Position of Bond Cleavage in the Acid-catalysed Hydrolysis of Methyl Methylarylphosphinates

By ROBERT A. MCCLELLAND

(*Department of Chemistry, University of Toronto, Toronto, Ontario* M5S 1A1, *Canada*)

Summary The hydrolysis of methyl methylarylphosphinate esters in 1·0 M $HClO_4$ at 67 °C is found to proceed with *ca.* 90% P–O and 10% C–O bond fission.

RATE data have recently been reported for the acid-catalysed hydrolysis of phosphinate esters,[1–3] implying an *A*2 mechanism. The tracer studies necessary to determine the position of water attack were not carried out however, although suggestions of both P–O[1] and C–O[3] bond fission were advanced. We report here a study for methyl methylarylphosphinate esters which shows that in fact both occur, the former dominating.

Esters containing *ca.* 12% ^{18}O in the methoxy oxygen were prepared by treating $Me^{18}OH$[4] with the phosphinic acid chloride. These were allowed to undergo hydrolysis in normal abundance 1·0 M $HClO_4$ at 67·0 °C, and the methanol recovered and analysed for ^{18}O content as its *p*-nitrobenzoate derivative. Control experiments demonstrated that there is no exchange of methanol oxygen under the hydrolysis conditions. Also, using samples of methanol of varying ^{18}O content the analysis procedure was established to be capable of a precision of ± 0·05 or better in determining the percentage of ^{18}O.

TABLE. Bond cleavage during hydrolysis of methyl methylarylphosphinates, ArMeP(:O)–O–Me, in 1·0M $HClO_4$ at 67·0 °C.

Aryl group	^{18}O in MeO of ester/%[a]	^{18}O in MeOH/%[a,b]	P–O Bond cleavage/%
C_6H_4Cl-4	12·20	11·40	93·3
Ph	12·13	11·02	90·7
C_6H_4Me-4	12·16	11·00	90·2

[a] Determined mass spectrometrically from $(M+2)/M$ intensity ratios; values are corrected for naturally occurring isotopes in other positions. [b] As *p*-nitrobenzoate derivative.

The results are summarized in the Table and show that these hydrolyses proceed with 90—93% P–O bond cleavage, this result being relatively insensitive to the nature of the aromatic substituent. The *ca.* 10% C–O cleavage which is observed is outside the limit of experimental error however, so that the competition between the two types of processes is very close and could be influenced by other variations (*e.g.*, structural, solvent, or temperature), making it dangerous to predict the exact situation without labelling studies. In fact, our result is anticipated by previous studies on phosphate esters, where again acid hydrolysis proceeds *via* both pathways.[5]

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