A Reappraisal of the Role of the *E*1cB Mechanism of Hydrolysis of Phosphoramidic Derivatives

By **Neil K. Hamer** * and **Robert D. Tack**, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW

Rates of alkaline solvolysis of a series of aryl methyl phosphoramidates and phosphoramidothioates have been measured; the results lead to the conclusion that, despite considerable differences in rate with varying degree of *N*-substitution, there is no important contribution from an *E*1cB process such as operates for related phosphoramidic halides and acyl carbamates. On the basis of the results of studies on the relative rates and direction of cleavage in the basic solvolysis of some *OS*-dimethyl phosphoramidothioates and phosphoramidodithioates it is proposed, contrary to an earlier suggestion, that both P–O and P–S cleavage arise predominantly from nucleophilic attack, although some contribution to the latter may arise from an elimination mechanism.

BASE-CATALYSED solvolysis of fully esterified derivatives of phosphoramidic acids bearing good leaving groups has generally been thought to involve a unimolecular elimination from the conjugate base of the substrate (*E*1cB).[1-4] The justification for such an assumption is that considerable differences in rates of hydrolysis are observed between esters bearing a proton attached to nitrogen and related esters in which the nitrogen is fully substituted. However the evidence is far from unequivocal[3,5,6] and several observations are more in accord with an S_N2(P) rather than an *E*1cB mechanism as the major breakdown pathway.[3,5] Our present interest in reinvestigating the question arose from observations of Fahmy *et al.*[7] on the basic hydrolysis of *OS*-dimethyl phosphoramidothioate and its methylated derivatives; not only did they observe considerable rate differences with increasing *N*-substitution, but the principal direction of cleavage of compound (1ao) was different from that of (1bo) and (1co). To account for this these authors suggested tentatively that the P–O cleavage of (1ao) and (1bo) involved nucleophilic attack by hydroxide ion, whereas the P–S cleavage of these two compounds arose from an *E*1cB process. Although basic nucleophilic attack on acyclic *OS*-diesters of P^V acids appears always to result in P–S fission,[8] our earlier work had shown that derivatives of cyclic *OS*-ethylene phosphorothioate may, depending on the structure, undergo P–O or P–S fission on attack by hydroxide ion.[9] Since these last observations are explicable in terms of phosphorane intermediates it seemed possible that the results of Fahmy might be similarly accommodated.

The most convincing evidence to support an *E*1cB mechanism in the solvolysis of phosphoramidate derivatives comes from the basic hydrolysis of phosphoramidic chlorides which, in contrast to the neutral solvolysis, proceeds faster by a factor of 10^6—10^7 when the nitrogen atom bears a proton than when it is fully substituted.[2,3] Further, racemisation of the chiral phosphorus centre in compound (2s) occurs during the basic hydrolysis, whereas the neutral solvolysis is stereospecific.[3] Finally, although nucleophilic substitution at a thiophosphoryl centre (P=S) is almost invariably slower (by a factor in the range 5—50) than

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[4] I. Oney and M. Caplow, *J. Amer. Chem. Soc.*, 1967, **89**, 6972.
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[6] A. Williams and K. T. Douglas, *J.C.S. Perkin II*, 1972, 1454; 1973, 318.
[7] M. A. H. Fahmy, A. Khasairinah, and T. R. Fukuto, *J. Org. Chem.*, 1972, **37**, 517.
[8] L. P. Rieff, L. J. Szafraniec, and H. S. Aaron, *Chem. Comm.*, 1971, 366.
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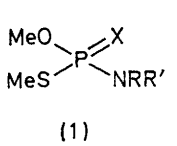
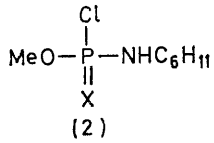
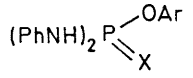
at an analogous phosphoryl (P=O) centre,[10-12] the basic (but not the neutral) solvolysis of compound (2s) is 400 times faster than that of the corresponding P=O compound. Although no one of these observations is in itself conclusive,[8] taken together they appear to exclude a bimolecular nucleophilic mechanism and leave the *E*1cB as the only reasonable alternative. However, with poorer leaving groups than chloride ion the enhancements of the rates of hydrolysis of esters bearing a proton attached to nitrogen, although still considerable, are much smaller, and evidence has accumulated to imply that for the esters (3o) and (3s) base-catalysed nucleophilic substitution proceeds by a *B*Ac2 rather than an *E*1cB process. With a view to settling this question we have examined the effect of varying degrees of *N*-substitution on the basic hydrolysis of a series of aryl methyl phosphoramidates and their P=S analogues. In the light of these results we then investigated the rates and the relative amounts of P–S and P–O cleavage in the alkaline hydrolysis of *OS*-dimethyl phosphoramidodithioates [(1as)—(1cs)] to determine whether the apparently complex behaviour of the *OS*-dimethyl phosphoramidothioates [(1ao)—(1co)] may be reasonably attributed to the operation of two distinct mechanisms.



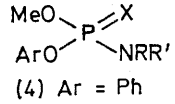
(1)



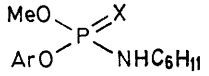
(2)



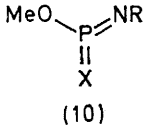
(3)



(4) Ar = Ph
(5) Ar = *p*-ClC$_6$H$_4$
(7) Ar = *m*-NO$_2$·C$_6$H$_4$
(8) Ar = *p*-NO$_2$·C$_6$H$_4$



(6) Ar = *p*-ClC$_6$H$_4$
(9) Ar = *p*-NO$_2$·C$_6$H$_4$



(10)

Where applicable:

a; NRR′ = NH_2 o; X = O
b; NRR′ = NHMe s; X = S
c; NRR′ = NMe_2

RESULTS

Rates of hydrolysis of the aryl esters (4)—(9) in sodium hydroxide solution were followed by observing the u.v. absorbance of the phenoxide released. Although ammonia and methanol were also trace products of the hydrolysis, infinity values were always within the range 90—98% of those calculated. The reactions in all cases were first-order in substrate and hydroxide ion and the second-order rate constants are given in Table 1. For the hydrolysis of *OS*-dimethyl esters the complication of dealkylation of substrate by liberated thiolate was obviated by monitoring the reaction by u.v. absorbance [13] at 235 nm, since this permits the use of very low concentrations (*ca.* 5 × 10^{-4}M) of substrate. In the case of compounds (1as) and (1bs), initial rates were also determined titrimetrically (pH-stat) and by the use of di-2-pyridyl disulphide [14] to estimate the liberated thiolate, as an independent check. Overall second-order rate constants for the hydrolysis of these compounds are given in Table 2 together with the relative proportions of P–O and P–S cleavage, these latter being determined both by ^{1}H n.m.r. measurements on the hydrolysate and by estimation of the thiolate liberated.

TABLE 1

Rates of basic hydrolysis of *O*-aryl *O*-methyl phosphoramidates and phosphoramidothioates at 28·0°

Compound	Rate constant (l mol^{-1} min^{-1})
(4ao)	21·6 ± 1·7
(4as)	3·14 ± 0·04
(5ao)	39·1 ± 2·7
(5as)	6·0 ± 0·4
(5bo)	1·09 ± 0·02
(5bs)	0·162 ± 0·001;[a] 0·11 [b]
(5co)	1·96 ± 0·02 × 10^{-3}
(6s)	0·04 [b]
(7ao)	101 ± 4
(7as)	15·9 ± 0·6
(8ao)	258 ± 1
(8as)	27·4 ± 0·9
(9o)	5·66 ± 0·11 [c]
(9s)	0·275 [d,c]

[a] In 3% v/v dioxan–water [check with (7as) gave no detectable difference from the rate in water at the same alkali concentration]. [b] In 26% v/v dioxan–water. [c] In 40% v/v dioxan–water at 29·0°. [d] Lit. value.[3]

TABLE 2

Rates of basic hydrolysis of *OS*-dimethyl phosphoramidothioates and phosphoramidodithioates at 28·0°

Compound	Rate constant (l mol^{-1} min^{-1})	% P–S cleavage
(1ao)	10·5 ± 0·2 [a]	13 [c]
(1bo)	0·29 ± 0·2 [a]	46 [c]
(1co)	*ca.* 10^{-4} [a,b]	
(1as)	3·25 ± 0·05 (3·3,[d] 2·6 [e])	14 (15 [f])
(1bs)	0·15 ± 0·01 (0·15 [d])	59 (50 [f])
(1cs)	*ca.* 10^{-4} [b]	

[a] For these compounds, Fahmy *et al.* report values of 9·0, 4·5 × 10^{-2}, and 1·5 × 10^{-4}, respectively; we have not been able to reproduce their result for (1bo). [b] These values are from the initial rates of thiol release. [c] N.m.r. spectra of the hydrolysates are reported to give values of 18 and 52%, respectively. [d] Rate from estimation of thiol by di-2-pyridyl disulphide after allowing for proportion of hydrolysis by P–S cleavage obtained from the n.m.r. of the hydrolysate. [e] Titrimetric result. [f] Proportions from the n.m.r. spectra of the hydrolysates.

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DISCUSSION

The data in Table 1 show that the variation in rate constant of the unsubstituted aryl methyl phosphoramidates with pK_a of the leaving group has a Brønsted slope (β) of -0.41 ± 0.05; for the P=S analogues $\beta = -0.32 \pm 0.05$. These values are very similar to those reported for the alkaline hydrolysis of dialkyl aryl phosphates (-0.5).[15,16] In contrast, the solvolysis of monoaryl phosphate dianions, which is believed to proceed by a unimolecular elimination (or something very close to it), shows $\beta = -1.23$.[17] Although for a true comparison with the present system one must allow a contribution to β of -0.4 for the ionisation of the monoanion,[18] it seems clear that a β value of -0.8 to -0.9 would be anticipated for an *E*1cB mechanism. In addition, alkaline hydrolysis of aryl *N*-methylcarbamates, for which an *E*1cB mechanism has been established, has $\beta = -1.1$, as opposed to $\beta = -0.3$ for the aryl *NN*-dimethylcarbamates which must necessarily use an addition–elimination process.[19-21] Thus the Brønsted slopes support a nucleophilic displacement rather than an *E*1cB process for the hydrolysis of these aryl esters.

Table 1 also shows that the phosphoramidates are hydrolysed considerably faster than the corresponding phosphoramidothioates, by a factor in the range 6—10 (18 in the case of *N*-cyclohexyl compounds but these reactions were conducted in aqueous dioxan). A factor of this magnitude is reasonably typical of the relative rates of hydroxide attack on dialkyl aryl phosphates and phosphorothioates but, as mentioned earlier, is in complete contrast to the relative rates for (2s) and (2o). Since replacement of P=O by P=S should stabilise the intermediate (10) in the *E*1cB reaction by more efficient p_π–p_π bonding we consider that this mechanism is excluded and that all the available data point to a bimolecular nucleophilic attack by hydroxide ion at phosphorus.

N-Methylation is seen to lead to a monotonic decrease in hydrolysis rate in these aryl methyl esters, by a factor in the range 35—50 fold for monosubstitution and a further 100—500 fold for *NN*-disubstituted esters. For the aryl carbamates these factors are *ca.* 10^2 and *ca.* 10^6. Thus we feel that our observation of rate variation with increasing *N*-alkylation provides no positive reason for preferring the *E*1cB mechanism and could equally well be attributed to steric effects on the nucleophilic attack. In comparison with the effect of methylation on the rates of alkaline hydrolysis of diethyl methylphosphonates (roughly a 4-fold decrease in rate per methyl group) [22,23] the effect of *N*-methylation on our phosphoramidate esters might appear unexpectedly large. Nevertheless similar conclusions concerning the relative steric requirements of these groups have been drawn from conformational studies on 2-amino-5-t-butyl-1,3,2-dioxaphosphorinans.[24] The size of these ' steric ' effects suggests that they include an electronic effect in which delocalisation of the nitrogen lone pair into the vacant 3*d* orbitals on phosphorus increases substantially with increasing *N*-alkylation. Thus the rate differences reflect a decreased electrophilicity of the phosphorus in addition to increased non-bonding interactions of the substrate with the nucleophile.

We shall now examine the suggestion that P–S cleavage of compounds (1ao) and (1bo) results from an *E*1cB mechanism; methoxide, being a poorer leaving group than phenoxides, can safely be assumed to be lost in a nucleophilic displacement process. From Table 2 we can deduce the partial rate constants for loss of thiolate from the *OS*-dimethyl esters (1) and see that:

$$k_2(1ao)/k_2(1as) \simeq 3 \quad \text{and} \quad k_2(1bo)/k_2(1bs) \simeq 1.5$$

In addition,

$$k_2(1ao)/k_2(1bo) \simeq 10; \quad k_2(1as)/k_2(1bs) \simeq 5;$$

$$k_2(1bo)/k_2(1co) \simeq 10^3; \quad k_2(1bs)/k_2(1cs) \simeq 2 \times 10^2.$$

In magnitude these figures are similar, to within a factor of 10, to those for the above aryl esters, which implies that a nucleophilic displacement process provides the major reaction pathway for the hydrolysis. However, the rather low values for $k_2(1ao)/k_2(1as)$ and $k_2(1bo)/k_2(1bs)$ do suggest that a significant proportion of the hydrolysis of the P=S compounds may be proceeding by the elimination mechanism. We conclude that these *OS*-dimethyl phosphoramidates do appear to be the first reported examples of nucleophilic displacements on P^V esters in which loss of alkoxide competes with loss of thiolate. Unfortunately the proportion of P–S cleavage by the alternative mechanism may be significant yet cannot be accurately assessed, with the result that a detailed interpretation of the mixed behaviour of these *OS*-diesters in terms of phosphorane intermediates is not yet justified.

EXPERIMENTAL

Solvents and reagents were purified according to published procedures. Inorganic reagents were AnalaR grade. ^{1}H N.m.r. spectra were recorded on a Perkin-Elmer R-12B spectrometer. Preparative t.l.c. was carried out on 2 mm plates of Merck Kieselgel $60PF_{254}$, developed with chloroform in most cases; for the more polar (1bo) and (1co) it was necessary to use chloroform–ethanol (9 : 1).

O-*Aryl* O-*Methyl Phosphoramidates and Phosphoramidothioates* (4)—(9).—To solutions of the appropriate phosphoro-

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[19] From data of M. J. Kolbenzene, R. L. Metcalf, and T. R. Fukuto, *J. Agric. Food Chem.*, 1954, **2**, 864.
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dichloridates [25-31] (typically 5 mmol) and methanol (5 mmol) in dry ether (50—100 ml), pyridine (5 mmol) in ether (20 ml) was added dropwise with stirring. The solutions were kept at 0° till no more pyridine hydrochloride separated (3 h to 1 week), then filtered. The filtrate was concentrated and treated with the appropriate amine (11 mmol) in ether [32] (acetonitrile was used for ammonia itself), and the product was isolated by the usual procedure. Those compounds which were liquids were purified by preparative t.l.c. and the remainder by recrystallisation. The n.m.r. spectra of these compounds were consistent with the structures assumed.

TABLE 3

Properties of the substrates

Compound	M.p. (°C)	Found (%) C	H	N	P	Calc. (%) C	H	N	P
(1as)	liq.	14·9	4·8	9·2		15·3	5·1	8·9	
(1bs)	liq.	20·7	5·7	8·0		21·0	5·9	8·2	
(1cs)	liq.	25·6	6·4	7·3		25·9	6·5	7·6	
(4ao)	90·5—92·5	45·3	5·4	7·7		44·9	5·4	7·5	
(4as)	36·0—36·5	41·7	5·0	6·4		41·4	5·0	6·9	
(5ao)	64—67	37·8	4·3	7·0		37·9	4·1	6·3	
(5as)	liq.	35·7	4·4	6·3		35·4	3·8	5·9	
(5bo)	24—28	40·4	4·8	5·6		40·8	4·7	5·9	
(5bs)	liq.	38·2	4·4	5·4		38·2	4·4	5·6	
(5co)	liq.	43·0	4·8	4·8		43·3	5·2	5·6	
(6s)	102—104	48·5	6·2	4·0		48·8	6·0	4·4	
(7ao)	94—95	36·3	4·1	11·9		36·2	3·9	12·1	
(7as)	liq.	34·4	3·7	10·9		33·9	3·8	11·3	
(8ao)	99—101	36·5	3·8	11·0	13·3	36·2	3·9	12·1	13·4
(8as)	44—47	34·5	3·7	11·1		33·9	3·8	11·3	
(9o)	118—120	49·8	6·1	9·6	9·9	49·7	6·1	8·9	9·9

liq. = liquid, purified by preparative t.l.c.

OS-*Dimethyl Phosphoramidothioate* (1ao) *and* N-*Methylphosphoramidothioate* (1bo).—These compounds were prepared by the alkaline hydrolysis of the phenyl methyl diesters (4as) and (4bs) followed by treatment of the hydrolysate (after removal of the liberated phenol) with dimethyl sulphate. Their spectral properties were as reported.[7]

OS-*Dimethyl* NN-*Dimethylphosphoramidothioate* (1co).—*NN*-Dimethylphosphoramidothioic dichloride (6 g) [27] was treated with sodium methoxide (1 g) in methanol (50 ml) at 0° for 30 min. The methanol was removed by evaporation and the residue was hydrolysed by sodium hydroxide (5 g) in water–dioxan (50 and 20 ml). After treatment of the hydrolysate in water (30 ml) with dimethyl sulphate (4 ml) and sodium hydrogen carbonate (1 g) the product was extracted with dichloromethane (3 × 20 ml) and purified by preparative t.l.c. Its n.m.r. spectrum was as reported.

OS-*Dimethyl Phosphoramidodithioate* (1as).—Prepared by a reported procedure,[33] this had b.p. 98° at 0·2 mmHg (lit.,[33] 86° at 0·2 mmHg).

OS-*Dimethyl* N-*Methylphosphoramidodithioate* (1bs).—Methyl phosphorodichloridodithioate (9·0 g; prepared by the reaction of methyl phosphorodichloridate with phosphorus pentasulphide) [34] and methanol (2 ml) in dry ether (80 ml) were treated with pyridine (4·0 ml) in ether (20 ml). After 1 day at 5°, the pyridine hydrochloride was filtered off and methylamine was passed through half the filtrate for 10 min at 0°. Filtration followed by evaporation gave crude product (2 g), which was purified by preparative t.l.c.; τ (CCl_4) 6·3 (3H, d, *J* 15 Hz), 6·5—6·9 (1H, m), 7·3 (3H, d, *J* 15 Hz), and 7·8 (3H, d, *J* 16 Hz).

OS-*Dimethyl* NN-*Dimethylphosphoramidodithioate* (1cs).—To methyl phosphorodichloridodithioate (9 g) in dry ether (100 ml) was added dimethylamine (4·5 g) in ether (50 ml) at 0°, dropwise with stirring. After 15 min the mixture was filtered and the residue distilled to give an oil (4·5 g), b.p. 62—64° at 0·1 mmHg, which was shown by n.m.r. to be methyl *NN*-dimethylphosphoramidochloridodithioate. This was refluxed with pyridine (2 ml) in methanol (20 ml) for 1 day and the product isolated as before; τ (CCl_4) 6·3 (3H, d, *J* 14 Hz), 7·2 (6H, d, *J* 13 Hz), and 7·8 (3H, d, *J* 16 Hz).

O-*Aryl* O-*Methyl Phosphoramidates and Phosphoramidothioates*.—Solutions of compounds (4ao), (4as), (5ao), (5as), (5bo), (5co), (7ao), (7as), (8ao), and (8as) ($0·3—8 \times 10^{-4}$M) in aqueous alkali, made up to ionic strength 0·050 with KCl, were placed in thermostatted cells in a Zeiss PMQ II spectrometer and the absorbance of the phenoxide was measured at intervals. The hydrolyses were followed for at least 10 half-lives and the observed infinity absorbance values were used to calculate rate constants. The hydrolyses of (5bs), (6s), and (9o) were similarly followed but, as these compounds were not sufficiently soluble in water, aqueous dioxan was used as solvent.

OS-*Dimethyl Phosphoramidothioates and Phosphoramidodithioates*.—Solutions of compounds (1ao), (1bo), (1co), (1as), (1bs), and (1cs) ($2—8 \times 10^{-4}$M) in aqueous alkali were made up in deoxygenated water containing ethylenedinitrilotetra-acetic acid (EDTA) (10^{-4}M) and sufficient potassium chloride to bring the ionic strength to 0·050. The EDTA inhibits oxidation of the thiolate but does not affect hydrolysis rates; in its absence, final absorbances slowly decreased. These solutions were placed in thermostatted cells in a Zeiss PMQ II spectrometer and the change in the absorbance due to methanethiolate was followed at 235 nm. The expected final absorbances were calculated from the experimentally determined extinction coefficients of thiolate and, after allowance for the absorbance of other species present, this permitted an estimate to be made of the proportion of reaction by P–S cleavage.

The initial rate of hydrolysis of (1as) was determined on a $3·2 \times 10^{-2}$M-solution by following its uptake of alkali at constant pH (9—11·5) with a pH-stat (Radiometer TTT11).

Initial rates of thiolate release from (1as) ($3·2 \times 10^{-2}$M) and (1bs) ($2·2 \times 10^{-2}$M) in carbonate buffers were determined by performing the hydrolysis at 27·0° in sealed tubes and estimating the thiol, after suitable time intervals, with di-2-pyridyl disulphide.

Product Studies.—Solutions of hydrolysate, after complete hydrolysis, were evaporated to dryness *in vacuo* below 40°; the residues were then taken up in D_2O and the relative amounts of products were estimated from the ^1H n.m.r. spectrum.

This work was supported by a grant from the S.R.C.

[4/485 *Received*, 12*th March*, 1974]

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