

## The Quest for Carbanion-promoted Dissociative Pathways in the Hydrolysis of Aryl Phosphinates

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Results of a kinetic study on the alkaline hydrolysis of the aryl (methylsulfonyl)methylphenylphosphinates **3a–i** show that a dissociative mechanism is not operating in this reaction. Activation entropy data ( $\Delta S^\ddagger = -59.5 \text{ J mol}^{-1} \text{ K}^{-1}$  for the 4-nitrophenyl ester) and good Hammett  $\sigma$  relationship ( $\rho = 1.45 \pm 0.07$ ) strongly suggest that an associative bimolecular mechanism occurs, in which negligible negative charge is generated on the leaving group in the rate-determining step.

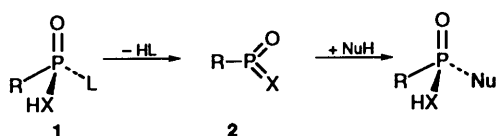
The hydrolysis reactions of phosphate, phosphonate and phosphinate esters have attracted considerable attention. This is due not only to the importance of the role of phosphorus in living systems<sup>1</sup> but also because of the variety of mechanisms displayed by these compounds.<sup>2</sup>

It is now generally believed that nucleophilic substitution at a tetracoordinate pentavalent phosphorus occurs by associative (AE) mechanisms through a pentacoordinate trigonal bipyramidal (TBP) intermediate or transition state.

The mechanism giving rise to a TBP transition state is denoted as  $S_N2(P)$  since it resembles the one occurring in bimolecular nucleophilic substitution reactions at a saturated carbon atom. Such a concerted process will take place with inversion of configuration at phosphorus.

If the transition state is long-lived enough to turn into an intermediate then the mechanism is referred to as an addition–elimination. In the framework of this stepwise process formation of the intermediate is followed by the detachment of the leaving group, again with inversion of configuration at phosphorus. However, the intermediate can undergo pseudo-rotation<sup>3</sup> prior to the departure of the leaving group and in such case retention of configuration at phosphorus will be observed. The first two mechanisms are often denoted as ‘in-line displacement’ and the last one as an ‘adjacent’ mechanism.<sup>4</sup>

A dissociative (elimination–addition or EA) mechanism is also possible if the substrate (**1**; L = leaving group) possesses a suitable ligand (HX-) bound to the phosphorus atom. As shown in Scheme 1, this process involves the participation of a



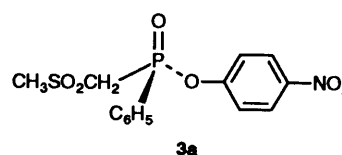
Scheme 1

tricoordinate intermediate or transition state (**2**) analogous to monomeric metaphosphate.<sup>2</sup>

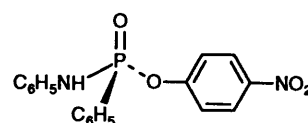
There is now good evidence for the intervention of a dissociative mechanism in the reactions of some phosphoric acid derivatives when X is oxygen<sup>5</sup> or nitrogen<sup>6</sup> even if the existence in solution of the free metaphosphate-like intermediate is still debated.<sup>5,7</sup> However, to the best of our knowledge, there is no evidence in the literature that such a mechanism may operate when X is a carbon atom. This fact is rather surprising since it is well known that a carbanion is an efficient internal nucleophile<sup>8</sup> in both acyl<sup>9</sup> and sulfonyl<sup>10</sup> transfer processes. This observation, coupled with our interest in the dissociative pathway in acyl transfer reactions,<sup>11</sup> prompted us to undertake a study on the hydrolysis of substrates that could, in principle,

react *via* a dissociative mechanism promoted by carbanionic internal nucleophiles.

A large amount of data on acyl transfer at carbon-, phosphorus- and sulfur-based acyl sites, shows that the reaction flux (associative *versus* dissociative) is controlled by: (i) leaving group ability; (ii) internal nucleophilicity of the substrate (related to the  $pK_a$  of the ionizable proton) and (iii) stability of the putative unsaturated intermediate (**2**). It is well established that the dissociative route requires a reasonably (although not exceedingly) low substrate  $pK_a$ , a good nucleofuge and a ‘stable’ intermediate.



**3a**



**4**

In this connection, we have chosen to investigate the alkaline hydrolysis of 4-nitrophenyl (methylsulfonyl)methylphenylphosphinate (**3a**). This ester has strict analogies with 4-nitrophenyl *N*-phenyl-*P*-phenylphosphonamidate (**4**) which hydrolyses in alkaline solution through an E1cB mechanism.<sup>6b,c</sup> These two esters differ indeed only in the nature of the ligand carrying the ionizable hydrogen atom (the potential internal nucleophile) and have in common the other three ligands (the double-bonded oxygen atom, the phenyl group and the nucleofugal 4-nitrophenoxy group) attached to phosphorus. Moreover, the acidity of the  $\alpha$ -hydrogen should be similar in both esters. This appraisal is based on the reasonable assumption that the  $pK_a$  difference between 4-nitrophenyl *N*-methylaminosulfonate (8.88 in 50% aqueous dioxane)<sup>12</sup> and **4** (12.37 in 50% aqueous ethanol)<sup>6b</sup> holds for 4-nitrophenyl (methylsulfonyl)methanesulfonate (9.03 in water)<sup>13</sup> and **3a** as well. From this comparison a value of about 12.5 is estimated for the  $pK_a$  of the ester **3a**. Therefore this ester could reasonably undergo hydrolysis through a dissociative pathway.

In order to obtain a better understanding of the mechanism we have also examined the effect of the variation of the leaving group on reactivity through the series **3a–i** (*vide infra*).

## Experimental

**General.**—Starting reagents and solvents were purified and/or distilled before use. Buffer materials were analytical reagent grade. Dioxane was purified by passage of the analytical grade material through an activated alumina column. Water was double distilled and preboiled to free it from dissolved carbon dioxide.

**Synthesis.**—Aryl (methylsulfonyl)methylphenylphosphinates (**3a–i**). The general procedure for the synthesis of the esters is reported. The first step is the preparation of (methylthio)methylphenylphosphinic acid by a slight modification of a described procedure:<sup>14</sup> chloromethyl methyl sulfide and phenylphosphonous dichloride were treated at 0 °C with AlCl<sub>3</sub>; after completion of the addition the mixture was allowed to reach room temperature and then heated at 80 °C for 30 min. The resulting complex was hydrolysed with water, the mixture was concentrated and the phosphinic acid was extracted with diethyl ether in a yield of about 60%. The acid was successively coupled with the appropriate phenol in the presence of dicyclohexylcarbodiimide by refluxing in anhydrous tetrahydrofuran for several hours. The resulting esters were finally oxidized to the desired products with a hydrogen peroxide/acetic acid/acetic anhydride mixture at room temperature for a few hours. In the last two steps the yields were generally good. For the esters **3g** and **3i** the oxidation was carried out with hydrogen peroxide/trifluoroacetic anhydride; hydrolysis of the expected product was observed when the standard oxidizing system was employed. The crude products were recrystallized to constant melting point from toluene, unless otherwise stated, and their <sup>1</sup>H NMR spectra recorded with a Varian Gemini 200 spectrometer (200 MHz) with tetramethylsilane as internal standard and CDCl<sub>3</sub> as solvent. Together with the signals due to the methyl and aromatic hydrogen atoms spectra showed a multiplet at *ca.* 4 ppm due to the P–C–H coupling of the diastereotopic methylenic hydrogen atoms. The characteristics of the products were as follows. 4-Nitrophenyl ester (**3a**): m.p. 160–161 °C from ethanol (Found: C, 47.8; H, 4.3; N, 3.1. C<sub>14</sub>H<sub>14</sub>NO<sub>6</sub>PS requires C, 47.3; H, 4.0; N, 3.9%); δ<sub>H</sub> 3.29 (3 H, s, CH<sub>3</sub>), 3.80–4.11 (2 H, m, CH<sub>2</sub>) and 7.32–8.21 (9 H, m, aromatic). Phenyl ester (**3b**): m.p. 120–121 °C from ligroin (Found: C, 54.4; H, 4.9. C<sub>14</sub>H<sub>15</sub>O<sub>4</sub>PS requires C, 54.2; H, 4.9%); δ<sub>H</sub> 3.26 (3 H, s, CH<sub>3</sub>), 3.75–4.05 (2 H, m, CH<sub>2</sub>) and 7.15–7.99 (10 H, m, aromatic). Chlorophenyl ester (**3c**): m.p. 136–137 °C (Found: C, 48.8; H, 4.0. C<sub>14</sub>H<sub>14</sub>ClO<sub>4</sub>PS requires C, 48.8; H, 4.1%); δ<sub>H</sub> 3.25 (3 H, s, CH<sub>3</sub>), 3.76–4.06 (2 H, m, CH<sub>2</sub>) and 7.08–7.96 (9 H, m, aromatic). 3-Cyanophenyl ester (**3d**): m.p. 124–125 °C (Found: C, 54.7; H, 4.5; N, 4.7. C<sub>15</sub>H<sub>14</sub>NO<sub>4</sub>PS requires C, 53.7; H, 4.2; N, 4.2%); δ<sub>H</sub> 3.27 (3 H, s, CH<sub>3</sub>), 3.72–4.09 (2 H, m, CH<sub>2</sub>) and 7.37–7.92 (9 H, m, aromatic). 4-Cyanophenyl ester (**3e**): m.p. 166–167 °C (Found: C, 52.6; H, 4.3; N, 4.2. C<sub>15</sub>H<sub>14</sub>NO<sub>4</sub>PS requires C, 53.7; H, 4.2; N, 4.2%); δ<sub>H</sub> 3.28 (3 H, s, CH<sub>3</sub>), 3.78–4.10 (2 H, m, CH<sub>2</sub>) and 7.28–7.96 (9 H, m, aromatic). 3-Nitrophenyl ester (**3f**): m.p. 127 °C (Found: C, 47.5; H, 4.0; N, 4.0. C<sub>14</sub>H<sub>14</sub>NO<sub>6</sub>PS requires C, 47.3; H, 4.0; N, 3.9%); δ<sub>H</sub> 3.29 (3 H, s, CH<sub>3</sub>), 3.82–4.12 (2 H, m, CH<sub>2</sub>) and 7.44–8.06 (9 H, m, aromatic). 3,5-Dinitrophenyl ester (**3g**): m.p. 184–185 °C from ethanol (Found: C, 42.7; H, 3.1; N, 6.8. C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>O<sub>8</sub>PS requires C, 42.0; H, 3.3; N, 7.0%); δ<sub>H</sub> 3.32 (3 H, s, CH<sub>3</sub>), 3.85–4.15 (2 H, m, CH<sub>2</sub>) and 7.58–8.84 (8 H, m, aromatic). 2-Chloro-4-nitrophenyl ester (**3h**): m.p. 176 °C from ethanol (Found: C, 43.3; H, 3.5; N, 3.5. C<sub>14</sub>H<sub>13</sub>ClNO<sub>6</sub>PS requires C, 43.1; H, 3.4; N, 3.6%); δ<sub>H</sub> 3.27 (3 H, s, CH<sub>3</sub>), 3.85–4.14 (2 H, m, CH<sub>2</sub>) and 7.49–8.29 (8 H, m, aromatic). 2,4,5-Trichlorophenyl ester (**3i**): m.p. 142–143 °C (Found: C, 40.9; H, 3.0. C<sub>14</sub>H<sub>12</sub>Cl<sub>3</sub>O<sub>4</sub>PS requires C, 40.6; H, 2.9%); δ<sub>H</sub> 3.27 (3 H, s, CH<sub>3</sub>), 3.82–4.11 (2 H, m, CH<sub>2</sub>) and 7.51–8.03 (7 H, m, aromatic).

(Methylsulfonyl)methylphenylphosphinic acid. This was obtained by oxidizing (methylthio)methylphenylphosphinic acid in the presence of hydrogen peroxide/acetic acid/acetic anhydride. M.p. 176 °C; δ<sub>H</sub> 3.14 (3 H, s, CH<sub>3</sub>), 3.82 (2 H, d, *J* 12.4, P–CH<sub>2</sub>) and 7.42–7.88 (5 H, m, aromatic).

**Product Analysis.**—UV spectra (in the 240–450 nm range) showed by direct comparison that the sole products of the hydrolysis of **3a** were 4-nitrophenol and (methylsulfonyl)methylphenylphosphinic acid. For the other substrates, the stoichiometry of the reaction was checked, after complete hydrolysis, at the λ<sub>max</sub> of the relevant phenolate, on the basis of the independently measured extinction coefficients of the products.

**Kinetics.**—The hydrolyses of the esters in 20% v/v dioxane–water solvent were followed spectrophotometrically by monitoring the release of the phenolate at the appropriate wavelength. In a typical kinetic run, the buffered solution (2.5 cm<sup>3</sup>) was allowed to equilibrate to the required temperature (±0.1 °C) in a 1 cm path length quartz cell placed in the thermostatted cell holder of a Kontron Uvikon 941 spectrophotometer and the reaction was initiated by adding a small aliquot (10 mm<sup>3</sup>) of a stock solution of the ester (*ca.* 10<sup>–2</sup> mol dm<sup>–3</sup> in dioxane). Reactions were usually followed for at least seven half-lives. Hydrolyses were carried out with potassium hydroxide at several different concentrations, and with phosphate, carbonate, benzylamine, borate and Tris buffers; in all cases at least three different buffer concentrations were employed. The pH of the buffered solutions were measured before and after the reaction. Buffer effects were observed for some substrates and the rate constants at zero buffer concentration were obtained by extrapolation. The ionic strength was maintained at 0.1 mol dm<sup>–3</sup> with potassium chloride. Calculations of the pseudo-first-order rate constants were performed by standard methods. Tables of primary kinetic data have been deposited as a Supplementary Publication.\*

## Results and Discussion

The pseudo-first-order rate constants for release of phenolates from the corresponding esters **3** were proportional to hydroxide ion concentration, in the pH range employed, according to the following rate law:

$$k_{\text{obs}} = k_{\text{OH}}[\text{OH}^-]$$

As above stated, the p*K*<sub>a</sub> of the 4-nitrophenyl ester (**3a**) is *ca.* 12.5 but the high reactivity of this compound prevents the observation of the curvature, due to the ionization of the substrate, in the pH–rate profile. The curvature is experimentally inaccessible also for the less reactive esters, since the decrease in reactivity, related to the presence of worse leaving groups, is probably coupled with an increase of the p*K*<sub>a</sub> values of the substrates, as was previously shown for phosphonamides.<sup>6c</sup> Values of the second-order rate constant *k*<sub>OH</sub> together with the pH range spanned are reported in Table 1.

Indeed, *k*<sub>OH</sub> may be either a true bimolecular rate constant related to attack of hydroxide ion on the neutral substrate (*k*<sub>b</sub> in Scheme 2) or a composite, apparent second-order rate constant (*k*<sub>a</sub>*K*<sub>a</sub>/*K*<sub>w</sub>) related to unimolecular expulsion of the leaving group from the conjugate base of the substrate.

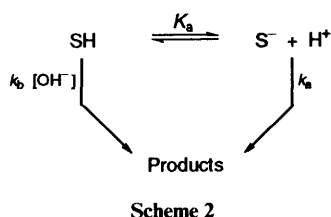
The second-order rate constant for the hydrolysis of **3a** is two orders of magnitude larger than the values reported<sup>15</sup> for the

\* Suppl. Pub. No. 56945 (3 pages). For details of the deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1993, issue 1.

**Table 1** Second-order rate constants for the hydrolysis of esters **3a**–**i** in 20% dioxane at 25 °C and  $\mu = 0.1$ 

Entry (3)	Substituent	$\lambda/\text{nm}^a$	pH range	$n^b$	$k_{\text{OH}}/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$\sigma^c$
<b>a</b>	4-NO <sub>2</sub>	400	8.20 ÷ 11.10	7	$(7.84 \pm 0.14) \times 10^2$	0.78
<b>b</b>	H	236	10.28 ÷ 12.36	7	$(4.78 \pm 0.11) \times 10$	0.00
<b>c</b>	4-Cl	299	9.33 ÷ 12.36	8	$(1.35 \pm 0.04) \times 10^2$	0.23
<b>d</b>	3-CN	320	9.33 ÷ 11.50	5	$(4.60 \pm 0.07) \times 10^2$	0.63
<b>e</b>	4-CN	275	9.33 ÷ 10.99	5	$(6.11 \pm 0.14) \times 10^2$	0.68
<b>f</b>	3-NO <sub>2</sub>	252	10.28 ÷ 11.50	5	$(6.22 \pm 0.05) \times 10^2$	0.71
<b>g</b>	3,5-(NO <sub>2</sub> ) <sub>2</sub>	266	8.20 ÷ 10.11	4	$(5.15 \pm 0.34) \times 10^3$	1.42 <sup>d</sup>
<b>h</b>	2-Cl-4-NO <sub>2</sub>	405	8.20 ÷ 10.57	4	$(2.11 \pm 0.26) \times 10^3$	0.98 <sup>d</sup>
<b>i</b>	2,4,5-Cl <sub>3</sub>	247	8.20 ÷ 11.05	5	$(8.61 \pm 0.43) \times 10^2$	0.80 <sup>d</sup>

<sup>a</sup> Wavelength for kinetic runs. <sup>b</sup> Number of data points, not including duplicates. <sup>c</sup> H. H. Jaffè, *Chem. Rev.*, 1953, **53**, 191. <sup>d</sup>  $\Sigma\sigma$ . A  $\sigma_p$  value of +0.20 was employed for 2-Cl. (J Shorter, in *Advances in Linear Free Energy Relationships*, eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, ch. 2, pp. 76–77).

**Table 2** The effect of temperature on the rate of hydrolysis of **3a**<sup>a</sup>

$T/\text{K}$	$k_{\text{obs}}/\text{s}^{-1}$
290.6	$(1.27 \pm 0.04) \times 10^{-4}$
298.2	$(2.73 \pm 0.04) \times 10^{-4}$
308.0	$(7.85 \pm 0.03) \times 10^{-3}$

<sup>a</sup> Conditions: Tris buffer in 20% dioxane,  $\mu = 0.1$ , pH = 8.20.

hydrolysis, under similar conditions, of 4-nitrophenyl diphenylphosphinate ( $7.3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) and dimethylphosphinate ( $16 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) which unambiguously react through the bimolecular mechanism. This difference could suggest that a different mechanism carries the reaction flux in the hydrolysis of the ester **3a**. Nevertheless, it seems likely that substitution of a phenyl with a (methylsulfonyl)methyl group causes an increase in rate because of the higher positive character of phosphorus due to the electron-withdrawing power of the (methylsulfonyl)methyl group. Furthermore, steric effects have been previously invoked to explain differences of this magnitude in reactions at tetracoordinate phosphorus.<sup>6c</sup>

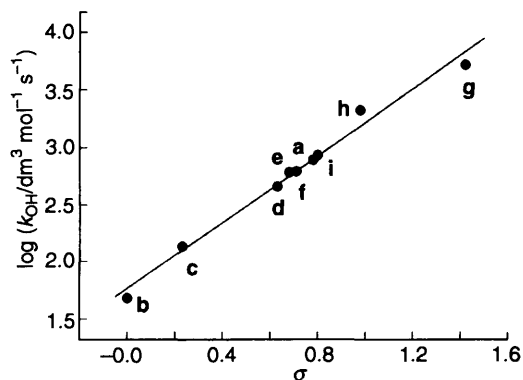
The pseudo-first-order rate constants increase, at a constant pH, with increasing total buffer concentration even with non-nucleophilic buffers such as carbonate; this observation is also consistent with a bimolecular mechanism.

Support for an AE mechanism is offered also by the effect of the temperature on the reaction rate. In Table 2 are reported the observed rates for the hydrolysis of **3a** at different temperatures. The entropy of activation is decidedly negative ( $\Delta S^\ddagger = -59.5 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and this result is not consistent with a dissociative mechanism for which a positive or slightly negative value of the entropy of activation should be expected.

Further, strong kinetic evidence for an associative mechanism comes from a linear free energy relationship for the hydrolysis of the substituted aryl phosphinates (**3a**–**i**). Fig. 1 shows a plot of  $\log k_{\text{OH}}$  against the Hammett  $\sigma$  constants: a good linearity is observed and the relationship is expressed by eqn. (1).

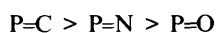
$$\log k_{\text{OH}} = (1.76 \pm 0.05) + (1.45 \pm 0.07)\sigma \quad (1)$$

The  $\rho$  value is close to that previously reported by Williams<sup>15a</sup> for the associative hydrolysis of substituted phenyl

**Fig. 1** Hammett plot of  $\log k_{\text{OH}}$  versus substituent constant  $\sigma$ . Data are from Table 1 and the line is calculated from eqn. (1).

diphenylphosphinates (1.55 in 10% dioxane at 25 °C).  $\rho$  values ranging from 0.9 to 1.9 have been reported for the alkaline hydrolysis of other phosphorus esters<sup>6c,16</sup> following AE mechanisms; by contrast, E1cB reactions show a much higher sensitivity of the apparent second-order rate constant on  $\sigma^-$ .<sup>6c,16b</sup> Finally, dependence of the rate constants on  $\sigma$  rather than  $\sigma^-$  suggests that little P–O bond cleavage in the transition state has occurred, thus indicating that there is little charge generation on the leaving group in the rate-determining step. However, since the leaving groups employed are less basic than the attacking nucleophile (hydroxide ion) the dependence of rate constants on  $\sigma$  cannot differentiate between a concerted displacement,  $\text{S}_{\text{N}}2(\text{P})$ , with a very early transition state, and a stepwise process in which the formation of the pentacoordinate intermediate is probably the rate-determining step.

From this work it appears that carbanionic internal nucleophilic centres are not able to foster dissociative pathways in the alkaline hydrolysis of phosphorus derivatives like **3**. As stressed above, the driving force for switching the mechanism of hydrolysis from an associative to a dissociative one is, other things being equal, the stability of the putative intermediate **2**. The esters **3a** and **4** follow different pathways in their hydrolysis and this may be attributed to a greater stability of the nitrogen intermediate (**2**,  $\text{X} = \text{C}_6\text{H}_5\text{N}$ ,  $\text{R} = \text{C}_6\text{H}_5$ ) due, as recently suggested by Jencks for a somewhat similar case,<sup>17</sup> to a more favourable p–d orbital overlap between phosphorus and two electron pairs of nitrogen in the conjugate base of **4** compared with the single electron pair of the putative carbanionic species arising from **3a**. The higher stability of the nitrogen intermediate as compared to the carbon one is suggested also by the calculated<sup>18</sup> sequence of the  $\pi$  orbital energy of the PX double bond:



even if this order refers, adopting the  $\sigma\lambda$  terminology employed in the description of phosphorus compounds,<sup>19</sup> to  $\sigma^2\lambda^3$  phosphorus derivatives since, to our knowledge, unfortunately nothing is reported for compounds of the type  $\sigma^3\lambda^5$  like **2**. From this standpoint further work is required to shed more light on the factors that cause the different behaviour between the esters **3a** and **4** pointed out in the present work.

### Acknowledgements

The authors gratefully thank Mr. Andrea Galatini for his valuable technical assistance in the synthesis of the compounds employed in this work.

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Paper 3/00667K

Received 2nd February 1993

Accepted 5th March 1993