A Duality of Mechanism in the Hydrolysis of Acyclic Phosphoranes

Nicholas Lowther and C. Dennis Hall*

Department of Chemistry, King's College, Strand, London WC2R 2LS, U.K.

Acyclic phosphoranes, $Ar_nP(OR)_{5-n}$ with $n = 0$—3 are shown to hydrolyse in neutral conditions by an S_N1 (P) mechanism for $n = 1, 2$, and 3 but by an S_N2 (P) or addition–elimination mechanism for $n = 0$; this is analogous to the classical S_N1 *vs.* S_N2 mechanisms observed for solvolysis reactions at tetrahedral carbon.

The reaction of three-co-ordinate phosphorus compounds (**1**), $n = 0$—3, with 2,2,2-trifluoroethyl phenylsulphenate (**2**) is now a well established and efficient route to acyclic phosphoranes (**3**) [reaction (1)].[1] The reaction must be carried out in aprotic and preferably non-polar media (*e.g.* toluene) since the phosphoranes, although thermally stable, are sensitive to moisture. The hydrolysis of acyclic phosphoranes [generalised by reaction (2)] has been studied for penta-aryloxyphosphoranes[2,3] and monocyclic tetra-alkoxyphenylphosphoranes[3] and in both cases it was concluded that the reactions proceeded through either an addition–elimination mechanism *via* a six-co-ordinate intermediate or an S_N2 (P) mechanism with the six-co-ordinated species as a transition state. We now report a series of experiments for acyclic phosphoranes (**3**), $n = 0$—3, which reveals a duality of mechanism analogous to that obtained in the classical studies of solvolysis at tetrahedral carbon.[4]

$$\underset{(\mathbf{1})\ n = 0\text{—}3}{Ar_nP(OR)_{3-n}} + \underset{(\mathbf{2})}{2PhSOCH_2CF_3} \rightarrow \underset{(\mathbf{3})}{Ar_nP(OR)_{3-n}(OCH_2CF_3)_2} + Ph_2S_2 \qquad (1)$$

$$Ar_nP(OR)_{5-n} + H_2O \rightarrow Ar_nP(O)(OR)_{3-n} + 2\,ROH \qquad (2)$$

A number of phosphoranes (**3**), $n = 0$—3 and $R = OCH_2CF_3$, were prepared in high yield ($\geqslant 95\%$) in toluene and were characterised by mass spectral, and ^1H, ^{13}C,

Table 1. ^{31}P N.m.r. data (in C_7D_8) at 36.4 MHz for phosphoranes, $Ar_nP(OR)_{5-n}$ and oxides, $Ar_nP(O)(OR)_{3-n}$, p.p.m. *vs.* 85% H_3PO_4.

Phosphorane	$\delta(^{31}P)$	Oxide	$\delta(^{31}P)$	$\Delta\delta(^{31}P)$ (oxide)/Hz
$Ph_3P(OCH_2CF_3)_2$	−59.1	Ph_3PO	+28.1	1.22
$Ph_2P(OCH_2CF_3)_3$	−45.6	$Ph_2P(O)(OCH_2CF_3)$	+33.1	1.46
$PhP(OCH_2CF_3)_4$	−61.0	$PhP(O)(OCH_2CF_3)_2$	+20.6	1.71
$P(OCH_2CF_3)_5$	−77.1	$(CF_3CH_2O)_3PO$	− 2.6	1.29
$(o\text{-}MeOC_6H_4)Ph_2P(OCH_2CF_3)_2$	−54.5	$(o\text{-}MeOC_6H_4)Ph_2PO$	+26.5	—
$PhP(OEt)_2(OCH_2CF_3)_2$	−61.3	$PhP(O)(OEt)_2$	+19.3	—
$o\text{-}MeC_6H_4P(OEt)_2(OCH_2CF_3)_2$	−57.6	[a]	+17.2	—
$(Pr^iO)_3P(OCH_2CF_3)_2$	−79.4	[b]	− 5.0	—

[a] Either $o\text{-}MeOC_6H_4P(O)(OEt)_2$, $o\text{-}MeOC_6H_4P(O)(OCH_2CF_3)_2$, or $o\text{-}MeOC_6H_4P(O)(OEt)(OCH_2CF_3)$. [b] Either $(Pr^iO)_3PO$, $(Pr^iO)_2P(O)(OCH_2CF_3)$, or $(Pr^iO)P(O)(OCH_2CF_3)_2$.

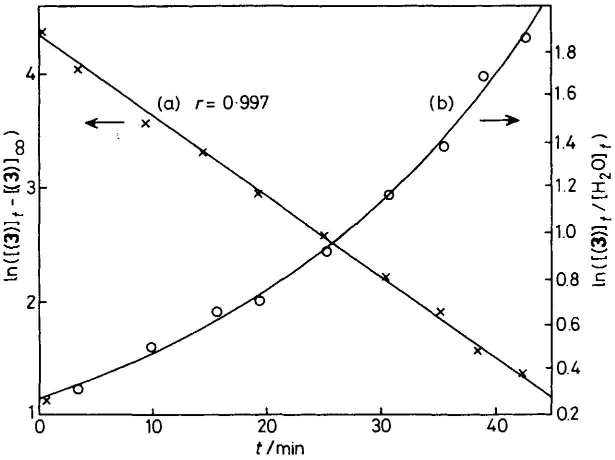
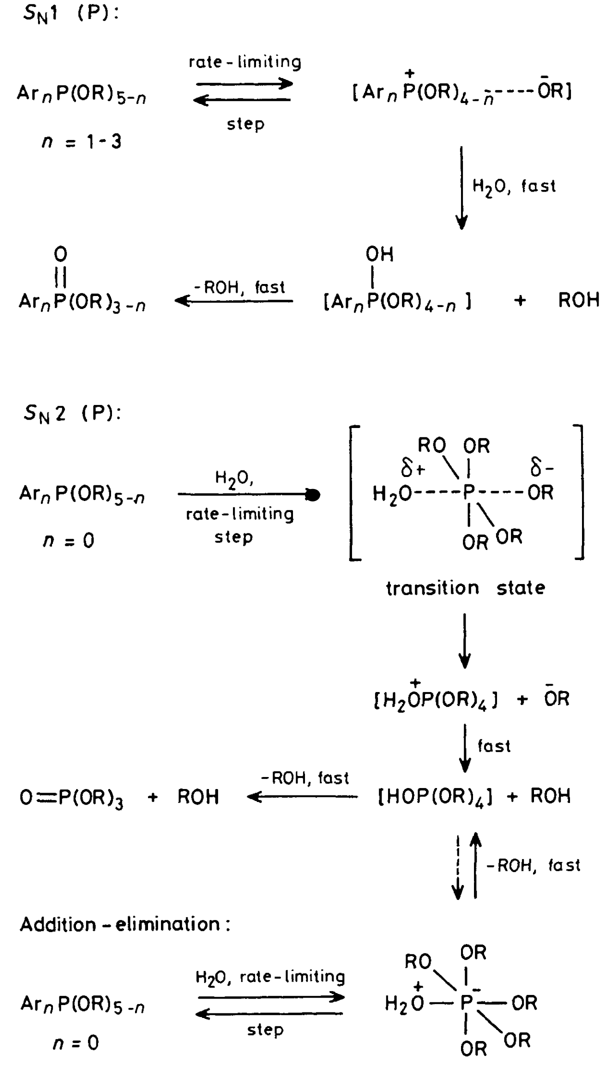


Figure 1. (a) ln $([(3)]_t - [(3)]_\infty)$ *vs.* time and (b) ln $([(3)]_t/[H_2O]_t)$ *vs.* time for the hydrolysis of $PhP(OCH_2CF_3)_4$ in toluene–12% MeCN at 31 °C; $[(3)]_0$ = 0.0788 M; $[H_2O]_0$ = 0.0737 M.

^{19}F, and ^{31}P n.m.r. data, the latter being given in Table 1 (*cf.* ref. 1). Hydrolysis of each of these phosphoranes by addition of a solution of $H_2{}^{18}O$ in acetonitrile (to effect solubilisation of the water) gave the corresponding oxide and alcohol [reaction (2)] as the exclusive products. In each case the ^{18}O was contained in the phosphoryl group as shown by isotope-induced chemical shift differences of *ca.* 1.5 Hz in the ^{31}P n.m.r. spectra of the oxides (Table 1) and no ^{18}O was detected in the product alcohol by g.c.–mass spectroscopy. Thus the products arise from attack of water at phosphorus leading to P–O cleavage rather than O–alkyl cleavage.

Equimolar mixtures of pairs of phosphoranes were then hydrolysed by addition of an amount of water† equivalent to half the total phosphorane concentration in each mixture. The relative amounts of hydrolysis of each phosphorane were then estimated by the ^{31}P n.m.r. signals of (i) the oxides formed and (ii) the residual phosphoranes. The response factors for the phosphoranes were established from the initial mixtures and the response factors for the oxides were determined by a total hydrolysis subsequent to each competitive experiment. The relative rates for hydrolysis are shown in Table 2. In one case (n = 1) the hydrolysis was slow enough to be followed by ^{31}P n.m.r. spectroscopy and the rate of reaction was shown to follow first-order kinetics for the disappearance of (**3**) (Figure 1). The data suggest a change of mechanism from S_N1 (P) for n = 1—3 to S_N2 (P) or addition–elimination for n = 0‡



Scheme 1

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† The water was dissolved in acetonitrile to effect solubilisation and unless otherwise stated the final solvent composition was 12% (v/v) MeCN in toluene.

‡ This is substantiated by the fact that for n = 1 with 5% MeCN for solubilisation the reaction becomes overall second-order, *i.e.* first-order in both (**3**) and H_2O. This will be discussed in more detail in the full report but is what one would expect in a lower polarity medium.

Table 2. Relative rates of hydrolysis of phosphoranes, $Ar_nP(OCH_2CF_3)_{5-n}$, in toluene–12% MeCN at 31 °C.

n	0	1^a	2	3
Relative rate	23	1	2	16

[a] For $n = 1$, $k_{obs.} = 1.20 \pm 0.05 \times 10^{-3}\ s^{-1}$.

Table 3. Hammett data from competitive experiments on the hydrolysis of $Ar_nP(OCH_2CF_3)_{5-n}$ with $n = 3$ and $n = 1$ in toluene–12% MeCN at 31 °C.

(A) $n = 3$; $Ar_3P(OCH_2CF_3)_2$ *vs.* $Ar'_3P(OCH_2CF_3)_2$

Ar_3	Ar'_3	k/k'	$\Delta\Sigma\sigma$	ρ
$(p\text{-}Me_2NC_6H_4)Ph_2$	$(p\text{-}MeOC_6H_4)_2Ph$	1.73	0.294	−0.81
$(p\text{-}MeOC_6H_4)_3$	$(p\text{-}MeOC_6H_4)_2Ph$	2.21	0.268	−1.29
$(p\text{-}MeC_6H_4)_3$	$(p\text{-}MeOC_6H_4)Ph_2$	1.43	0.242	−0.64
$(p\text{-}MeOC_6H_4)Ph_2$	$(p\text{-}MeC_6H_4)Ph_2$	1.27	0.098	−1.06
Ph_3	$(p\text{-}FC_6H_4)_3$	1.72	0.186	−1.27
$(m\text{-}MeC_6H_4)_3$	Ph_3	1.68	0.207	−1.09
$(m\text{-}MeC_6H_4)_3$	$(p\text{-}FC_6H_4)_3$	3.51	0.393	−1.39
$(p\text{-}MeC_6H_4)Ph_2$	Ph_3	1.30	0.170	−0.67
$(p\text{-}ClC_6H_4)_3$	$(m\text{-}ClC_6H_4)_3$	3.39	0.438	−1.21
$(p\text{-}MeOC_6H_4)_2Ph$	$(p\text{-}MeC_6H_4)_3$	1.05	0.026	−0.81
$(p\text{-}MeOC_6H_4)_2Ph$	$(p\text{-}MeOC_6H_4)Ph_2$	1.64	0.268	−0.80
$(p\text{-}Me_2NC_6H_4)Ph_2$	$(p\text{-}MeC_6H_4)_3$	2.18	0.320	−1.06
$(p\text{-}MeOC_6H_4)Ph_2$	$(m\text{-}MeC_6H_4)_3$	1.14	0.061	−0.93
$(p\text{-}MeC_6H_4)Ph_2$	$(p\text{-}FC_6H_4)_3$	2.14	0.356	−0.93

Average $\rho = -1.00 \pm 0.2$

(B) $n = 1$; $ArP(OCH_2CF_3)_4$ *vs.* $Ar'P(OCH_2CF_3)_4$

Ar	Ar'			
$p\text{-}MeC_6H_4$	$m\text{-}MeC_6H_4$	1.24	0.101	−0.92
Ph	$p\text{-}ClC_6H_4$	2.43	0.227	−1.70
$p\text{-}MeOC_6H_4$	Ph	2.37	0.268	−1.40
$p\text{-}Me_2NC_6H_4$	$p\text{-}MeOC_6H_4$	5.29	0.562	−1.29
$p\text{-}MeOC_6H_4$	$p\text{-}ClC_6H_4$	6.66	0.495	−1.66
$p\text{-}Me_2NC_6H_4$	Ph	9.22	0.830	−1.16
$p\text{-}MeOC_6H_4$	$p\text{-}MeC_6H_4$	1.22	0.098	−0.88
$p\text{-}MeOC_6H_4$	$m\text{-}MeC_6H_4$	2.01	0.199	−1.52

Average $\rho = -1.30 \pm 0.3$

(Scheme 1). One of the principal criteria used to establish the latter mechanism[2] was the observation of steric retardation of the rate by increasing the bulk of the substituents around phosphorus. Accordingly, we determined the relative rate of hydrolysis for $(Pr^iO)_3P(OCH_2CF_3)_2$ *vs.* $P(OCH_2CF_3)_5$ to be 1 : 9.7. This is clearly another example of steric retardation and in agreement with literature data reveals an S_N2 (P) or addition–elimination mechanism with the addition step being rate-limiting. Conversely and in accord with an S_N1 (P) mechanism, *ortho*-substituents introduced into the aryl groups of (**3**), $n = 1$ or 3, caused steric acceleration of the reaction with $o\text{-}MeC_6H_4P(OEt)_2(OCH_2CF_3)_2 : PhP(OEt)_2(OCH_2CF_3)_2 = 6.8 : 1$ and $(o\text{-}MeOC_6H_4)Ph_2P(OCH_2CF_3)_2 : Ph_3P(OCH_2CF_3)_2 = 7.0 : 1$.

The ρ-values for a series of phosphoranes derived from Ar_3P and $ArP(OCH_2CF_3)_2$ were −1.0 (±0.2) and −1.3 (±0.3) respectively (Table 3). Thus a low degree of positive charge develops on phosphorus in reaching the transition state in accord with the proposal of an S_N1 (P) mechanism for both series of phosphoranes and in contrast to the *positive* ρ-values expected for an addition–elimination route.[2] Finally it is interesting that the magnitude of ρ observed in these experiments is small enough to suggest that the transition state for $n = 1$—3 resembles the ion-pair rather than solvent-separated ions in which a full positive charge would be developed on phosphorus.

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References

1 D. B. Denney, D. Z. Denney, P. J. Hammond, and Yu-Pin Wang, *J. Am. Chem. Soc.*, 1981, **103**, 1785.

2 W. C. Archie, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, 1973, **95**, 5955.

3 A. Queen, A. E. Lemire, and A. F. Janzen, *Int. J. Chem. Kinet.*, 1981, **13**, 411.

4 E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1935, 244; E. D. Hughes, *ibid.*, 1935, 255; E. D. Hughes, C. K. Ingold, and U. G. Shapiro, *ibid.*, 1936, 225; L. C. Bateman, K. A. Cooper, E. D. Hughes, and C. K. Ingold, *ibid.*, 1940, 925.