Phosphorus-31 NMR Investigation of the Heterogeneous Hydrolytic Decomposition of Zinc(II) Bis(*O,O*-Dialkyl Dithiophosphate) Lubricant Additives

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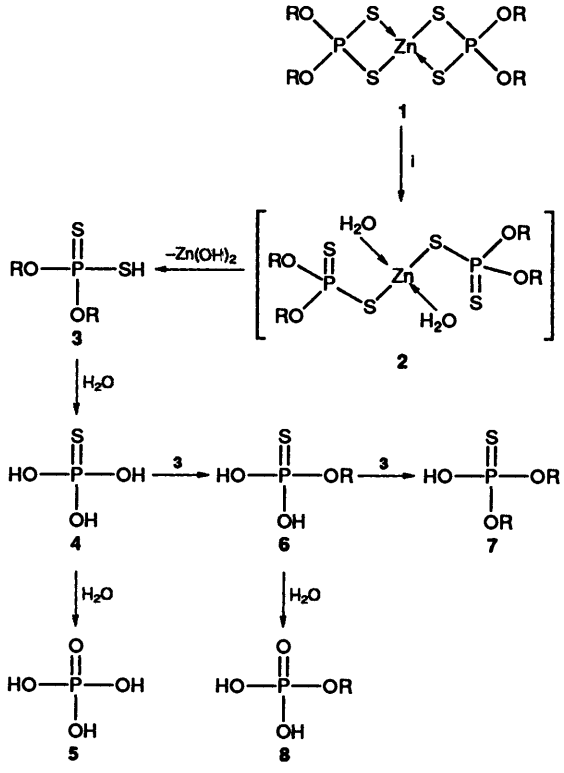
^{31}P NMR spectroscopy has been used to investigate the heterogeneous-phase hydrolysis of zinc(II) bis(*O,O*-dialkyl dithiophosphates) (ZnDTP), $Zn[S_2P(OR)_2]_2$ **1** where R = 2-propyl **1a**, 2-butyl **1b**, 4-methyl-2-pentyl **1c** and 2-ethylhexyl **1d** in a 1:1 mixture of heptane–*p*-xylene to which a ten-fold excess of water (relative to ZnDTP) was added. In each case, the process leads to end-products identical to those previously found for homogeneous-phase hydrolysis, *viz.* thiophosphoric acid **4**, phosphoric acid **5** and alkyl dihydrogen phosphate **8**. All hydrolyses are found to follow first-order kinetics and the calculated relative rates of hydrolytic breakdown (k_{HET} = 4.16–0.66 × 10^{-5} s^{-1}) show a significant decrease as the size of alkyl group increases. This is attributed to the rate-limiting step for hydrolysis being the diffusion of the ZnDTP across the solvent–water interface.

In previous papers we have described in some detail ^{31}P NMR spectroscopic studies on the mechanism and kinetics of the homogeneous hydrolysis of 'normal' zinc(II) bis(*O,O*-dialkyl dithiophosphates), $Zn[S_2P(OR)_2]_2$, (ZnDTP) **1**[1–3] and their nickel and cadmium analogues.[4] These studies have established that under homogeneous conditions, using 1,2-dimethoxyethane as solvent and an excess of water at 85 °C, dialkyl ZnDTPs are hydrolysed to phosphoric acid **5** *via O,O*-dialkyl dithiophosphoric acid **3** and thiophosphoric acid **4**, as well as the transesterification products **6**, **7** and **8** (Scheme 1). Kinetic analysis of the homogeneous hydrolysis reaction by quantitative ^{31}P NMR spectroscopy has shown that for a range of ZnDTPs (R = ethyl, 2-propyl, 2-butyl, hexyl, 4-methyl-2-pentyl and 2-ethylhexyl), the size and nature (*i.e.* primary or secondary) of the alkyl group has little or no observable effect upon the rate of hydrolysis (k_{HOM} = 2.34–2.96 × 10^{-4} s^{-1}). This null effect of the alkyl groups was attributed to hydrophobic interactions between the hydrocarbon chains in the polar solvent that left the central zinc atom exposed to attack by water irrespective of their size. In this paper we present findings of further kinetic studies into the heterogeneous-phase hydrolysis of a number of ZnDTPs of varying chain length in consideration of the important and well documented[5,6] role of these complexes as anti-oxidant and anti-wear agents in lubricating oils.



Scheme 1 *Reagents and conditions:* i, H_2O (10 equiv.), 85 °C

Results and Discussion

Heterogeneous Hydrolysis of Zinc(II) *Bis*(O,O-*Dialkyl Dithiophosphates*) **1**.—The hydrolytic studies were carried out using freshly prepared zinc dialkyl dithiophosphates and a 1:1 mixture of heptane and *p*-xylene as solvent to which a 10-fold excess of water (relative to the ZnDTP) was added. This mixture was heated to 85 °C and emulsified by vigorous stirring at a constant rate. Aliquots of the reaction mixture were sampled at periodic intervals and their ^{31}P NMR hydrogen decoupled (broad band) spectra monitored for the disappearance of the ZnDTP and the formation of intermediates and products. Identification of these species was made on the basis of peak enhancement techniques by addition of authentic samples and by consideration of the peak multiplicities obtained from ^{31}P NMR hydrogen-coupled spectra in conjunction with results obtained from our previous studies.[1–4] To allow kinetic analysis, an inert internal standard of triphenyl phosphate was used to compare peak intensities and the ^{1}H-decoupled spectra obtained under conditions in which the longitudinal relaxation times (T_1) of the species concerned were taken into account. Our previous work had shown that a pulse delay of 5 s satisfies these requirements.

Hydrolysis was carried out on the following ZnDTP derivatives: 2-propyl, **1a**; 2-butyl, **1b**; 4-methyl-2-pentyl, **1c**; and 2-ethylhexyl, **1d**. Diethyl ZnDTP, used extensively in previous studies, was found to be unsuitable in these circumstances due to its poor solubility in the chosen solvent system. In each case, monitoring of the hydrolysis reaction by ^{31}P NMR spectroscopy gave rise to spectra which showed a gradual decay in the resonance due to the ZnDTP. Somewhat surprisingly these spectra showed little evidence for the formation of any

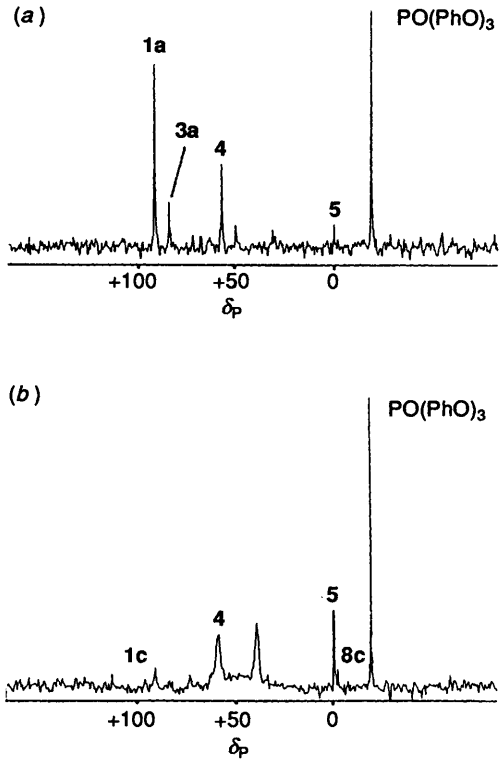


Fig. 1 ^{31}P NMR spectrum of the homogenised hydrolysis products for the heterogeneous hydrolysis of (*a*) 2-propyl ZnDTP **1a**, t = 18 h and (*b*) 4-methyl-2-pentyl ZnDTP **1c**, t = 42 h in 1:1 heptane–*p*-xylene at 85 °C

soluble hydrolysis products. However, the existence of such products was confirmed by homogenising the reaction mixture with a few drops of DME or acetone, the acidic species clearly being insoluble in the heptane–*p*-xylene solvent and associating with the aqueous layer which settled out at the bottom of the sample vessel. Fig. 1(*a*) shows the products observed for the hydrolysis of 2-propyl ZnDTP **1a**, these being identified as *O,O*-bis(2-propyl) dithiophosphoric acid **3a** (δ_P +85), thiophosphoric acid **4** (δ_P +58) and phosphoric acid **5** (δ_P 0). These species were similarly identified as being the products of ZnDTPs **1b–d**. Furthermore, in the case of 4-methyl-2-pentyl ZnDTP **1c** [Fig. 1(*b*)] and 2-ethylhexyl ZnDTP **1d** a resonance at δ_P −2.0 was observed and identified as being due to the respective *O*-alkyl phosphoric acid **8**. In addition to these familiar hydrolysis products, the spectra also showed the appearance of a resonance occurring in the chemical shift range δ_P +40–50. Such resonances had not been encountered previously in homogeneous hydrolyses and could not be associated with any known products of hydrolysis. It was necessary therefore to determine whether this species occurred due to hydrolytic processes, or was a consequence of the non-hydrolytic thermal decomposition of the ZnDTP. It is generally accepted [7] that ZnDTPs are thermally stable up to temperatures of *ca.* 130 °C and given that the hydrolyses were performed at 85 °C it seemed unlikely that thermal decomposition was playing a significant role. However, given the long periods over which the ZnDTPs were subjected to heating during heterogeneous reactions, it seemed prudent to undertake some investigation of this matter. This was accomplished by heating 4-methyl-2-pentyl ZnDTP **1c** (which had shown the greatest tendency to form the unidentified product) in anhydrous heptane–*p*-xylene at 85 °C whilst monitoring the reaction by ^{31}P NMR spectroscopy. No products, soluble or insoluble were observed, even after heating for 72 h, thus confirming that thermal decomposition of the ZnDTP is not responsible for the resonance occurring at δ_P +40–50, and that this product is more likely the result of the hydrolysis process. This chemical shift is characteristic of a (mono)thiophosphate anion [8] and is probably due to a zinc thiophosphate salt, formed in the aqueous layer by the reaction of a thiophosphoric acid and zinc hydroxide.

Table 1 First-order rate constants k_{HET} for the heterogeneous hydrolysis of zinc(II) *O,O*-dialkyl dithiophosphates **1a–d** in 1:1 heptane–*p*-xylene at 85 °C

ZnTDP	$k_{HET}/10^{-5}$ s^{-1}	$k_{HOM}/10^{-4}$ s^{-1} [a]
2-propyl **1a**	4.16	2.57
2-butyl **1b**	2.23	2.96
4-methyl-2-pentyl **1c**	1.61	2.74
2-ethylhexyl **1d**	0.66	2.55

[a] From ref. 3.

Kinetic analysis of the ^{31}P NMR spectroscopic data for the heterogeneous hydrolyses of ZnDTPs **1a–d** (Fig. 2) shows that in each case the reaction obeys a first-order relationship described by the first-order rate eqn. (1), where a_o is the

$$k = \ln [a_o/(a_o - x)]/t \qquad (1)$$

initial concentration of ZnDTP and x the amount consumed after time, t, determined by monitoring the solvent phase. The calculated relative rate constants (k_{HET}) are presented in Table 1 and show that the rate of hydrolysis exhibits a marked decrease as the size of the alkyl group increases, and that their magnitudes are between 6- and 40-fold smaller than those values obtained for homogeneous hydrolysis. We have previously shown[1,3] that under homogeneous conditions the kinetics of ZnDTP hydrolysis can be approximately described as being initially pseudo-first-order, due to water being present in large excess, after which an exponential increase in the rate is observed due to acid catalysis of the reaction by the phosphoric acid products that are formed. This approximation was later amended with a complex two parameter kinetic analysis, which takes into account both the uncatalysed and catalysed contributions to the reaction.[4] In the case of heterogeneous hydrolysis, it is clear that the reaction is genuinely first-order and that there is no evidence of acid catalysis occurring as the reaction proceeds. As water is not available to the ZnDTP in excess under heterogeneous conditions due to its immisibility with the solvent the kinetics of the hydrolyses clearly cannot be described in pseudo-first-order terms. Hydrolysis of the ZnDTP can only occur after it has diffused across the solvent–water interface into the aqueous layer. The diffusion process is driven by osmotic forces and studies [9–11] have shown this to be a unimolecular process which can be described by first-order kinetics. These investigations of such systems involving a liquid–liquid interface have also demonstrated that the rate-limiting factor is the transport of the substrate across the surface between the two phases, whereafter reaction occurs rapidly to give the products. Consequently, for heterogeneous ZnDTP hydrolyses, it is clear that the observed first-order rate constant, k_{HET} is actually a measure of the rate of diffusion of the ZnDTP across the solvent–water interface rather than a direct measurement of the rate of hydrolysis. Hydrolysis of the ZnDTP occurs rapidly in the aqueous phase to give the products. The rate of diffusion is affected by the nature of the substrate which is demonstrated by those ZnDTPs with larger alkyl substituents and therefore a greater efficacy for the solvent phase diffusing at a slower rate relative to those with smaller groups.

In conclusion, these investigations establish that whilst the heterogeneous hydrolysis of the ZnDTPs studied occurs *via* the

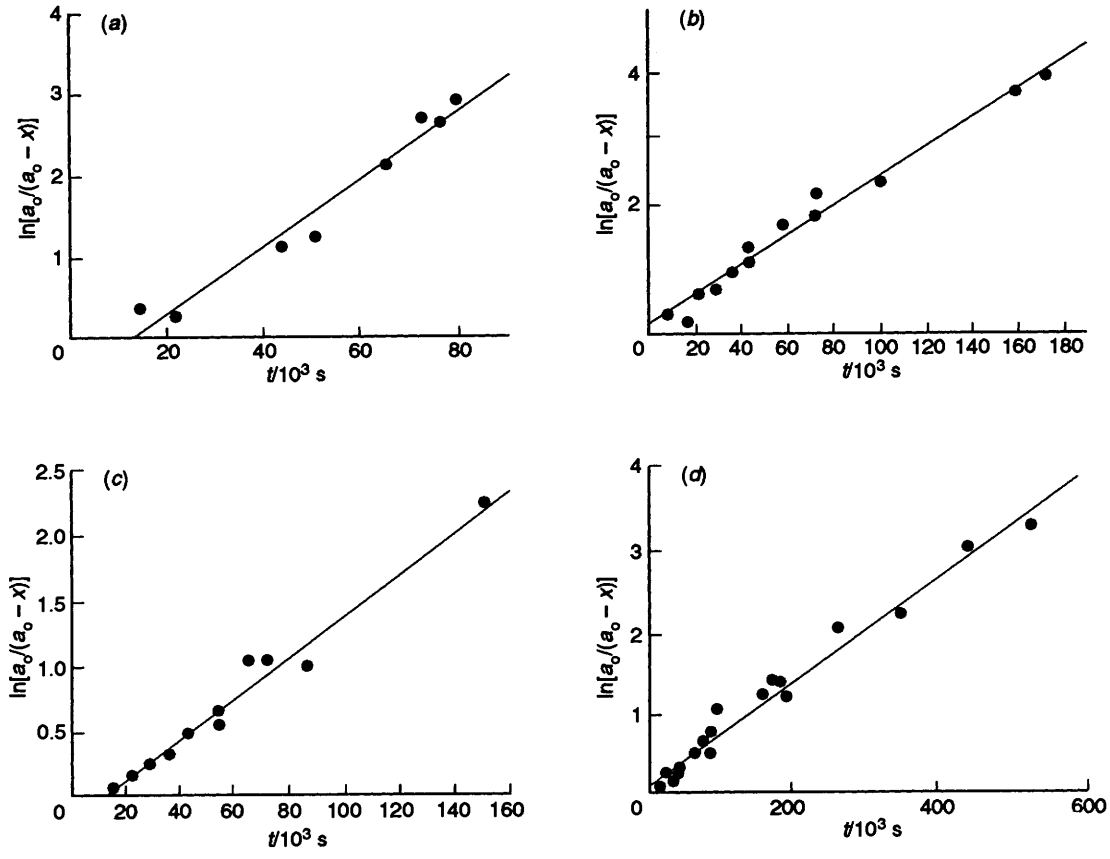


Fig. 2 First-order kinetic plots for the heterogeneous hydrolysis of: (*a*) 2-propyl ZnDTP **1a**; (*b*) 2-butyl ZnDTP **1b**; (*c*) 4-methyl-2-pentyl ZnDTP **1c**; and (*d*) 2-ethylhexyl ZnDTP **1d** in 1 : 1 heptane–*p*-xylene at 85 °C

same mechanism and intermediates to give the same products as the corresponding homogeneous reaction, summarised in Scheme 1, there are some notable differences in the nature of the kinetics of the two reactions: whereas the rate of homogeneous hydrolysis is governed by acid catalysis, with the rate determining step being the attack of water at the zinc atom, heterogeneous hydrolysis is limited by the rate of diffusion of the ZnDTP between the solvent and aqueous phases.

Experimental

^{1}H NMR spectra were obtained on a Bruker WP200SY instrument operating at 28 °C: *J* values given 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 capillary 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°), and a pulse delay of 5 s were used. Accumulation of 100 scans per spectrum gave a signal : noise ratio of > 10 : 1. All solvents were of AnalaR grade, and dried by an appropriate means. Water used in hydrolysis reactions was deionised and distilled.

'Normal' Zinc(II) *Bis*(*O,O-Dialkyl Dithiophosphates*) **1**.[12]—*O,O*-Dialkyl dithiophosphoric acid **3** (0.162 mol) (prepared by the reaction of phosphorus pentasulfide and the corresponding alcohol)[13] in water (400 cm^3) at 60 °C under argon gas was neutralised with a 5 mol dm^{-3} sodium hydroxide solution using phenolphthalein indicator. Zinc sulfate (25.9 g, 0.090 mol) in water (60 cm^3) was added and the solution stirred for 2 h. On cooling, the reaction was extracted with diethyl ether (2 × 100 cm^3) and the dried extract filtered through Kieselguhr. The solvent was evaporated *in vacuo* to give the ZnDTP **1**. 'Normal' zinc(II) bis[*O,O*-bis(2-propyl) dithiophosphate] **1a** (85%), m.p. 144–145 °C (heptane) (lit.,[7] 144.5), δ_P($CDCl_3$) +94.8, (DME) +97.1. 'Normal' zinc(II) bis[*O,O*-bis(2-butyl) dithiophosphate] **1b** (83%), oil, δ_P($CDCl_3$) +87.8, (DME) +97.1, δ_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) and 4.66 (4 H, m, CH). 'Normal' zinc(II) bis[*O,O*-bis(4-methyl-2-pentyl) dithiophosphate] **1c** (93%), oil, δ_P($CDCl_3$) +93.1, (DME) +96.6, δ_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, CH_3), 1.73 (8 H, m, CH_2) and 4.77 (4 H, m, CH). 'Normal' zinc(II) bis[*O,O*-bis(2-ethylhexyl) dithiophosphate **1d** (79%), oil, δ_P($CDCl_3$) +100.6, (DME) +101.4, δ_H($CDCl_3$) 0.87 (12 H, t, ^3J_H 6.5, CH_3), 0.89 (12 H, t, ^3J_H 7.4, CH_3), 1.26 (32 H, m, CH_2), 1.58 (4 H, m, CH) and 3.85 (8 H, m, CH_2).

Heterogeneous Hydrolysis of Zinc(II) *Bis*(O,O-*Dialkyl Dithiophosphate*) **1**.—The ZnDTP (8.75 mmol) and triphenyl phosphate (1.385 g, 4.37 mmol) in 1 : 1 heptane–*p*-xylene were mixed with distilled water (1.575 g, 87.5 mmol). The reaction mixture was heated at 85 °C with vigorous stirring maintained at a constant 750 rpm using a high speed Heidolph magnetic stirrer. Aliquots of the mixture were sampled at appropriate time intervals and the progress of the reaction monitored by ^{31}P NMR spectroscopy.

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