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A MASS SPECTROMETRIC STUDY OF SOME DIALKYLPHOSPHINIC ACIDS AND THEIR ALKYL ESTERS

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Abstract—The fragmentation patterns of dialkylphosphinates show predominance of species corresponding to phosphinate molecular ions and phosphacylium ions. A preferred path of fragmentation appears to be alkyl—P → alkene + H—P, with alkyl groups larger than Me. For example, in the spectrum of diethylphosphinic acid, the base peak corresponds to HPO_2H^+ presumably produced from the initially formed parent ion by loss of Et radical and ethylene. It thus appears possible to predict the modes of fragmentation of alkyl-P(V) compounds enabling mass spectrometry to be of considerable utility in structural analysis. The predominant species and pathways of fragmentation provide some interesting chemistry of energetic species.

INTRODUCTION

There have been some reports of mass spectra of organophosphorus compounds. Methylphosphines have been shown[1] to give molecular ions of high intensity and to lose Me groups without rearrangements. However, ethylphosphines lose ethylene —$C_2H_5PH_2^+$ is responsible for the base peak in the mass spectrum of triethylphosphine and the H_3P^+ peak is second in intensity to the molecular ion in the spectrum of ethylphosphine.[2] The heterocycle, tetramethylenephosphine, also loses ethylene to give the base peak at M-28.[3] Loss of alkene is common in compounds with alkyl-heteroatom groups where the alkyl group is larger than Me.[4]

Halmann and Klein studied the mass spectrum of trimethylphosphine oxide and found Me_3PO^+, Me_2PO^+ (base), H_2PO^+, and PO^+ to be the major fragments.[5]

Trialkyl phosphates fragment on electron impact to give $P(OH)_4^+$, $ROP(OH)_3^+$, and $(RO)_2P(OH)_2^+$ as the most abundant ions. Studies of mixed alkyl aryl phosphates show that alkyl groups undergo elimination and are lost much more readily than aryl groups.[6] Triaryl phosphates lose ArO and ArOH in contrast to the trialkyl phosphates.[6] The mass spectrum of trimethyl phosphite indicates loss of OMe or Me, but triethyl phosphite undergoes elimination; $P(OH)_2^+$, $P(OH)_3^+$, and $HP(OH)_3^+$ correspond to the three most intense peaks.[7] Dialkyl phosphonates (B), commonly (and incorrectly) called dialkyl phosphites (A) (Eq. 1), show similar results in their mass spectra: dimethyl phosphonate (B, R = Me) loses Me groups to give mainly

$$RO-\overset{OR}{P}-OH \rightleftharpoons RO-\underset{H}{\overset{OR}{P}}{=}O \qquad (1)$$

A B

HPO_3^+, PO_3^+ and PO^+, but diethyl, dipropyl and dibutyl phosphonates give $HP(OH)_3^+$ as the base peak.[8] In dialkyl alkylphosphonates, O-alkyls are lost more readily than P-alkyls.[7]

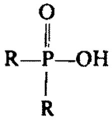
The Me esters of phenylphosphinic acid, phenylmethylphosphinic acid, and phenylethylphosphinic acid fragment on electron impact to give ϕPO_2Me^+ as the most abundant fragment for the latter two esters and the second most abundant phosphorus-containing ion (next to PO^+) in the mass spectrum of the former ester. Propyl phenylphosphinate, however, loses C_3H_5 and C_3H_6 preferentially.[9]

RESULTS

Table 1 summarizes the data collected from a study of the mass spectra of dimethyl-, diethyl-, and diisopropylphosphinic acids. The data for the diethyl compound represent average values from two spectra.

The mass spectra of the Me and Et esters of dimethylphosphinic acid, the Me esters of diethylphosphinic and diisopropylphosphinic acids, and isopropyl diethylphosphinate were studied, and the data obtained are summarized in Table 2. The data given for ethyl dimethylphosphinate represent average values for two spectra.

TABLE 1. NORMALIZED INTENSITIES OF PEAKS IN MASS SPECTRA OF DIALKYLPHOSPHINIC ACIDS[a]



$$R_2P(O)OH$$

Fragment[b]	R = Me		R = Et		R = i-Pr	
	m/e	% of base	m/e	% of base	m/e	% of base
$R_2PO_2H^{+\cdot}$	94	40	122	8	150	9
$R_2P(OH)_2^+$	95	17	123	5	151	32
$R(H)P(OH)_2^+$	81	—	95	3	109	8
$R(H)PO_2H^{+\cdot}$	80	—	94	72	108	96
RPO_2H^+	79	100	93	37	107	6
R_2PO^+	77	22	105	6	133	—
$R(H)PO^+$	63	4	77	5	91	2
$RPO^{+\cdot}$	62	2	76	2	90	2
$H_2PO_2H^{+\cdot}$	66	—	66	6	66	31
HPO_2H^+	65	—	65	100	65	100
H_2PO^+	49	9	49	6	49	2
$HPO^{+\cdot}$	48	4	48	4	48	—
PO^+	47	28	47	13	47	6
			121	3	93	6
			108	5	80	14
			103	3	79	9
Metastables:	66·2	(94 → 79)	87·8	(121 → 103)	77·8	(150 → 108)
			72·3	(122 → 94)	59·2	(108 → 80)
			45·3	(93 → 65)	39·1	(108 → 65)
			44·9	(94 → 65)		

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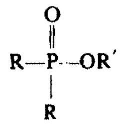
[a] All fragments present to the extent of 2% of the most abundant fragment and with m/e ⩾ 47 are included.

[b] Fragments are given as most likely structures; see discussion section.

TABLE 2. NORMALIZED INTENSITIES OF PEAKS IN MASS SPECTRA OF ALKYL DIALKYLPHOSPHINATES[a]



$R{-}P(=O)(R){-}OR'$

Fragment[b]	R = Me R' = Me m/e	 % of base	R = Me R' = Et m/e	 % of base	R = Et R' = Me m/e	 % of base	R = i-Pr R' = Me m/e	 % of base	R = Et R' = i-Pr m/e	 % of base
$R_2PO_2R'^{+\cdot}$	108	16	122	3	136	6	164	5	164	—
$R_2PO_2H_2^{+}$	95	—	95	51	123	—	151	—	123	100
$R_2PO_2H^{+\cdot}$	94	3[c]	94	5[c]	122	—	150	—	122	3
$R(H)PO_2R^{+\cdot}$	94	3[c]	108	2	108	53	122	32	136	4
$RPO_2R'^{+}$	93	100	107	7[d]	107	70	121	16	135	39
$R_2P(O)H^{+\cdot}$	78	45	78	37	106	—	134	—	106	11
R_2PO^{+}	77	14	77	56	105	2	133	—	105	43
$H_2PO_2R'^{+\cdot}$	80	—	94	5[c]	80	2	80	5	108	—
$HPO_2R'^{+}$	79	—	93	—	79	100	79	100	107	—
$R(H)PO_2H^{+\cdot}$	80	—	80	2	94	—	108	—	94	27
RPO_2H^{+}	79	—	79	100	93	—	107	—	93	94
$R(H)P(O)H^{+\cdot}$	64	—	64	—	78	—	92	—	78	6
$R(H)PO^{+}$	63	48	63	14	77	3	91	—	77	15
$RPO^{+\cdot}$	62	3	62	4	76	—	90	—	76	2
HPO_2H^{+}	65	2	65	4	65	2	65	—	65	38
H_2PO^{+}	49	3	49	8	49	6	49	—	49	5
$HPO^{+\cdot}$	48	2	48	4	48	4	48	—	48	2
PO^{+}	47	10	47	22	47	12	47	3	47	4
$M\text{-}CH_3$									149	20
Metastables:	56·5	(108 → 78)	66·4	(94 → 79)	85·8	(136 → 108)	90·8	(164 → 122)	92·3	(164 → 123)
	42·8	(93 → 63)	62·4	(95 → 77)	58·3	(107 → 79)	51·6	(121 → 79)	89·7	(123 → 105)
			58·3	(107 → 79)	57·8	(108 → 79)	51·2	(122 → 79)	74·0	(149 → 105)
			55·4	(107 → 77)					72·4	(122 → 94)
			50·8	(78 → 63)					64·1	(135 → 93)
			49·8	(122 → 78)					57·3	(106 → 78)
									56·4	(105 → 77)
									45·3	(93 → 65)

[a] All fragments present to the extent of 2% of the most abundant fragment and with m/e ≥ 47 are included, except for those mainly due to C^{13}.

[b] Most likely structures are given for fragments—see discussion.

[c] Sum of intensities of indistinguishable isomeric ions.

[d] Could also be $M\text{-}CH_3$.

Because a different fragmentation pattern is found for di-n-butylphosphinic acid, its spectrum is shown separately (Table 3).

The duplicated spectra generally agreed to ± 10% of peak intensities for major peaks. Spectra of the solid acids were also run by direct insertion procedures, but these spectra were found to be much less reproducible than those from the heated inlet procedures. However, a correlation does exist between the major peaks of the spectra obtained by both procedures.

TABLE 3. NORMALIZED INTENSITIES OF PEAKS IN THE MASS SPECTRUM OF DI-N-BUTYLPHOSPHINIC ACID[a]

m/e	% of base	*m/e*	% of base	*m/e*	% of base
149	10	95	3	66	2
136	6	94	100	65	29
131	2	93	12	63	2
123	2	92	2	57	7
122	6	80	36	56	3
121	6	79	13	55	5
108	7	78	2	49	2
107	9	77	2	48	2
96	2	75	2	47	5
Metastables:	115·2	(149 → 131)		66·4	(94 → 79)
	103·9	(178 → 136)		59·3	(108 → 80)
	72·4	(122 → 94)		52·4	(122 → 80)
				45·3	(93 → 65)

[a] All fragments present to the extent of 2% of the base peak and with *m/e* ⩾ 47 are included.

The phosphinic acids exhibit a tendency to form anhydrides on heating under vacuum; in fact, it has been observed in this laboratory that diethylphosphinic acid may be converted to its anhydride by simple vacuum distillation. Anhydride formation was minimized by use of higher inlet temperatures so that less time was required; however, traces of anhydride were indicated in the mass spectra of the acids.

DISCUSSION

Dialkylphosphinic acids. The mass spectrum of dimethylphosphinic acid differs considerably from the others studied. The molecular ion (C)* shows considerable intensity and the base peak represents loss of a Me group to give a fragment which almost certainly must have structure D (*m/e* 79). A metastable was found corresponding to this fragmentation. Besides PO^+ and the M + 1 peak (due to ion-molecule reactions and to ^{13}C) which are to be expected, the only other large peak corresponds to E (*m/e* 77). The origin of PO^+ (*m/e* 47) is an unresolved and interesting problem.

Structures D and E belong to a common class of ions (F) which probably should be called by the general name *phosphacylium ions.* If R and R′ in F are both alkyl groups, the positive charge would be distributed between phosphorus and oxygen in the ground state in analogy to acylium ions, but when an OR or OH group is present (as in D)

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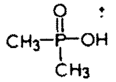
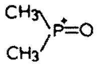
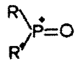
* In this paper, odd-electron ions (such as C) are not charged on any single atom, but even-electron ions (such as D, E, F) are charged on the appropriate atom in the valence bond structure which we think is the predominant contributor to the structure of the ion.



C

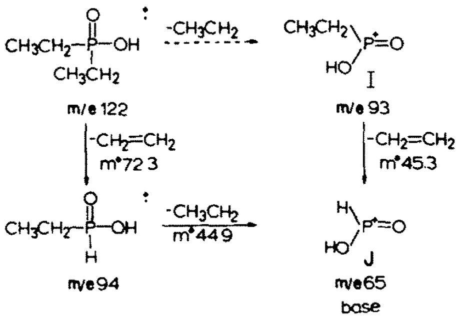


E



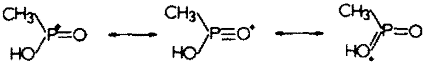
F

CHART I Dialkylphosphinic Acids — Alkyl > Methyl[a]



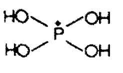
[a] Fragmentation pathways for which metastable peaks were found are indicated by solid arrows; dashed arrows indicate no metastable was found.

additional stabilization is possible (2). The bonding in F would depend on the hybridization at phosphorus; the most reasonable hybridization appears to be trigonal with a p-p π bond in D and the additional π bonding indicated in G and H due to d-p overlap.

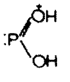


(2)

The mass spectra of the other phosphinic acids are quite different from that of dimethylphosphinic acid. The second largest peaks in the spectra of diethyl- and diisopropylphosphinic acid correspond to loss of one mole of alkene from the parent ion (Chart I). The largest peak in both spectra corresponds to loss of alkene from the type of phosphacylium ion (I) that is most intense in the spectrum of dimethylphosphinic acid. There are metastables (Chart I and Table 1) corresponding to *J* being formed by at least two different pathways. These metastables and the fact that *J* is the base peak in the spectra of diethyl- and diisopropylphosphinic acid indicate that *J* is a particularly stable ion. This fragment, $P(OH)_2^+$, has been noticed in other studies,[7,8] but we propose *J* as the most reasonable structure. The kind of stabilization cited[6] for K probably would not be as important in the alternative structure (L) suggested for $PO_2H_2^+$.[7] The known preference[10] of phosphorus for pentavalent structure over trivalent, which has a primary source the larger bond strengths of P=O and O—H bonds (Eq. 1),[10] supports J as the structure of $PO_2H_2^+$. If L were formed it should very rapidly relax into J.

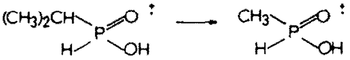


K

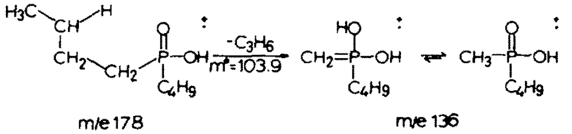


L

Another interesting result is the occurrence of Me transfer after electron impact on diisopropylphosphinic acid. Peaks at mass 80 and 79 correspond to loss of C_2H_4 with Me transfer from peaks at mass 108 and 107, and a metastable is found for 108 → 80 (Table 1) corresponding to



Di-n-butylphosphinic acid. In this phosphinic acid the alkyl groups are of sufficient length to observe the McLafferty rearrangement[4] which is observed in carboxylic acids and esters.[11, 12] From the fragmentation pattern (Table 3), the McLafferty rearrangement apparently occurs (Eq. 3). The tautomeric change indicated in Eq. 3 should be fast and might precede a second rearrangement to give the base peak at $m/e = 94$. Certainly the P=O tautomer for m/e 136 should be considerably more stable.[10] There is an indication of a metastable for 136 → 94, but it is at 65·0 and therefore cannot be definitely detected under the intense 65 peak. The metastable for 122 → 94 indicates that an alternative fragment with $m/e = 94$ can be formed by another pathway.


(3)

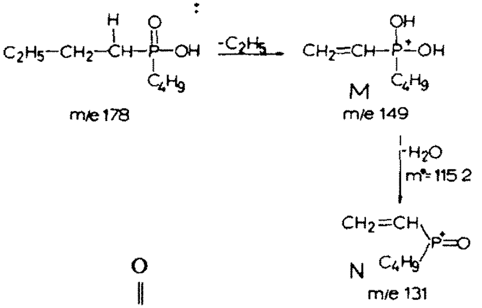
The fragmentation pattern and metastables (Table 3) give evidence of fragmentation processes mentioned above for the lower phosphinic acids:

(1) Phosphacylium ion formation by loss of R is indicated in 94 → 79, for which a metastable is found, and in the probable processes 178 → 121, 122 → 93, and several species → 65.

(2) Elimination of ethylene with H transfer to phosphorus: 93 → 65 ($m^* = 45{\cdot}3$) and 108 → 80 ($m^* = 59{\cdot}3$).

(3) Elimination of ethylene with R transfer to phosphorus appears necessary to explain 122 → 94 ($m^* = 72{\cdot}4$) and formation of ions with $m/e = 93$ and 108.

The 149 peak and the m^* for 149 → 131 can best be explained by another elimination (Eq. 4). Although it is possible that 149 has structure O in analogy to the proposal for carboxylates,[12] the metastable for 149 → 131 lends support to the fragmentation 178 → 149 shown in Eq. 4.*


(4)

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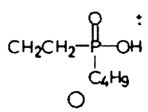
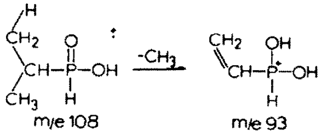
* It is possible that the $+CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}OR$ fragment suggested in studies on carboxylates[12] is actually $CH_2 = CH—\overset{+}{C}\begin{smallmatrix}OH\\OR\end{smallmatrix}$ The latter should be a more stable structure.



We also observe a metastable for 121 → 103 in the mass spectrum of $(Et_2)PO_2H$ (Table 1) analogous to the 149 → 131 process in Eq. 4. The 93 peak in the mass spectrum of $(i\text{-}Pr)_2PO_2H$ can be attributed to another vinyl fragment (Eq. 5).

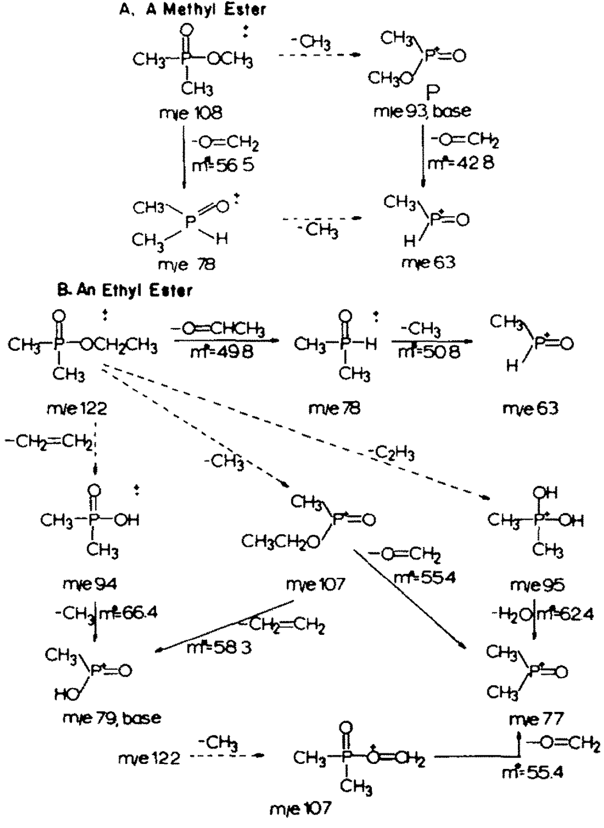
Alkyl Dialkylphosphinates. As has been previously found,[7, 11b] Me esters (Chart IIA) differ from higher alkyl esters (Chart IIB) because of the ease of elimination in the latter. Considering first the three Me esters (Table 2), methyl dimethylphosphinate



(5)

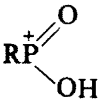
gives a base peak corresponding to a phosphacylium ion (P), but methyl diethylphosphinate and methyl diisopropylphosphinate give base peaks corresponding to Q. This difference is analogous to the results for the acids and supports the stability of phosphacylium ions and their frequent appearance after electron impact on organophosphorus compounds.

CHART II Alkyl Dialkylphosphinates[a]

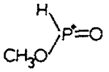


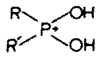
[a] Fragmentation pathways for which metastable peaks were found are indicated by solid arrows; dashed arrows indicate no metastable was found.

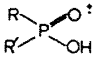
In regard to our discussion of elimination in fragmentations, peaks corresponding to $Me_2P(O)H^+$ are found in the spectra of Me_2PO_2R. It is likely that $>C{=}O$ is eliminated to give this fragment (and in both esters appropriate metastables are found). In higher dialkylphosphinates, the $R_2P(O)H^+$ fragment is less intense; presumably elimination occurs preferentially in the R-P portion of the molecule.

Both dimethylphosphinates give large Me_2PO^+ and $Me(H)PO^+$ peaks which again indicates the tendency for fragmentations to give phosphacylium ions even when there is no OR group for stabilization of that ion. The ethyl and isopropyl esters also give strong phosphacylium ion peaks of the  $R\overset{+}{P}(=O)OH$ type (Table 2) after formation of acid by elimination.

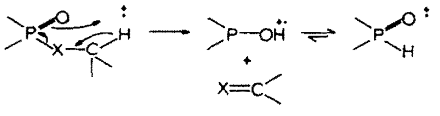
To summarize, phosphacylium ions (F), protonated phosphinate ions (R), and phosphinate ions (S) appear to be the most common fragments in the mass spectra of dialkylphosphinates. The prevalence of phosphacylium ions will probably be a general phenomenon in the mass spectra of organophosphorus compounds.

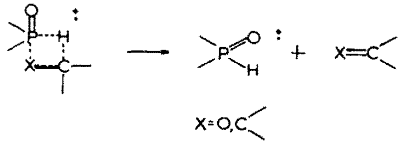

Q


R


S

Elimination at pentavalent phosphorus. The occurrence of elimination after electron impact on phosphines[2] is not surprising since the unshared pair of electrons on phosphorus can participate in the fragmentation. In the examples reported in this paper, phosphorus does not have an unshared pair of electrons, so two explanations are possible for the eliminations we find to be prevalent (Eqs 6, 7). Although carboxylates appear to show some of this process (in propionic acid M-28/M = 0·1),[11a] it is much more common in phosphinates (in diethylphosphinic acid (M-28/M = 9·0). Therefore, although (6) has a less strained transition state, (7) would permit the molecule to fall further in energy (without the secondary tautomerism in Eq. 6). Also, d orbitals could participate in (7), and this would explain the differences between phosphinates and carboxylates.


(6)


(7)

EXPERIMENTAL

The mass spectra were measured with an AEI MS-9 instrument using the heated inlet system, with ionization energy 70 eV and source temp about 200°.

Preparation of the compounds. All the compounds studied were synthesized by known methods[10] and exhibited NMR spectra with expected integrations, chemical shifts, and coupling constants.

The dimethyl- and diethylphosphinic acids were prepared by reaction of the appropriate Grignard with thiophosphoryl chloride to produce the intermediate tetraalkylbiphosphine disulfide which could be oxidized with either H_2O_2 or HgO to the corresponding phosphinic acid.[20] The diisopropylphosphinic acid was prepared by addition of isopropyl Grignard to diethyl phosphonate followed by oxidation with H_2O_2. The dimethyl and diisopropyl acids were easily purified by sublimation; the diethylphosphinic acid was distilled under vacuum.

Typical ester preparations involved formation of the acid chloride either by treatment of the parent acid with a 10% excess of $SOCl_2$ and several drops of N,N-dimethylformamide, or by treatment of the appropriate tetraalkylbiphosphine disulfide with SO_2Cl_2·. To the crude acid chloride was then added a soln of the appropriate RONa, and the esters were purified by vacuum distillation. In the case of methyl diisopropylphosphinate, Cl_3PS was added to isopropyl Grignard, hydrolysis was effected by 10% H_2SO_4, and the thiophosphinic acid (in the ether phase) was converted to acid chloride with SO_2Cl_2. The methyl ester was then obtained by addition of NaOMe to the acid chloride which had been purified by distillation. (Found: C, 51·0; H, 10·3. Calc for $C_7H_{17}PO_2$: C, 51·2; H, 10·4%); NMR spectrum (neat): 6·32 τ, doublet, J = 10 c/s, area $\propto$ 3·4; multiplet centered at 8·1 τ, area $\propto$ 2·2; 8·90 τ, doublet of doublets, J = 15, 7 c/s, area $\propto$ 12.

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