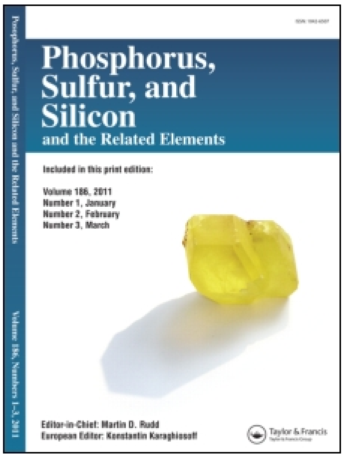

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THE MASS SPECTRA OF PHOSPHONYL COMPOUNDS PART 2[1] PHOSPHONYL DIHALIDES

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THE MASS SPECTRA OF PHOSPHONYL COMPOUNDS PART 2[1] PHOSPHONYL DIHALIDES

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The mass spectra of two series of alkane- and substituted-methanephosphonyl dichlorides have been studied together with the spectrum of benzenephosphonyl dichloride. The molecular ions are of low abundance. Ions corresponding to hydrocarbon or halomethyl groups, which occur by cleavage of the P—C bond, are usually abundant, producing the base peaks in most of the spectra.

The mass spectra of phosphonyl dichlorides have been studied very little.[2,3] Their characterization by mass spectrometry has not been important probably because of their reactivity and ready conversion to stable derivatives such as esters. However, the mass spectra of the derivatives are complicated by the fragmentations of the additional groups. The dihalides promised to give much simpler spectra and be more volatile than the phosphonic acids upon which we have already reported.[1]

The electron-inpact mass spectra of methane-, ethane-, 2-propane-, 1,1-dimethylethane-, benzene- and phenylmethanephosphonyl dichlorides (**1**), the mono-, di-, and trichloromethanephosphonyl dichlorides (**2**), and the bromomethanephosphonyl dibromide (**3**) were determined. The characteristic ions are given in the Table.

TABLE

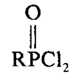
Characteristic ions in the mass spectra of phosphonyl dichlorides 1–3[a]

	M^+		R^+		$POCl_2^+$	PO^+
Compound	*m/e*	%	*m/e*	%	%	%
1, R = Me	132	0	15	0	100	25
1, R = Et	146	9	29	100	6	33
1, R = Pr^i	160	4	43	100	30	13
1, R = Bu^t	174	15	57	100	17	9
1, R = CH_2Ph	208	14	91	100	3	4
1, R = Ph	194	34	77	100	45	42
2, *n* = 1	166	16	49	100	38	95
2, *n* = 2	200	2	83	100	25	35
2, *n* = 3	234	0	117	<52[b]	<52[b]	100
3	298	4	93	50	—	100

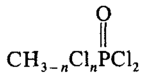
[a] The Table records abundancies of ions relative to the base peaks arbitrarily taken as 100%. The quoted *m/e* values of chlorine-containing ions correspond to the ^{35}Cl isotopes only; the appropriate ^{37}Cl isotope-containing peaks were also observed.

[b] Both ions appear at a similar mass and were not distinguished.

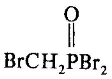
Inlet temperatures in the range 100–150°C were usually sufficient although higher temperatures were used for the di- and trichloromethanephosphonyl dichlorides. The molecular ions are generally of low abundance and are absent from the spectra of the methane and trichloromethane compounds. Cleavage of the P—C bond is a facile process and gives rise to base peaks or second-most abundant ions, i.e. R^+ or $POCl_2^+$ as indicated in the Table. The ion at *m/e* 47 (PO^+) is an abundant ion in all the


$RP(=O)Cl_2$

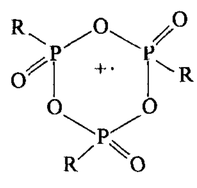
(**1**)

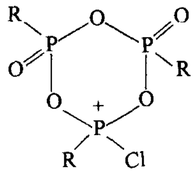

$CH_{3-n}Cl_nP(=O)Cl_2$

(**2**)


$BrCH_2P(=O)Br_2$

(**3**)


(**4**)


(**5**)

spectra and it is the base peak in the spectra of the trichloromethane compound (**2**, $n = 3$) and the bromide (**3**). Peaks at m/e 101 (PCl_2^+), 82 ($POCl^+$) and 36 (HCl^+) were also present in most of the spectra, although their abundances varied considerably. All halogen containing ions appeared as multiplets appropriate to the expected isotopic ratios. Ions corresponding to M-halogen, which dominate the spectra of phosphoryl trichloride,[4] are abundant only in the spectrum of the dibromide (**3**) and benzenephosphonyl dichloride (**1**, R = Ph).

Meta-stable ions are rare. They appear only in the spectra of phenylmethane- and 1,1-dimethylethanephosphonyl dichlorides and correspond to fragmentations of the hydrocarbon groups.

Some of the first spectra which we determined contain peaks at high mass which correspond to cyclic anhydrides such as (**4**) and (**5**). These obviously arose via partial hydrolysis of the acid chlorides.

In conclusion we find that mass spectrometry is a convenient method for the characterization of phosphonyl dihalides provided care is taken to minimize exposure of the compounds to moist air. The spectra are much less complex than those of phosphonic acids and their esters although this is offset by the low abundance of the molecular ions.

EXPERIMENTAL

The mass spectra were determined on a Perkin–Elmer Hitachi RMU6 instrument at 70 eV by the direct insertion method.

The phosphonyl dihalides were prepared by the Kinner–Perren reaction[5] or treatment of the corresponding phosphonic acid with phosphorus pentachloride[6] or thionyl chloride.[7] The identity and purity of the dihalides were established by ir, ^1H and ^{31}P nmr spectroscopy and comparison of mp or bp with literature values.

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