

Preliminary communication

ANALOGIES BETWEEN THE DYNAMIC STEREOCHEMISTRY AT SILICON AND PHOSPHORUS. KINETIC EVIDENCE OF NUCLEOPHILIC SOLVENT PARTICIPATION IN THE HYDROLYSIS OF MENTHYLCHLORO(PHENYL)PHOSPHONATE

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Summary

Kinetic evidence for nucleophilic participation of external nucleophiles in the hydrolysis of menthylchloro(phenyl)phosphonate is presented. The results, which are similar to those for silicon compounds, are consistent with a mechanism involving extension of coordination at the central atom.

Recently, we reported kinetic and stereochemical evidence for nucleophilic assistance in the hydrolysis of chlorosilanes [1–3]. Furthermore, we have shown the very close behaviour of chlorophosphonates and chlorosilanes in the racemization scheme, catalysed by nucleophilic agents [4, 5]. It thus appears of interest to study the possibility of nucleophilic participation of external nucleophiles, viz. dimethylformamide (DMF) and dimethylacetamide (DMA), in the hydrolysis of menthylchloro(phenyl)phosphonate (I).

Phosphorylation of alcohols catalysed by nucleophilic agents in aprotic solvents has been extensively studied [6, 7]. Mikolajczyk reported the catalytic effect of DMF in reactions of chlorophosphonothioate with water or amines [8].

Preliminary experiments showed that the chlorophosphonate ($\approx 10^{-2}$ M) did not react with low contents of water (10^{-3} – 10^{-1} M) in aprotic solvents but addition of ten equivalents of DMF caused direct formation of phosphonic acid. We then carried out kinetic studies of the hydrolysis of I in carbon tetrachloride (CCl_4), catalysed by the nucleophilic agents DMF and DMA. Starting material and the product menthylphenylphosphonic acid are normally the only compounds detected by ^{31}P NMR spectroscopy*. Polarimetry and NMR we used to measure the rates of reactions, and the results are shown in Table 1,

*In some experiments at lower concentrations of I (5×10^{-2} M), water ($\approx 10^{-3}$ M), and nucleophilic agent (5% v/v.), pyrophosphonate was also observed by ^{31}P NMR spectroscopy (yield < 30%).

TABLE 1

ACTIVATION PARAMETERS FOR HYDROLYSIS OF MENTHYLCHLORO(PHENYL)PHOSPHONATE

	$k_t^{25^\circ\text{C}}$ ($\text{mol}^{-2} \text{l}^{-2} \text{s}^{-1}$)	E_a (kcal mol^{-1})	ΔH^\ddagger (kcal mol^{-1})	ΔG^\ddagger (kcal mol^{-1})	ΔS^\ddagger ($\text{kcal}^{-1} \text{mol}^{-1}$)
DMF	2.6×10^{-3}	7.3	6.7	21	-47.7
DMA	1.6×10^{-3}	5.0	4.4	21	-56.0

ACTIVATION PARAMETERS FOR EPIMERISATION OF MENTHYLCHLORO(PHENYL)PHOSPHONATE

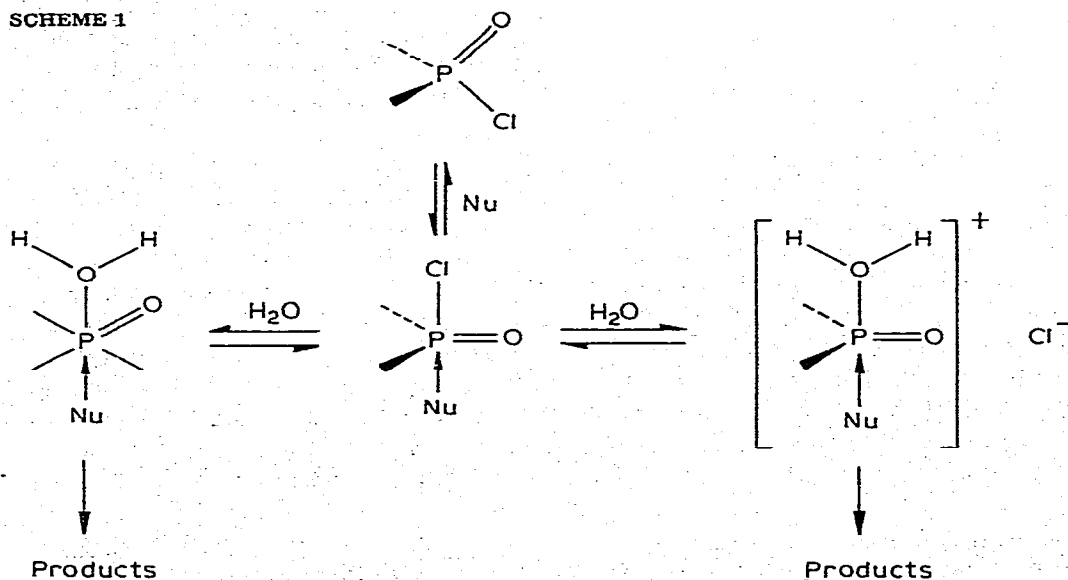
DMF	4.5×10^{-5}	10.4	9.8	23.3	-45
DMA	1.8×10^{-5}	6.5	5.9	23.8	-60

which also includes data for epimerisation. The reaction is first order in each of the chlorophosphonate, water and nucleophile. ^{31}P NMR showed that the chlorophosphonate was not epimerised during hydrolysis, consistent with the fact that hydrolysis is 80–100 times faster than epimerisation in CCl_4 .

As for the epimerisation, there is a large negative activation entropy, while the activation enthalpies have comparable values in hydrolysis and epimerisation of I.

Reports of analogous dynamic stereochemistries at silicon and phosphorus can be found in the literature [2, 9–11]. Since we observe the same rate-law for hydrolysis and epimerisation of $\text{P}(\text{O})\text{Cl}$ and $\text{Si}-\text{Cl}$ bonds catalysed by nucleophiles, it seems reasonable to assume similar mechanisms for both reactions. We propose a two-step process (Scheme 1), the first step being the reversible coordination of the nucleophilic agent to phosphorus, followed by rate-determining attack of water (hydrolysis) or nucleophile (epimerisation) on the penta-

SCHEME 1



coordinated phosphorus, giving either a direct displacement of Cl^- or a hexacoordinated intermediate.

However, two results reveal differences between phosphorus and silicon. The activation parameters we have now observed ($\Delta H_p^\ddagger \approx 7$) and ($\Delta S_p^\ddagger = -40-55$ e.u.) are markedly different [12] compared with the very low enthalpy values ($\Delta H_{\text{Si}}^\ddagger \approx 0$) but large entropy ones ($\Delta S_{\text{Si}}^\ddagger \approx -45-60$ e.u.) observed for silicon. Secondly, the mechanism proposed for hydrolysis of chlorosilanes is well supported by changes of the stereochemistry (retention instead inversion). On the other hand, hydrolysis of (—)ethylchloro(ethyl)phosphonothioate which has been studied by Mikolajczyk [8] in water/DMF mixture, is non stereospecific (e.g. only 69% inversion instead of complete inversion in alkaline medium).

Nevertheless, the basic feature of these reactions at silicon and phosphorus is the same, namely, nucleophilic participation in the hydrolysis. Without any assistance, the reaction does not take place in non polar aprotic solvents. Moreover, substitutions are accompanied by marked changes in stereochemistry. Full retention is observed at silicon. With phosphorus, extensive racemization is expected from the reaction process, since the starting chlorophosphonate (I) is not epimerised during the hydrolysis. Kinetic and stereochemical studies of hydrolysis of chlorophosphonothioates catalysed by nucleophiles are being studied.

References

- 1 R.J.P. Corriu, G. Dabosi and M. Martineau, *J. Chem. Soc. Chem. Commun.*, (1977) 649.
- 2 L.H. Sommer, *Stereochemistry, Mechanism and Silicon*, McGraw-Hill, New York, 1965.
- 3 R.H. Prince, *Inorg. Chem.*, **1**, 9 (1972) 353 from *M.T.P. International Review of Sciences*.
- 4 R.J.P. Corriu, G.F. Lanneau and D. LeClerq, *J. Chem. Soc. Chem. Commun.*, (1978) 104.
- 5 R.J.P. Corriu and M. Henner, *J. Organometal. Chem.*, **74** (1974) 1.
- 6 F. Ramirez and J.F. Marecek, *Tetrahedron Lett.*, **42** (1976) 3791; *J. Org. Chem.*, **40** (1975) 2849.
- 7 F. Ramirez, J.C. Marecek and H. Okazaki, *J. Amer. Chem. Soc.*, **98** (1976) 5310.
- 8 M. Mikolajczyk, *Tetrahedron*, **23** (1967) 1543.
- 9 D.B. Cooper, C.R. Hall, J.M. Harrison and T.D. Inch, *J. Chem. Soc. Perkin I*, (1977) 1969 and ref. therein.
- 10 W.S. Wadsworth, Jr., *J. Org. Chem.*, **38** (1973) 2921.
- 11 R. Corriu and C. Guerin, unpublished work.
- 12 R.F. Hudson and L. Keay, *J. Chem. Soc.*, (1960) 1865.