called hydrophobic bonding),[18] whereby the hydrocarbon parts of the complexes in an aqueous environment tend to cluster together and leave the zinc exposed to attack by water.

These observations are in sharp contrast to the aforementioned findings by Cote and Bauer[16] on the hydrolytic stability of *O*,*O*-dialkyl dithiophosphoric acids **3**, which are the primary products of the hydrolysis of ZDTP **1**. They found that the long-chain derivatives are distinctly more stable against hydrolysis than the short-chain ones. An explanation for this divergence in behaviour may lie in the closer proximity of the alkyl groups in these species to the centre of hydrolytic attack, *i.e.* the phosphorus atom, thereby leading to greater hindrance to the approach by water. Secondly, in the case of the dithiophosphoric acids, hydrolysis involves cleavage of the RO–P bond, which is more likely to be influenced by changes in the attached alkyl group.

The implication of these observations for the hydrolyses of ZDTPs seems to be that although the rate of their initial hydrolysis to the corresponding *O*,*O*-dialkyl dithiophosphoric acid is independent of the nature of the alkyl group, the latter does exert an influence to a varying degree on subsequent steps to secondary hydrolysis products.

Experimental

Melting points were determined on a Gallenkamp m.p. apparatus. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker WP200SY instrument operating at 28 °C. *J* values are in Hz. All ^{31}P NMR spectra were recorded on a JEOL FX90Q spectrometer operating at 36.23 MHz and 27 °C with either a deuteriated solvent or an internal coaxial C_6D_6 lock. ^{31}P chemical shifts are referred to 85% phosphoric acid, with shifts to higher frequency positive. For kinetic measurements, a spectral window of 5200 Hz, a pulse width of 4 μs (20°), an acquisition time of 0.787 s and a pulse delay of 5 s were used. Accumulations over 50 scans in the proton decoupled mode were found to give a satisfactory signal to noise ratio. pH measurements were made using a Kent EIL 7015 pH meter equipped with a model 1160 glass combination electrode.

All solvents used were of AnalaR grade, and dried by appropriate means. Water used in the hydrolysis was deionised and distilled. 'Ether' refers to diethyl ether throughout.

Potassium O,O-*Dialkyl Dithiophosphate*.—Prepared by the neutralisation of the corresponding *O,O'*-dialkyl dithiophosphoric acid (prepared by reaction of the appropriate alcohol with P_2S_5[19]) with a saturated solution of potassium hydrogen carbonate. Extraction with ether removed any unreacted acid and impurities and the remaining aqueous layer was evaporated *in vacuo*. The resulting residue was warmed in acetone and hot filtered to remove inorganic solids. On evaporation of the acetone, the potassium salt was obtained. Potassium *O,O*-diethyl dithiophosphate, m.p. 191–195 °C (acetone–ether) (lit.,[20] 194–195 °C), $\delta_P(D_2O)$ + 110.6 (lit.,[21] +110.5). Potassium *O,O*-bis(2-propyl)dithiophosphate, m.p. 203 °C (lit.,[22] 193 °C), $\delta_P(D_2O)$ + 107.1 (lit.,[21] +107.4). Potassium *O,O*-bis(2-butyl)dithiophosphate, m.p. 126.5–128 °C (acetone), $\delta_P(CDCl_3)$ +108.5. Potassium *O,O*-bis(4-methyl-2-pentyl)dithiophosphate, m.p. 153–157 °C (acetone), $\delta_P(CDCl_3)$ + 111.6. Potassium *O,O*-bis(2-ethylhexyl)dithiophosphate, oil, $\delta_P(CDCl_3)$ + 109.3.

'Normal' Zinc(II) *Bis*(O,O-*dialkyl dithiophosphates*) **1**.—Prepared by the reaction of potassium *O,O*-dialkyl dithiophosphate with zinc(II) sulfate in a 2:1 molar ratio in aqueous solution. Extraction with ether followed by evaporation *in vacuo* gave the ZDTP. 'Normal' zinc(II) *O,O*-diethyl dithiophosphate **1a** (85%), m.p. 76–78 °C (heptane) (lit.,[23] 77 °C), $\delta_P(CDCl_3)$ + 96.5. 'Normal' zinc(II) bis[*O,O*-bis(2-propyl)dithiophosphate] **1b** (85%), m.p. 144–145 °C (heptane) (lit.,[11] 144.5 °C), $\delta_P(CDCl_3)$ + 94.8. 'Normal' zinc(II) bis[*O,O*-bis(2-butyl)dithiophosphate] **1c** (83%), oil, $\delta_P(CDCl_3)$ + 87.8, $\delta_H(CDCl_3)$ 0.94 (12 H, t, ^3J_H 7.4, CH_3), 1.37 (12 H, d, ^3J_H 6.2, CH_3), 1.70 (8 H, m, CH_2), 4.66 (4 H, m, $^3J_{PH} < 1$ Hz, CH). 'Normal' zinc(II) bis[*O,O*-bis(hexyl)dithiophosphate] **1d** (85%), oil, $\delta_P(CDCl_3)$ + 97.9, $\delta_H(CDCl_3)$ 0.87 (12 H, t, ^3J_H 6.4, CH_3), 1.32 (24 H, m, 3 × CH_2), 1.71 (8 H, m, CH_2), 4.14 (8 H, dt, $^3H_{PH}$ 9.0 Hz, ^3J_H 6.5, CH_2O). 'Normal' zinc(II) bis[*O,O*-bis(4-methyl-2-pentyl)dithiophosphate] **1e** (93%), oil, $\delta_P(CDCl_3)$ + 93.1, $\delta_H(CDCl_3)$ 0.90 (12 H, d, ^3J_H 6.5, CH_3), 0.94 (12 H, d, ^3J_H 6.5, CH_3), 1.32 (4 H, m, CH), 1.40 (12 H, d, ^3J_H 6.2 Hz, CH_3), 1.73 (8 H, m, CH_2), 4.77 (4 H, m, CH). 'Normal' zinc(II) bis[*O,O*-bis(2-ethylhexyl)dithiophosphate] **1f** (79%), oil, $\delta_P(CDCl_3)$ + 100.6, $\delta_H(CDCl_3)$ 0.89 (24 H, m, CH_3), 1.26 (32 H, m, CH_2), 1.58 (4 H, m, CH), 3.85 (8 H, m, CH_2O).

Hydrolysis of 'Normal' Zinc(II) *Bis*(O,O-*dialkyl dithiophosphates*).—The ZDTP (3.50 mmol), triphenyl phosphate (0.554 g; 1.70 mmol) and distilled water (0.630 g; 35.0 mmol) were mixed in DME (10.0 cm^3). The resulting solution was transferred to a series of NMR tubes which were sealed and heated in a water bath at 85 ± 0.2 °C. Kinetic measurements were obtained by monitoring the ^{31}P NMR spectra for the disappearance of the ZDTP at time interval, *t*, at which point the NMR tube was removed from the water bath and quenched in ice.

Hydrolysis of Zinc(II) *Bis*[O,O-bis(4-*methyl*-2-*pentyl*)*dithiophosphate*] **1e** *in Acid Conditions*.—The hydrolysis of 4-methyl-2-pentyl ZDTP was carried out using mixtures prepared as described above, one using DME saturated with HCl gas to give a pH = 1 and another to which 3 drops of conc. hydrochloric acid had been added to give a pH < 0. Both solutions were transferred to NMR tubes and hydrolysed in the usual way, along with a similarly prepared neutral solution for comparison.

References

1 T. Colclough and J. I. Cuneen, *J. Chem. Soc.*, 1964, 4790.
2 A. J. Burn, *Tetrahedron*, 1966, **22**, 2153.
3 A. J. Bridgewater, J. R. Dever and M. D. Sexton, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1006 and references cited therein.
4 A. J. Burn, R. Cecil and V. O. Young, *J. Inst. Petroleum*, 1971, 319.
5 H. Luther and S. K. Sinha, *Erdol Und Kohle*, 1964, **17**, 91.
6 H. Luther, E. Baumbarten and K. U. Islam, *Erdol Und Kohle*, 1973, **26**, 509.
7 F. G. Rounds, *A.S.L.E. Trans.*, 1975, **18**, 79 and references cited therein.
8 J. S. Ashford, L. Bretherick and P. Gould, *J. Appl. Chem.*, 1965, **15**, 170.
9 J. J. Dickert and C. N. Rowe, *J. Org. Chem.*, 1967, **32**, 647.
10 W. W. Hanneman and R. S. Porter, *J. Org. Chem.*, 1964, **29**, 2996.
11 C. N. Rowe and J. J. Dickert, *A.C.S. Pre-prints*, 1965, **10**, No. 2 (D6).
12 J. F. Ford, *J. Inst. Petroleum*, 1968, **54**, 198, and references cited therein.
13 G. J. J. Jayne and J. S. Elliott, *J. Inst. Petroleum*, 1970, **56**, 42.
14 A. J. Burn, S. K. Dewan, I. Gosney and P. S. G. Tan, *J. Chem. Soc., Perkin Trans. 2*, 1989, 753.
15 A. J. Burn, S. K. Dewan, I. Gosney and P. S. G. Tan, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1311.
16 G. Cote and D. Baur, *Anal. Chem.*, 1984, **56**, 2153.
17 P. G. Harrison, P. Brown, M. J. Haynes, J. M. Kiely and J. McManns, *J. Chem. Res.* (*M*), 1991, 174 and references cited therein.
18 E. M. Huque, *J. Chem. Educ.*, 1989, **66**, 581.
19 V. P. Wystrach, E. O. Hook and G. L. M. Christopher, *J. Org. Chem.*, 1956, **21**, 705.
20 N. I. Zemlyanskii, O. A. Prib and B. S. Drach, *Zhur. Obsh. Khim.*, 1961, **31**, 880; *Chem. Abstr.*, 1961, **55**, 23314b.
21 M. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. Van Waser, *Phosphorus-31 NMR* in *Topics in Phosphorus Chemistry*, eds. M. Grayson and E. J. Griffith, Interscience, New York, vol. 5, 1967.
22 G. I. Bolotava, G. G. Kotova, K. I. Zimina and V I Isagulyants, *Zh. Prikl. Khim.*, 1965, **38**, 1580; *Chem. Abstr.*, 1965, **63**, 13028a.
23 D. R. Dakternieks and D. P. Graddon, *Aust. J. Chem.*, 1970, **23**, 1989.

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