The Acid-catalysed Hydrolysis of *O*-Methyl Dimethylthiophosphinate. Direct Evidence for Pentaco-ordinate Intermediate Formation in the Conversion of the P=S Ester into the P=O Ester

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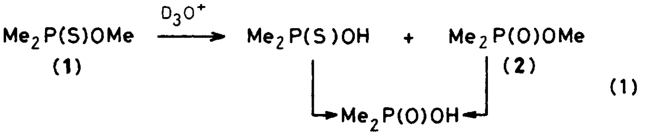
Hydrolysis of the title compound in strong acid leads not only to the phosphinic acid but also to methyl dimethylphosphinate which could only be formed by the intermediacy of a pentaco-ordinate species.

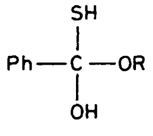
The hydrolysis of the title compound, (**1**), has been studied over the concentration range 25—85% D_2SO_4 at 75 °C. The reactions were followed by n.m.r. spectroscopy in a manner similar to that which has already been reported.[1] The most striking feature of this reaction is that (**1**) undergoes both loss of methanol and exchange of sulphur (equation 1).

Similar observations have been reported for the hydrolysis of thiobenzoates[2,3] and thiobenzoic acids.[4] Over a wide range of acid concentrations, the thiobenzoates hydrolyse by an $A_{ac}2$ mechanism with competitive loss of H_2S or alcohol from the tetrahedral intermediate (**3**).[2,3] The analysis of the kinetic data for the hydrolysis of (**1**) strongly supports the formation of a pentaco-ordinate intermediate of a type common to both processes.

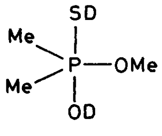


$$\begin{tikzcd} \underset{(1)}{\mathrm{Me_2P(S)OMe}} \arrow[r, "\mathrm{D_3O^+}"] & \mathrm{Me_2P(S)OH} \arrow[dr] & + & \underset{(2)}{\mathrm{Me_2P(O)OMe}} \arrow[dl] \\ & & \mathrm{Me_2P(O)OH} & \end{tikzcd} \qquad (1)$$

The pH–rate profiles for the hydrolysis reactions of (**1**) are shown in Figure 1. The bell-shaped parts of the curves are typical for $A2$ processes. In the lower part of the acidity range, the loss of methanol is faster than the exchange of sulphur which is contrary to that which is observed in thiobenzoates.[2,3] In (**1**), exchange of sulphur only becomes significant above 50% D_2SO_4 and reaches a maximum in the bell part of the curve at 70% acid; the rate then passes through a minimum of 75% acid after which it increases quickly such that at 95%



(**3**)



(**4**)

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D_2SO_4 and 75 °C complete conversion of (**1**) into (**2**) takes only a few minutes. Because of this fast exchange no hydrolysis of (**1**) is observed at these acidities. The product of the exchange reaction, (**2**), undergoes hydrolysis very slowly above 85% D_2SO_4.[1]

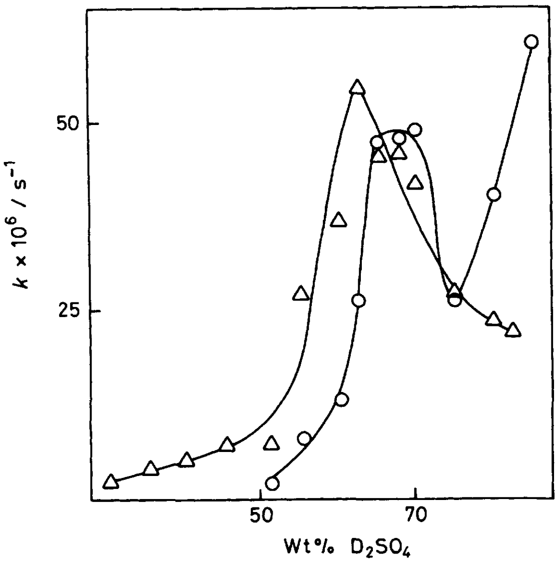

Figure 1. The rate profiles for *O*-methyl dimethylthiophosphinate hydrolysis (Δ) and desulphurisation (○) reactions in D_2SO_4 at 75 °C.

Table 1. Data obtained from the acid hydrolysis of (**1**) and (**2**).[a]

Compound	pK_a	A	B	C	D
(**1**)	−5.53	3.31	−0.21	0.82	6.56
(**2**)	−3.14	2.28	0.94	0.91	0.61

[a] Analysis of rate data was by the following methods: A and B, Bunnett equation (w and w*; ref. 5); C, Bunnett–Olsen equation (ref. 6); D, Yates–McClelland equation (ref. 7) using a modified Hammett acidity function ($H_x = mH_o$), where m = 0.49 for (**1**) and 1.73 for (**2**).

As well as the pH–rate profiles additional evidence for an *A*2 mechanism comes from the results of the analysis of the rate data using the Bunnett,[5] Bunnett–Olsen,[6] and Yates–McClelland[7] equations (Table 1).

The concomitant loss of the sulphur and methanol in an *A*2 process can best be explained by the formation of a pentacoordinate intermediate like (**4**). We believe this to be the strongest evidence yet reported for the formation of intermediates during the reactions of nucleophiles with phosphinic acid derivatives.

The high acidity catalysis of the sulphur exchange reaction will be commented on elsewhere.

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References

1 K. A. Abbas and R. D. Cook, *Can. J. Chem.*, 1977, **55**, 3740.
2 S. Smith and M. O'Leary, *J. Org. Chem.*, 1963, **28**, 2825.
3 J. T. Edward and S. C. Wong, *J. Am. Chem. Soc.*, 1977, **99**, 7224; J. T. Edward, S. C. Wong, and G. Welch, *Can. J. Chem.*, 1978, **56**, 931.
4 J. T. Edward, G. Welch, and S. C. Wong, *Can. J. Chem.*, 1978, **56**, 935.
5 J. F. Bunnett, *J. Am. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978.
6 J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, 1966, **44**, 1899, 1917.
7 K. Yates and R. A. McClelland, *J. Am. Chem. Soc.*, 1967, **89**, 2686.