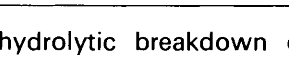
Phosphorus-31 NMR Investigation of the Comparative Hydrolytic Breakdown of Nickel(II) and Cadmium(II) *versus* Zinc(II) Bis(*O,O*-Diethyl Dithiophosphates) in an Aqueous Medium

Alan J. Burn,[a] Sharwan K. Dewan,[b] Ian Gosney,[b] Kenneth G. McKendrick,[b] Chris P. Warrens,[a] John P. Wastle[b] and Cameron W. Watson[b]
[a] *BP International Ltd., Sunbury Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex, UK TW16 7LN*
[b] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

The hydrolytic breakdown of nickel(II) and cadmium(II) bis(*O,O*-diethyl dithiophosphates) **1b** and **c**, respectively in aqueous dimethoxyethane at 85 °C have been studied using ^{31}P NMR spectroscopy. The complexes are hydrolysed at different rates although in each case the process leads to identical end-products, *viz.* phosphoric acid **7**, *O*-ethyl *O,O*-dihydrogen phosphorothioate **8**, *O,O*-diethyl *O*-hydrogen phosphorothioate **9**, and ethyl dihydrogen phosphate **10**. Comparison of the kinetic results obtained with those for the previously studied zinc(II) analogue **1a** show that there is *ca.* one hundred-fold decrease in the rate of hydrolysis for the nickel(II) complex, this being ascribed to the intervention of two hitherto unobserved hydrated species **11** and **12**, both of which are sufficiently stable to be observed by ^{31}P NMR spectroscopy. Similar intermediates are not observed with the cadmium(II) complex **1c** which hydrolyses at a comparable rate to its zinc counterpart. These results are explained in terms of the respective metal–sulfur bond strengths of the dithiophosphate complexes and further support the contention that hydrolysis occurs by attack of water at the metal centre followed by the loss of *O,O*-diethyl *S*-hydrogen phosphorodithioate **3**, the primary hydrolysis product.

Previously, we have described in some detail ^{31}P NMR spectroscopic studies of the kinetics and mechanism of the homogeneous hydrolysis of 'normal' zinc(II) *O,O*-diethyl dithiophosphate, $Zn[PS_2(OEt)_2]_2$ (diethyl ZnDTP) **1a**[1,2] and some other dialkyl ZnDTPs.[3] The role of these and other metal dialkyl dithiophosphates (MDTPs) as anti-oxidant and anti-wear agents in lubricating oils and as anti-oxidants in hydrocarbon polymers[4] has been extensively studied.



1 a M = Zn
b M = Ni
c M = Cd

In this paper we report a detailed investigation into the comparative hydrolytic behaviour of the related nickel(II) *O,O*-diethyl dithiophosphate, $Ni[PS_2(OEt)_2]_2$ (diethyl NiDTP) **1b** and cadmium(II) *O,O*-diethyl dithiophosphate, $Cd[PS_2(OEt)_2]_2$ (diethyl CdDTP) **1c**, using ^{31}P NMR spectroscopy as a tool for the identification of intermediates and final products. The ethyl derivatives were chosen for these studies for continuity and for their ease of preparation and purification. As before, we employed 1,2-dimethoxyethane (DME) as the reaction medium because of its miscibility with water and its boiling point (85 °C) which allows a homogeneous-phase hydrolysis of the MDTPs to be studied over a reasonable time-scale.

Results and Discussion

The hydrolysis of the metal dialkyl dithiophosphates $M[PS_2(OEt)_2]_2$ was carried out using freshly prepared samples and distilled water in a 1 : 10 molar ratio in DME heated at 85 °C. The ^{31}P NMR hydrogen-decoupled spectra were monitored for the disappearance of the MDTP until completion of hydrolysis as well as for 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.[1–3]

Hydrolysis of Nickel(II) O,O-*Diethyl Dithiophosphate* **1b**.— The ^{31}P NMR hydrogen-decoupled spectra for the hydrolysis of diethyl NiDTP **1b** are shown in Fig. 1 and indicate that there are a number of significant differences between this process and the hydrolysis of ZnDTPs previously investigated.[1,3] The most apparent of these differences is the time taken for the hydrolytic consumption of **1b** to occur. In the case of diethyl ZnDTP **1a**, hydrolysis is complete within 90 min at 85 °C in a ten-fold excess of water, whereas the disappearance of **1b** is *ca.* 100 times slower, requiring something in the order of six days under the same conditions. This striking divergence in hydrolytic stability cannot be ascribed to an induction period, as was the case for some ZnDTPs previously studied,[3] but may be explained by consideration of the respective M–S bond strengths and bond lengths for the nickel and zinc complexes. Typical single-bond energies for Ni–S and Zn–S are reported[5] to be 344 and 205 kJ mol^{-1}, respectively. Correspondingly, the reported Ni–S bond length[6] of 2.21 Å is considerably shorter than the value of 2.35 Å for the zinc dithiophosphate complex.[7] We have previously argued that hydrolytic attack occurs at the metal with cleavage of the M–S bond and the formation of the corresponding *O,O*-dialkyl *S*-hydrogen dithiophosphate **3** (Scheme 1). It is therefore clear that the increased energy required to cleave the much stronger Ni–S bond inhibits the rate at which the hydrolysis of the nickel complex **1b** occurs *vis-à-vis* its zinc counterpart.

From Fig. 1 it is also evident that there are significant differences in the nature of intermediate species formed in the hydrolytic breakdown of the nickel and zinc complexes. For

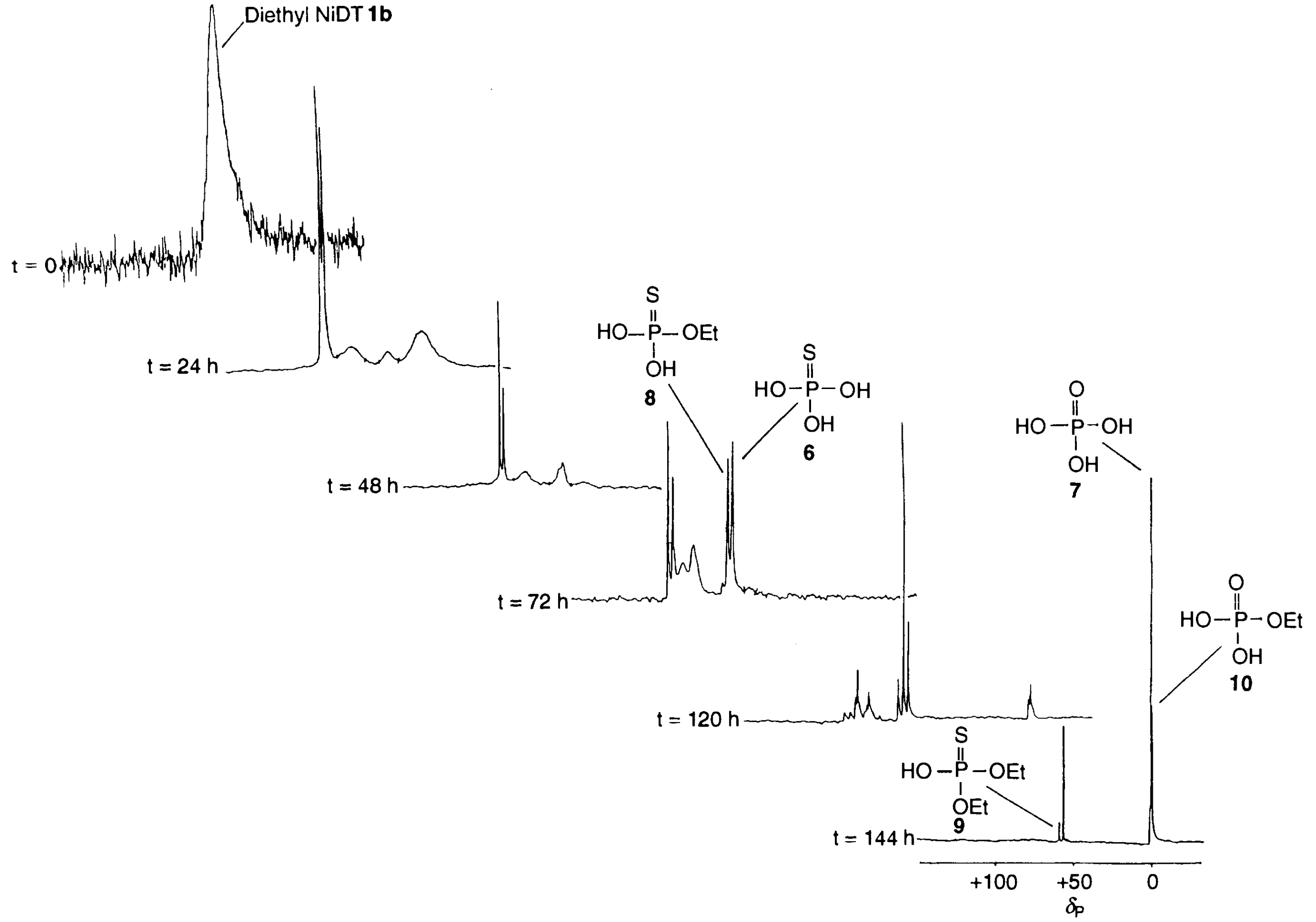
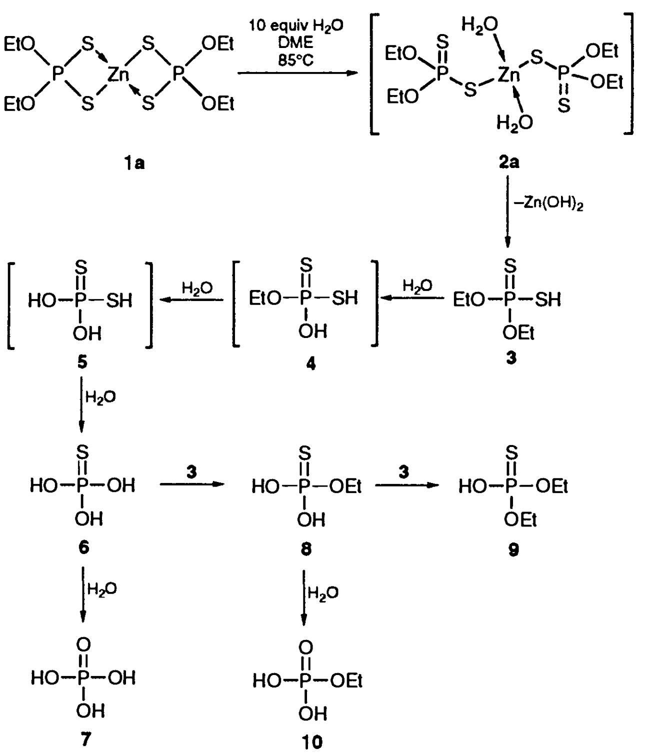


Fig. 1 ^{31}P NMR spectra of the hydrolysis of diethyl NiDTP **1b** at 85 ± 1 °C in DME with 10 equiv. water

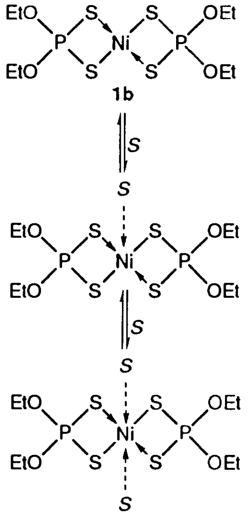
diethyl ZnDTP **1a**, our previous studies established that hydrolysis of the ZnDTP (δ_P +101) to the corresponding phosphorodithioate **3** (δ_P +84.6) is followed by further hydrolysis to phosphorothioic *O,O,O*-acid **6** (δ_P +58.7) *via* the two intermediates *O*-ethyl *O,S*-dihydrogen phosphorodithioate **4** (δ_P +78.1) and phosphorodithioic *O,O,S*-acid **5** (δ_P +71.3). The thiophosphoric acid **6** is then either hydrolysed to phosphoric acid **7** (δ_P 0.0) or undergoes a series of transesterification reactions with **3** to give *O*-ethyl *O,O*-dihydrogen phosphorothioate **8** (δ_P +61.3), its hydrolysis product ethyl dihydrogen phosphate **10** (δ_P −0.3), and *O,O*-diethyl *O*-hydrogen phosphorothioate **9** (δ_P +64.1). In the case of NiDTP **1b** we have shown by a combination of peak enhancement and spin multiplicity techniques that the hydrolysis products with ^{31}P NMR resonances at +64.5, +62.0, +59.7, +1.2 and +0.2 concur with species **9**, **8**, **6**, **7** and **10**, respectively. Accordingly the ultimate hydrolysis products of diethyl NiDTP **1b** are identical to those observed for diethyl ZnDTP **1a**. What is clearly different from the observations made for diethyl ZnDTP **1a** is the nature of the nickel complex in an aqueous environment and the subsequent appearance of the first-formed intermediates in the hydrolysis process. Initially at $t = 0$, the ^{31}P NMR spectrum for diethyl NiDTP exhibits a broad resonance at δ_P +55.7. This does not compare with typically observed sharp resonances at *ca.* +100 ppm for ZnDTPs, nor does it compare with the value of +94 ppm reported for dibutyl NiDTP in cyclohexane.[4] To clarify this anomaly, the ^{31}P NMR spectrum of diethyl NiDTP **1b** was recorded in various anhydrous solvents, the results of which are presented in Table 1. From this data it is clear that in the presence of electron-donating solvents such as DME and CH_3CN a broad resonance at a low chemical shift is observed for the complex **1b** whereas in less polar solvents such as chloroform, benzene and hexane, a sharp resonance occurs at around +90 ppm.

Unfortunately, diethyl NiDTP **1b** is insufficiently soluble in water for its ^{31}P NMR spectrum to be obtained in this solvent. However, it was found that addition of water to anhydrous solutions led to slight broadening and reduction in chemical shift of the diethyl NiDTP **1b**. Previous studies have shown that the latter exists as a four-coordinate diamagnetic (low spin) square-planar complex with a purple colour typical of its oxidation state.[8] Other studies have shown NiDTPs can form green six-coordinate paramagnetic (high spin) complexes with mono- and bi-dentate bases such as amines, *e.g.* $Ni[PS_2(OR)_2]_2$·Bipy,[9,10] as well as five-coordinate paramagnetic complexes with ligands such as 2,9-dimethyl-1,10-phenanthroline[11] and triphenyl phosphine.[12] We ascribe the observed broadening of the NiDTP resonance to complexation by electron-donating solvents such as DME and CH_3CN to the nickel atom, giving rise to a five- or six-coordinate complex which is paramagnetic in nature. However, irrespective of the nature of the solvent used, the solution remains a strong purple colour as verified by the lack of any appreciable change in the UV spectrum of diethyl NiDTP **1b** when recorded in both chloroform[7] and DME (Table 2).

On the basis of these results it is evident that **1b** does not exist entirely as a paramagnetic complex in electron-donating solvents, but that an equilibrium exists between the four-coordinate and five- and/or six-coordinate complexes as shown in Scheme 2. This explanation is also compatible with the observed ^{31}P NMR spectra since only small concentrations of paramagnetic species need be present to cause peak broadening.



Scheme 1 Mechanism for the hydrolysis of diethyl ZnDTP **1a** at 85 °C in DME with 10 equiv. water



Scheme 2 Proposed formation of paramagnetic five- and six-coordinate complexes of diethyl NiDTP **1b** in electron-donating solvents (*S*)

Table 1 ^{31}P NMR chemical shift values of diethyl NiDTP **1b** in various solvents

Solvent[a]	ε_r[b]	δ_P[c]
DME	7.20	+53.4 (br)
DME–H_2O	—	+55.7 (br)
$CDCl_3$	4.7	+92.9 (sh)
CH_3CN	38.8	+38.6 (br)
Benzene	2.3	+91.0 (sh)
Hexane	1.9	+88.7 (sh)[d]

[a] Anhydrous unless otherwise stated. [b] Relative permittivity. [c] In the absence of a deuteriated solvent, an internal capillary lock was used instead; ^1H-decoupled; sh = sharp, br = broad. [d] *cf.* δ_P +94 for *sec*-butyl analogue.[4]

Table 2 UV-VIS spectral data for diethyl NiDTP **1b** in chloroform and DME

Chloroform band max/cm^{-1} [a]	DME band max/cm^{-1} [a]
43 103 (9 090)	41 152 (8 320)
35 461 (6 460)	35 088 (5 090)
31 205 (2 310)	31 250 (17 800)
26 178 (1 000)	26 178 (826)
19 608 (95)	19 084 (85)
14 925 (75)	14 881 (119)

[a] ε/dm^3 mol^{-1} cm^{-1} in parentheses.

Furthermore, electron-donation by the solvent to the nickel atom is expected to cause an increase in electron density in the dithiophosphate ligand, and is consistent with an increased shielding around the phosphorus nucleus with a corresponding reduction in chemical shift as observed.

Further to these observations, hydrolysis of diethyl NiDTP **1b** in the initial stages gives rise to a number of intermediate species the like of which we had not previously encountered during our studies with ZnDTPs. After 24 h, four resonances are apparent, at +92.5 (sharp), +91.1 (sharp), +78.4 (broad) and +61.8 ppm (broad). The latter of these is probably due to unresolved resonances of the hydrolysis products, *i.e.* **6** and **8**, which occur in that region of the spectrum. The two sharp peaks at +92.5 and 91.1 ppm have the characteristic chemical shifts of the dithiophosphate group. Furthermore, if these species are associated with the metal atom, the implication is that they do so in the form of a diamagnetic complex. In order to assist in the identification of these species, peak enhancement studies were carried out, and the resulting spectra are shown in Fig. 2. Thus, when a fresh sample of NiDTP **1b** was added to the hydrolysis mixture, the resulting spectrum [Fig. 2(*b*)] showed an increase in the intensity of the peaks at +90.4 and +88.4 ppm relative to the other peaks in the spectrum, and the concomitant appearance of a broad resonance centred around +45 ppm due to the parent species. In another experiment, addition of a freshly distilled sample of the *O,O*-diethyl phosphorodithioate **3** to the reaction [Fig. 2(*c*)] produced no increase in intensity of either of the said two peaks, but instead led to their virtual eradication, and the simultaneous formation of peaks due to the hydrolysis products **6** and **8**, presumably by acid-catalysis.

The outcome of these peak enhancement studies is that neither of the two peaks at +92.5 and +91.1 ppm can be attributed to the presence of *O,O*-diethyl dithiophosphoric acid **3**. This is not surprising since we have shown previously[1] that under these conditions **3** undergoes very fast hydrolysis, and therefore will not be observed in any appreciable quantities over this time-scale.

What is clear is that the peaks at +92.5 and +91.1 ppm are associated with the nickel complex **1b** and that they readily decompose to the partially hydrolysed products **6** and **8** in the presence of **3**. Furthermore, the ^{31}P NMR hydrogen-coupled spectrum showed a quintet for each of these signals ($^3J_{PH}$ = *ca.* 10 Hz), which together with the value of their chemical shifts, established that both resonances are due to diethyl dithiophosphate species. On the basis of this evidence we propose that these resonances are due to the incursion in the initial stages of hydrolysis of hitherto unobserved hydrated NiDTP species **11** and **12** (Scheme 3) both of which are relatively stable to further hydrolysis, and consequently can be observed by ^{31}P NMR spectroscopy. Further evidence to support this concept of initial complexation is based upon molar extinction coefficient studies[13] which have shown that the diethyl NiDTP

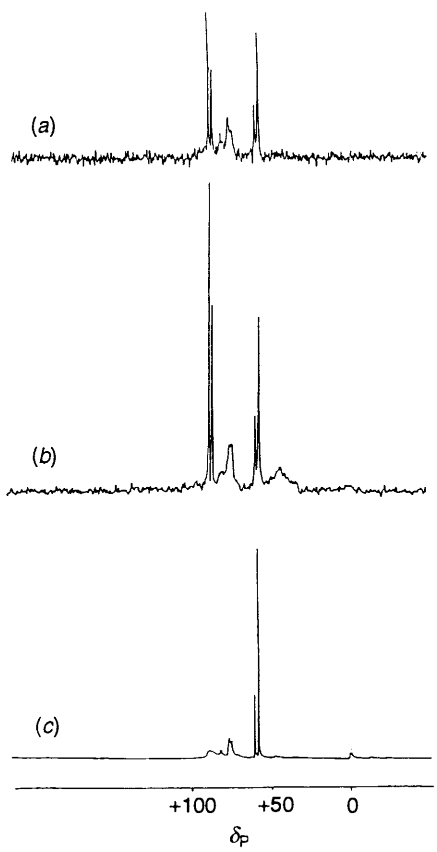
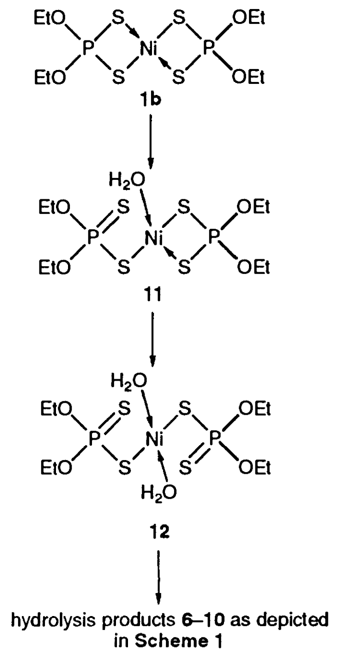


Fig. 2 ^{31}P NMR H-decoupled spectra of the hydrolysis of NiDTP **1b** in DME at 85 ± 1 °C with 10 equiv. water; (*a*) after 24 h; (*b*) peak enhancement with addition of **1b**; (*c*) peak enhancement with addition of diethyl phosphorodithioate **3**



Scheme 3 Mechanism for the hydrolysis of diethyl NiDTP **1b** in DME at 85 ± 1 °C

1b readily complexes with water. For example, addition of 20 volume % of water to an ethanolic solution of NiDTP decreases the apparent molar extinction coefficient to approximately one fifth of the original value without changing the position of the band maxima. After complete hydrolysis the maxima correspond to that for $Ni(H_2O)_6^{2+}$. Further, for the completely decomposed solution (above 60% water content) it is reported that there is some indication of the possible existence of high-spin $NiDTP{\cdot}(H_2O)_2$ or $NiDTP{\cdot}(H_2O)_4^{2+}$ in that the observed extinction coefficients are slightly higher than those of the ordinary aquo ion.

Hydrolysis of Cadmium(II) O,O-*Diethyl Dithiophosphate*.—Analysis of the hydrolytic instability of cadmium(II) *O*,*O*-diethyl dithiophosphate (CdDTP) **1c** at 85 °C in DME with 10 equiv. of water by ^{31}P hydrogen-decoupled NMR spectroscopy (Fig. 3) shows that the process occurs by the same mechanism observed for the hydrolysis of its zinc analogue **1a** with the formation of *O*,*O*-diethyl *O*-hydrogen phosphorothioate **9** (δ_P = +63.5), *O*-ethyl *O*,*O*-dihydrogen phosphorothioate **8** (δ_P +61.6), phosphorothioic *O*,*O*,*O*-acid **6** (δ_P +58.6), phosphoric acid **7** (δ_P +1.2) and ethyl dihydrogen phosphate **10** (δ_P +0.2) preceded by the intermediacy of *O*,*O*-diethyl *S*-hydrogen dithiophosphate **3** (δ_P +98.3). However, it did occur more slowly, taking 315 min for complete hydrolysis compared to 90 min for diethyl ZnDTP **1a** under identical conditions. The spectra verified that this difference arose by intervention of an induction period (*ca.* 210 min) before hydrolysis of **1c** commenced. This pattern of behaviour is akin to that observed previously with certain 'normal' ZnDTPs owing to contamination by trace amounts of the corresponding 'basic' form. In essence, the latter undergoes dissociation in solution to produce zinc(II) oxide which then reacts with the primary hydrolysis product phosphorodithioate **3** to reform the 'normal' salt, and thus inhibit hydrolysis. Apparently, in the case of the cadmium complex **1c** a similar phenomenon is occurring as expressed by the 'basic' $\rightleftharpoons$ 'normal' equilibrium (Scheme 4).

$$Cd_4[S_2P(OEt)_2]_6O \rightleftharpoons \underset{\mathbf{1c}}{3Cd[S_2P(OEt)_2]_2} + CdO$$

Scheme 4

As in the case of ZnDTP hydrolyses,[1–3] it is immediately apparent from attempts to plot the data in the standard pseudo-first order format that the kinetics are not particularly well described by such a simple model. The absolute rate of reaction initially increases with time (before declining as the reaction approaches completion), even for systems free from an induction period, with a corresponding monotonic increase in the effective first order rate constant. It has been concluded previously[1] that this effect results from acid auto-catalysis of the rate-determining hydrolysis step by the acidic products of the reaction.

We have therefore analysed the current data according to a two-parameter kinetic model, described in the Appendix, which takes explicit account of the auto-catalysis. Results for several ZnDTPs, previously treated by the less exact pseudo-first order approach,[1,3] have also been re-analysed for comparison. The effective first-order rate constant, k_{eff}, is assumed to be linearly proportional to the extent of the reaction, x, [eqn. (1)] and in

$$k_{eff} = k_0 + k_1x \qquad (1)$$

turn proportional to the H^+ concentration generated in the reaction. The parameters k_0 and k_1 are obtained from non-linear least squares fits to the observed variation of MDTP with time.

The 'uncatalysed' rate constant, k_0, is a relatively poorly determined quantity, particularly for those reactions which exhibit an induction period. There is naturally a severe correlation between the assumed length of the induction period and the resultant fitted value of k_0. In any case, k_0 does not really refer to an uncatalysed reaction but more correctly to the

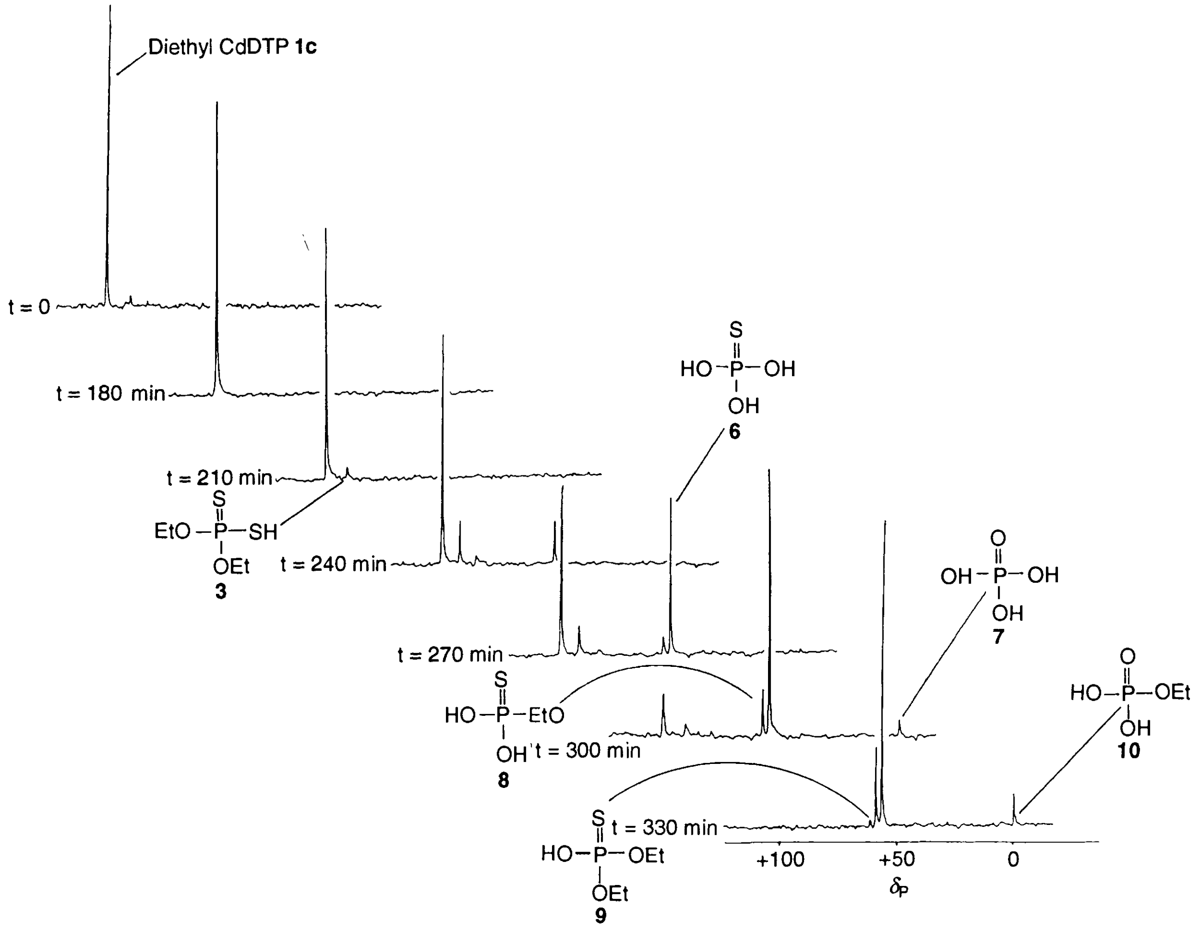


Fig. 3 ^{31}P NMR spectra of the hydrolysis of diethyl CdDTP **1c** in DME with 10 equiv. water at 85 ± 1 °C

Table 3 Best-fit kinetic parameters for the hydrolysis of MDTPs at 85 °C in DME with 10 mol equiv. of water

M	R	$10^{-3}\ t_0{}^a$/s	$10^5\ k_0$/s^{-1}	$10^3\ k_1$/dm^3 mol^{-1} s^{-1}
Cd	Ethyl	10.8	2.4	2.3
		12.0	5.4	2.0
		12.5	8.6	1.8
Zn	Ethyl	0.0	11.9	1.3
Zn	2-Prop-2-yl	0.0	9.4	2.0
Zn	But-2-yl	0.0	19.1	3.9

[a] Assumed induction period.

combination of any truly uncatalysed hydrolysis and the acid-catalysed rate at the initial pH of the system. In contrast, the 'catalytic' coefficient, k_1, is much less sensitive to the effect of any induction period, and is the quantity which can most sensibly be compared between different metal dialkyl DTPs for a fixed (excess) concentration of water. Consideration of the absolute values of k_0 and k_1 reveals that typically the auto-catalysed contribution to the rate exceeds the 'uncatalysed' component after only *ca.* 30% of the initial concentration of metal DTP has reacted. In some cases this fraction is considerably smaller.

Results for diethyl CdDTP **1c** and those ZnDTPs which are relatively free from an induction period are collected in Table 3. The quality of the fit to the diethyl CdDTP data, and its dependence on the assumed induction period, are illustrated in Fig. 4(*a*). The corresponding plot for diethyl ZnDTP **1a**, which is not subject to an induction period, is shown for comparison in Fig. 4(*b*). This slightly more sophisticated analysis does not affect the basic conclusion that the rates of the auto-catalysed hydrolyses of both diethyl CdDTP **1c** and diethyl ZnDTP **1a** are comparable (within a factor of *ca.* 1.5). The rates for the series of ZnDTPs also lie within a factor of *ca.* 3, confirming the previous conclusion that the identity of the alkyl substituent does not critically affect the rate-determining step. The diethyl NiDTP hydrolysis reaction was not amenable to an equivalent quantitative analysis due to the broad nature of the NiDTP resonance and the presence of other overlapping signals preventing accurate data being obtained from the ^{31}P NMR spectra, but it is nevertheless clear that the rates are some two orders of magnitude slower under equivalent conditions for the reasons discussed previously. This lack of influence by the central metal atom (Cd *vs.* Zn) on the rate of hydrolysis can be rationalised on the basis of our earlier findings that attack by water followed by rapid cleavage of the M–S bond (for ZnDTPs) is the rate-determining step in the overall process. Given that the single-bond energies for Cd–S (208.5 kJ mol^{-1}) and Zn–S (205 kJ mol^{-1}) are very similar, it is not surprising that the hydrolyses of the corresponding dithiophosphate complexes proceed at comparable rates.

Finally, the precipitates formed during hydrolysis were analysed to determine the composition of the metal-containing residues. Previously, analysis of the precipitate formed during the hydrolysis of diethyl ZnDTP **1a** had shown that the zinc(II) hydroxide formed by the initial hydrolysis of the ZnDTP reacted further with hydrogen sulfide and the various phosphoric acid derivatives present to give a mixture of zinc hydroxide, zinc oxide, zinc sulfide and zinc phosphates.[1] The results of this analysis, along with those for diethyl NiDTP **1b** and diethyl CdDTP **1c** are displayed in Table 4. From these

Table 4 Elemental analysis of precipitates from the hydrolysis of metal dithiophosphates **1a–c**

	ZnDTP **1a**[a]		NiDTP **1b**		CdDTP **1c**	
Element	% Weight	Elemental ratio	% Weight	Elemental ratio	% Weight	Elemental ratio
M	41.0	1	29.4	1	64.0	1
P	16.9	0.87	14.5	0.93	3.6	0.20
S	7.6	0.38	8.3	0.52	19.0	1.04
C	1.3	0.18	2.9	0.48	1.7	0.25
H	1.5	2.38	2.1	4.19	0.4	0.70
O	31.7	3.18	39.0	4.86	6.3	0.69

[a] From ref. 1.

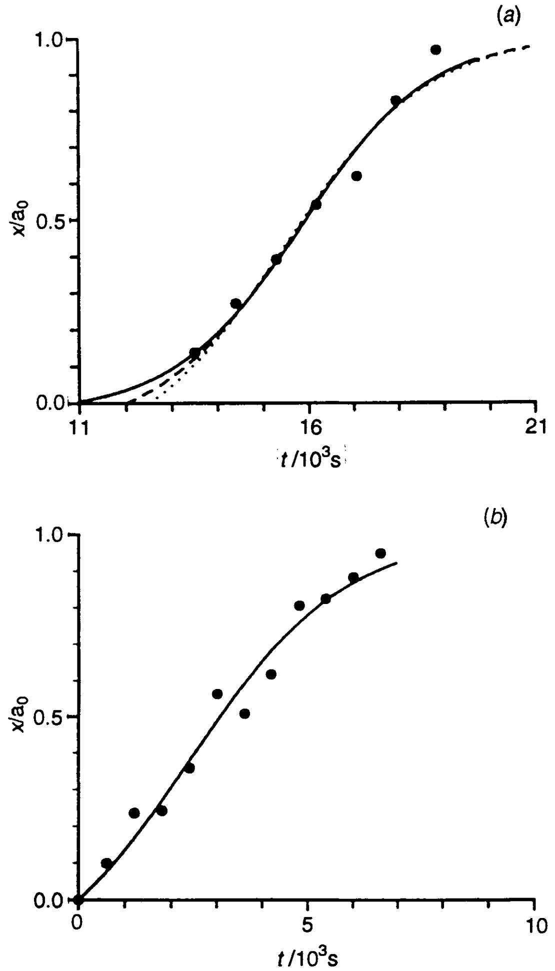


Fig. 4 Observed variation in MDTP concentration and best-fit curves derived from the kinetic model described in the text. (*a*) Diethyl CdDTP: assumed induction period of 10 800 s (———); 12 000 s (– – – –); 12 500 s (· · · ·). (*b*) Diethyl ZnDTP: no assumed induction period.

figures, it is clear that the precipitate formed by the hydrolysis of the NiDTP **1b** is similar in constitution to that of the ZnDTP **1a**. Treatment of the precipitate with dilute hydrochloric acid resulted in the evolution of hydrogen sulfide, confirming the presence of nickel sulfide in the precipitate. The ^{31}P NMR spectrum of a solution of the precipitate in sodium hydroxide (2 mol dm^{-3}) showed signals at +4.98 and −5.25 ppm which were identified as being due to sodium phosphate and sodium pyrophosphate, respectively by using peak enhancement methods with authentic samples.

Analysis of the hydrolysis precipitate from diethyl CdDTP **1c** showed it to be of markedly different composition to both the zinc and nickel precipitates. It is clear that the precipitate consists principally of cadmium and sulfur, with only a small proportion of phosphates present. Treatment of this precipitate with dilute hydrochloric acid results in copious evolution of hydrogen sulfide, indicating that cadmium sulfide was indeed the major constituent. Cadmium accounted for 64% of the precipitate's weight, and it is significant that CdS contains 63% cadmium by weight. The ^{31}P NMR spectrum of a solution of the precipitate in sodium hydroxide (2 mol dm^{-3}) showed only very small quantities of sodium phosphate and sodium pyrophosphate to be present, as indicated by the analysis results.

In conclusion, it is evident from the sequence of formation of the observed products and their nature that the hydrolysis of diethyl NiDTP **1b** proceeds by the same type of mechanism as that described previously for the corresponding zinc analogues[1,3] apart from its inception. Initially, the NiDTP **1b** exists in equilibrium with a six-coordinate paramagnetic solvated complex; thereafter the reaction pathway gives rise to two hydrated NiDTP species **11** and **12** whose formation is apparently facilitated by the much stronger Ni–S bond resisting further hydrolysis to *O*,*O*-diethyl dithiophosphate **3** and other subsequent hydrolysis products. In consequence, a slower rate of hydrolysis is observed compared to its zinc analogue. Similarly, for diethyl CdDTP **1c** the identity of the intermediates and end-products indicates that the mechanism of hydrolysis is the same as that for ZnDTPs. Furthermore it has been established that while the initiation of hydrolysis is inhibited by an induction period, its rate is almost the same as that previously measured for the corresponding ZnDTP.[1] This is a consequence of the similarity in energy of the respective M–S bonds, which being considerably less than that of their nickel counterpart, are more rapidly cleaved thereby reinforcing our claim that the initial and rate-determining step for hydrolysis in the zinc and cadmium complexes is attack of water at the metal centre.

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. All ^{31}P NMR spectra were recorded on a JEOL FX90Q spectrometer operating at 27 °C or at 50 °C for CdDTP samples due to low solubility with either a deuteriated solvent or an internal coaxial C_6D_6 lock. ^{31}P chemical shifts are quoted with reference to 85% phosphoric acid with shifts to high frequency being positive. The spectral window for kinetic measurements was 5200 Hz and a pulse width of 4 µs (20°) was used with acquisition time of 0.787 s and a pulse delay of 5 s; accumulations of 100 scans per spectrum gave a typical signal: noise ratio of $\geqslant 10:1$. UV and visible spectra were measured with a Unicam SP800A spectrophotometer. All solvents used were of AnalaR grade, and dried by an appropriate means. Water used in the hydrolysis was de-ionised and distilled.

Potassium O,O-*Diethyl Dithiophosphate*.—Prepared by the neutralisation of the corresponding *O,O*-diethyldithiophosphoric acid (prepared from the reaction [14] of ethanol with P_2S_5) 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 extracted with hot acetone and filtered to remove inorganic solids. On evaporation of the acetone, the potassium salt was obtained, m.p. 191–195 °C (acetone–ether) (lit.,[15] 194–195 °C); $\delta_P(D_2O)$ +110.6 (lit.,[16] +110.5).

'Normal' Metal(II) O,O-*Diethyl Dithiophosphates* **1**.—Prepared by the reaction of potassium *O,O*-diethyldithiophosphate with metal(II) sulfate in a 2:1 molar ratio in aqueous solution. Extraction with ether followed by evaporation *in vacuo* gave the MDTP.

'Normal' nickel(II) O,O-*diethyl dithiophosphate* **1b**. M.p. 105–106 °C (lit.,[17] 105 °C); $\delta_P(CDCl_3)$ +92.9; δ_P(DME) +53 (br).

'Normal' cadmium(II) O,O-*diethyl dithiophosphate* **1c**. (79%), m.p. 144–145 °C (lit.,[18] 144 °C); $\delta_P(CDCl_3)$ +107.7; δ_P(DME) +106.6.

Hydrolysis of 'Normal' Metal(II) O,O-*Diethyl Dithiophosphate* **1**.—A solution of the MDTP (0.35 mmol) and distilled water (0.630 g; 35.0 mmol) in DME (10.0 cm^3) was transferred to a series of 5 mm NMR tubes which were sealed and heated in a water bath at 85 ± 0.2 °C. At periodic time intervals, a sample was removed, quenched in ice and the progress of the reaction monitored by ^{31}P NMR spectroscopy. Triphenyl phosphate was used as an inert internal standard and the ^1H-decoupled spectra were obtained under conditions in which the T_1 values of the various species were taken into account (see ref. 1).

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Appendix

The rate-determining step of the reaction is assumed to be hydrolysis of the MDTP, initially present at a concentration, a_0. This process is autocatalysed by H^+ produced in the reaction. The pseudo-first-order rate constant is therefore assumed to obey the relationship (A1), where x is the

$$k_{\text{eff}} = k_0 + k_1 x \qquad \text{(A1)}$$

concentration of MDTP which has reacted. The water is considered to be in sufficient excess to remain at a constant concentration throughout the course of reaction. The differential equation for x is therefore (A2), which may be

$$\frac{dx}{dt} = k_0(a_0 - x) + k_1 x(a_0 - x) \qquad \text{(A2)}$$

integrated[19] to yield the solution (A3). The parameters α and

$$x/a_0 = \{\exp(\beta t) - 1\}/\{\exp(\beta t) + \alpha\} \qquad \text{(A3)}$$

β, which are derived from non-linear least squares fits[20] to the observed variation of the MDTP concentration with time, may be inverted to the kinetic parameters through (A4a) and (A4b)

$$k_0 = \beta/(1 + \alpha) \qquad \text{(A4a)}$$

$$k_1 = \alpha\beta/[a_0(1 + \alpha)] \qquad \text{(A4b)}$$

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