Evidence for a Sulphene Intermediate in the Base Hydrolysis of the Methanesulphonic Anhydrides of Phosphinothioic Acids

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Summary Isotope incorporation studies on the base hydrolysis of the methanesulphonic anhydrides of phosphinothioic acids (**1**) using ^{18}O enriched water and D_2O have shown that S–O bond cleavage occurs *via* a sulphene intermediate.

Mixed sulphonic–thiophosphorus anhydrides have been synthesized recently.[1] The enantiomeric methanesulphonic anhydrides of t-butylphenylphosphinothioic acid (**1**; R^1 = Ph, R^2 = Me) undergo base hydrolysis in dioxan–water with full retention of configuration at the phosphorus atom, whereas the acid catalysed hydrolysis is accompanied by inversion of configuration.[1] Our preliminary conclusion from these results was that nucleophilic attack of the hydroxide ion occurs at the sulphonyl group.[1]

Table 1. Incorporation of ^{18}O into the products obtained from the hydrolysis of (**1**) (% excess ^{18}O) (ref. 2)

Compound	$H_2{}^{18}O$ ($\pm$0·01)	S-Me ester of (**2**) ($\pm$0·01)	Me ester of (**3**)
(**1**; R^1=Ph, R^2=p-MeC_6H_4)	25·32	0·0	25·35±0·08
(**1**; R^1=Ph, R^2=Me)	25·32	0·0	26·44±0·2
(**1**; R^1=OMe, R^2=Me)	24·30	0·0	22·34±0·4
(**2**[a]; R^1=Ph)	25·32	0·0	—
(**2**[a]; R^1=OMe)	24·30	0·0	—
(**3**[a]; R^2=Me)	24·30	—	4·05±0·04

[a] Control experiments.

We now describe experiments which clearly demonstrate that the base hydrolysis of the anhydrides (**1**) proceeds with cleavage of the S–O bond, and in the case of mixed anhydrides derived from methanesulphonic acid (**1**; R^2 = Me) a sulphene intermediate is involved.

The hydrolysis of (**1**) in 4·0M NaOH in dioxan–water (4:1) containing *ca.* 25 atom % excess of ^{18}O, at 21 °C for 24 h gave, after acidification with HCl, the thioic acid (**2**) and sulphonic acid (**3**) (reaction 1). The acids (**2**) and (**3**) were separated quantitatively by selective extraction with $CHCl_3$. The aqueous solution remaining after the extraction of (**2**) was continuously extracted with ether and the extract treated with ethereal diazomethane to give the corresponding methylsulphonate. The chloroform solution was evaporated and treated with ethereal diazomethane to give the isomeric S–Me and O–Me esters of the acid (**2**). The isotope incorporation data presented in Table 1 were calculated from the mass spectra of the S–Me esters of (**2**) and the methyl esters of (**3**), which were obtained from the reaction mixture. The results show that O from the solvent is incorporated into the sulphonic acid (**3**) but not into the thioic acid (**2**). Control experiments showed that the thioic acid (**2**) did not undergo exchange under the reaction conditions. A significant but relatively small incorporation of ^{18}O into the sulphonic acid (**3**; R^2 = Me) was noted in control experiments under the same reaction conditions. The results presented in Table 1 show decisively that the base hydrolysis of (**1**) occurs with exclusive S–O cleavage. This finding correlates with our previous observation of the retention of configuration at the phosphorus atom.[1]

$$\underset{(\mathbf{1})}{\mathrm{Bu^tR^1P(S){-}O{-}SO_2{-}R^2}} \xrightarrow[\text{ii, HCl}]{\text{i, }^{18}\mathrm{OH}^-} \underset{(\mathbf{2})}{\mathrm{Bu^tR^1P(S)OH}} + \underset{(\mathbf{3})}{\mathrm{R^2SO_2{-}^{18}OH}} \qquad (1)$$

Table 2. Incorporation of ^2H into the products obtained from the hydrolysis[a] of (**1**) (% excess ^2H) (ref. 2)

Compound	Me-ester of (**3**)
(**1**; R^1 = Ph, R^2 = Me)	85·4 ± 0·9
(**1**; R^1 = OMe, R^2 = Me)	80·6 ± 2
$MeSO_2Cl$	82·4 ± 1
$MeSO_3H$[b]	0·00 ± 0·05

[a] Hydrolysis was carried out using 95% D_2O. [b] Control experiment.

Kinetic data showed that the second-order rates of the base hydrolysis of the methanesulphonic anhydrides (**1**; R^2 = Me) (k_{obs} = 10·5 l mol^{-1} s; H_2O–dioxan 50:30; t = 40 ± 0·1 °C) were considerably faster than those of the toluene-*p*-sulphonic anhydrides (**1**; R = p-MeC_6H_4) (k_{obs} = 0·03 l mol^{-1} s; H_2O–dioxan; t = 40 ± 0·1 °C), thus suggesting different mechanisms in the two cases. For this reason deuterium-incorporation studies (reactions 2 and 3) were carried out employing the method of King *et al.*[3] and Truce *et al.*[4] as a way of showing that the mechanism in the former case involved a sulphene intermediate.

$$\mathrm{Bu^tR^1P(S){-}O{-}SO_2Me} \xrightarrow[\mathrm{D_2O}]{\mathrm{OD^-}} \mathrm{Bu^tR^1P(S)O^-} + \mathrm{CH_2{=}SO_2} + \mathrm{DOH} \qquad (2)$$

$$\mathrm{CH_2{=}SO_2} \xrightarrow[\text{ii, OD}^-]{\text{i, D}_2\text{O}} \mathrm{CH_2DSO_2O^-} \xrightarrow[\text{ii, CH}_2\text{N}_2]{\text{i, HCl}} \mathrm{CH_2DSO_2OMe} \qquad (3)$$

The hydrolysis was carried out in 3·5M NaOH in dioxan–deuterium oxide at 24 °C for 6 h. Deuterium incorporation was determined by mass spectral analysis. The data in Table 2 show that the base hydrolysis of (**1**; R^2 = Me) in D_2O occurs with a very high formation of monodeuteriated methanesulphonic acid, but no di-or trideuteriated methanesulphonic acids are formed. It is of interest to note that the incorporation of deuterium during the base hydrolysis of methanesulphonyl chloride in D_2O was found to be of the same order of magnitude as that found for the anhydrides (**1**; R^2 = Me). The most significant conclusion from the above results is that the base hydrolysis of the anhydrides (**1**) proceeds either by direct attack of OH^- anion on the sulphonyl centre or *via* a sulphene intermediate. Both mechanisms are involved in the case of the anhydrides derived from the methanesulphonic acid (**1**; R^2 = Me). The kinetic data are consistent with sulphene formation by an E_2 mechanism.[5] As far as we are aware, sulphonic anhydrides of phosphorus have never been described previously as being sources of sulphene intermediates.

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