Tetrahedron, 1966, Vol. 22, pp. 1383 to 1389. Pergamon Press Ltd. Printed in Northern Ireland

THE REACTIONS OF DIALKYL HYDROGEN PHOSPHITES WITH ALKYL VINYL ETHERS THE MASS SPECTRA OF THE PHOSPHONATES

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(*Received* 13 *October* 1965; *in revised form* 7 *December* 1965)

Abstract—The mass spectra of eleven dialkyl alkylphosphonates have been determined. The rearrangement under the electron impact, which is found in trialkyl phosphates, trialkyl phosphites and dialkyl hydrogen phosphites, accounts for the major peaks of the phosphonates. The carbon-phosphorus bond shows appreciable cleavage.

MASS spectra of trialkyl phosphates,[1] trialkyl phosphites[2] and dialkyl hydrogen phosphites[3] have revealed a singular mode of cleavage and rearrangement under electron bombardment, giving the oxonium-type of ion as the most stable. This type of rearrangement has also been exemplified in diethyl ethylphosphonate and diisopropyl methylphosphonate.[2] But the cleavage pattern is very simple in alkylphosphine.[4,5]

In order to determine the behaviour of the phosphonates under electron impact, the mass spectra of (i) dialkyl β-alkoxyethylphosphonates (I–VIII; which are the addition products of dialkyl hydrogen phosphites with alkyl vinyl ethers, or the reaction products of β-alkoxyethyl bromide and trialkyl phosphites),[6] and (ii) dialkyl alkylphosphonates (IX–XI; in which the alkyl chain bonded to phosphorus consists of four or eight carbon atoms) were examined. As both ether and phosphonyl groups are present in the former phosphonate molecules, their break-down pattern under the electron impact proved very interesting.

$ROCH_2CH_2P(O)(OR')_2$

I (R = R′ = Et)
II (R = n—Pr R′ = Et)
III (R = n—Bu R′ = Et)
IV (R = *i*—Bu R′ = Et)
V (R = n—Bu R′ = i—Pr)
VI (R = R′ = n—Bu)
VII (R = 2—Ethylhexyl R′ = Et)
VIII (R = 2—Ethylhexyl R′ = n—Pr)

$RP(O)(OR')_2$

IX (R = n—Bu R′ = Et)
X (R = n—C_8H_{17} R′ = Et)
XI (R = 2—Ethylhexyl R′ = Et)

EXPERIMENTAL

Spectra were made with a Hitachi RMU 6D mass spectrometer at an ionization potential of 80 eV. Ion source temp. was 250°. Spectra were taken immediately after distillation for the reasons previously mentioned.[6]

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[1] F. McLafferty, *Analyt. Chem.* **28**, 306 (1956).
[2] J. Occolowitz and G. White, *Analyt. Chem.* **35**, 1179 (1963).
[3] R. Harless, *Analyt. Chem.* 33, 1387 (1961).
[4] M. Halmann, *J. Chem. Soc.* 3270 (1962).
[5] Y. Wada and R. Kiser, *J. Phys. Chem.* **68**, 2290 (1964).
[6] T. Nishiwaki, *Tetrahedron* **21**, 3043 (1965) and subsequent paper.

RESULTS AND DISCUSSION

The mass spectra of the phosphonates (I–XI) exhibit molecular ions of extremely low intensity. These ions are detected and serve for identification when the spectra are taken at maximum sensitivity. The abundance of the (M + 1) ion of dialkyl β-alkoxyethylphosphonates is large enough to be detected at minimum sensitivity. The protonated molecular ion has been observed in the case of ethers, esters, amines, etc. Loss of an hydrogen atom from the molecular ion was not observed.

In the spectrum of diethyl n-octylphosphonate (X), $(M\text{–}C_3H_7)^+$, $(M\text{–}C_4H_9)^+$, $(M\text{–}C_5H_{11})^+$, $(M\text{–}C_6H_{13})^+$ and $(M\text{–}C_7H_{15})^+$ ions were of moderate intensity (R.I. 10 ~ 40), but the $(M\text{–}C_4H_{10})^+$ ion, produced by the scission of both carbon–oxygen linkages of the $P(O)(OEt)_2$ group, was not observed. Similarly, the $(M\text{–}C_4H_9)^+$ ion (R.I. 18) was found for diethyl 2-ethylhexylphosphonate (XI), indicating the fragmentation of a butyl group from the molecular ion. But in the spectra of diethyl and di-n-propyl β-2-ethylhexyloxyethylphosphonates (VII and VIII), $(M\text{–}C_4H_9)^+$ or $(M\text{–}C_2H_5)^+$ were not formed. In VII, $(M\text{–}C_6H_{13})^+$, $(M\text{–}C_8H_{17})^+$ and $(M\text{–}C_{10}H_{21})^+$ and in VIII, $(M\text{–}C_8H_{17})^+$, $(M\text{–}C_{10}H_{21})^+$ and $(M\text{–}C_{12}H_{25})^+$ were of moderate intensity.

It has been shown by McLafferty[7] that in aliphatic ethers with primary alkyl chains, β-bond scission to the ether oxygen is the preferred mode of fragmentation, provided the alkyl chain is unbranched in the vicinity of the oxygen atom. α-Cleavage is another breakdown pattern of aliphatic ethers. The $(CH_2OCH_2CH_2P(O)(OR')_2)^+$ ion is of small to moderate abundance in II, III, IV, VII and VIII, which becomes less significant with increasing number of carbons, or branching of the ester group. The $ROCH_2^+$ ion, only possible by β-cleavage of dialkyl β-alkoxyethylphosphonates, could be detected in I, where the relative intensity of this ion is 14. An ion (*m/e* 31; $CH_2{=}OH^+$), usually observed in the mass spectra of primary alcohols and ethers, was also detected in the spectra of dialkyl β-alkoxyethylphosphonates (I–VIII; R.I. 10 ~ 20). This must be formed from $ROCH_2^+$ or $CH_2OCH_2CH_2P(O)(OR')_2^+$. On the other hand, α-cleavage yields the R^+ ion in greater abundance than the $(CH_2CH_2P(O)(OR')_2)^+$ ion. In this case also, the increased carbon chain reduces this ion to almost negligible abundance (Table 1).

TABLE 1. α- AND β-CLEAVAGES OF THE ETHER LINKAGE IN DIALKYL β-ALKOXYETHYLPHOSPHONATES $ROCH_2CH_2P(O)(OR')_2$

	$(CH_2OCH_2CH_2P(O)(OR')_2)^+$		$(CH_2CH_2P(O)(OR')_2)^+$		R^+	
	m/e	R.I.	*m/e*	R.I.	*m/e*	R.I.
I	195	1	165	14	29	44
II	195	23	165	15	43	39
III	195	15	165	19	57	35
IV	195	33	165	27	57	69
V	223	1	193	—	57	55
VI	251	—	221	—	57	64
VII	195	35	165	18	113	4
VIII	223	20	193	—	113	4

The formation of mass 28 in I, mass 42 in II and mass 56 in III, IV, V and VI are explained by postulating the following cyclic transition state. However, another

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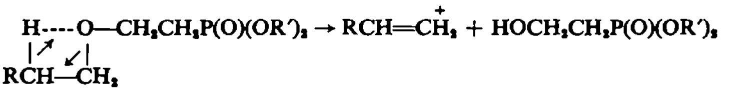
[7] F. McLafferty, *Analyt. Chem.* **29**, 1782 (1957).

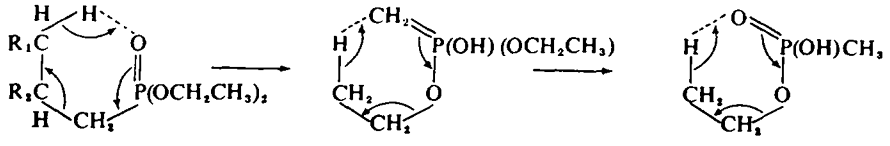
$(CH_2{=}CHP(O)(OR')_2)^+$ ion, capable of being produced by similar α-cleavage with



$$\overset{+}{\mathrm{H}}\text{----}O{-}CH_2CH_2P(O)(OR')_2 \rightarrow RCH{=}\overset{+}{C}H_2 + HOCH_2CH_2P(O)(OR')_2$$
$$RCH{-}CH_2$$

subsequent rearrangement of hydrogen, was not well exemplified.

β-Scission to double bonds such as carbonyl, nitrile, etc., with subsequent rearrangement of hydrogens under the electron impact is well known.[8] The occurrence of this breakdown is highly probable on the alkyl chain directly bonded to the P=O group, which can be demonstrated in the mass spectra of dialkyl alkylphosphonates (IX, X and XI). The ion (*m/e* 152), with the most abundant formation in the ethyl esters X and XI and second prominent in IX, is probably produced via the following six-membered transition state. Further multiple rearrangements of this ion result in



m/e 152
R.I. IX 87
X 100
XI 100

m/e 124
R.I. IX 5
X 4
XI 6

$\rightarrow CH_3P(O)(OH)_2^+ \rightarrow CH_3P(OH)_3^+$

m/e 96
R.I. IX 10
X 7
XI 5

m/e 97
R.I. IX 44
X 25
XI 21

the ultimate formation of the $CH_3P(OH)_3^+$ ion, *m/e* 97. This is supported by the absence of these ions in the spectrum of diethyl ethylphosphonate[2] and by the absence or the negligible amount of these ions in the spectra of diethyl β-alkoxyethylphosphonates, for in these phosphonate molecules the γ-methylene group on the alkyl group directly bonded to phosphorus is unavailable.

The carbon-phosphorus linkage in diethyl ethylphosphonate and diisopropyl methylphosphonate was reported to be stable under electron bombardment[2] and the base peak in the spectra of these compounds corresponded to the $RP(OH)_3^+$ ion. This ion must be formed by multiple stage rearrangement of hydrogens from the cleaved alkyl groups, which will be stabilized due to the resonance of the positive charge between the attached hydroxyl groups.

The formation of this $RP(OH)_3^+$ ion, in which the alkyl group directly bonded to phosphorus atom was not fragmented, could be ascertained in the dialkyl alkylphosphonates (IX, X and XI) although it was not the most prominent ion. This ion is in fairly high abundance in the spectrum of IX (*m/e* 139; R.I. 70), possibly due to the contribution from other ions having the same mass, but only of low abundance in the spectra of X (*m/e* 195; R.I. 14) and XI (*m/e* 195; R.I. 3). Therefore, the breakdown of the carbon chain is significant in the long-chain alkylphosphonates.

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[8] K. Biemann, *Mass Spectrometry, Organic Chemical Applications* Chap. 3. McGraw-Hill, New York (1962) and Refs therein.

Dialkyl β-alkoxyethylphosphonates exhibit a small to almost insignificant $(ROCH_2CH_2P(OH)_3)^+$ ion in which the alkyl group bonded to phosphorus is intact, but in diethyl β-isobutoxyethylphosphonate (IV), the relative abundance of this ion is 21. In several cases (Table 2) the $(ROCH_2CH_2P(O)(OH)_2\text{-}1)^+$ ion is in higher abundance than the $(ROCH_2CH_2P(OH)_3)^+$ ion and in the long-chain β-alkoxyethylphosphonates both ions are not observed.

TABLE 2. IONS IN WHICH THE CARBON–PHOSPHORUS LINKAGE OF DIALKYL β-ALKOXYETHYLPHOSPHONATES IS NOT BROKEN*

	$(ROCH_2CH_2P(O)(OH)(OR'))^+$		$(ROCH_2CH_2P(O)(OH)_2)^+$		$(ROCH_2CH_2P(O)(OH)_2\text{-}1)^+$	
	m/e	R.I.	*m/e*	R.I.	*m/e*	R.I.
I	182	4	154	3	153	34
II	196	1	168	1	167	10
III	210	—	182	8	181	88
IV	210	—	182	5	181	63
V	224	1	182	3	181	5
VI	238	8	182	19	181	1
VII	266	—	238	—	237	—
VIII	280	—	238	—	237	—

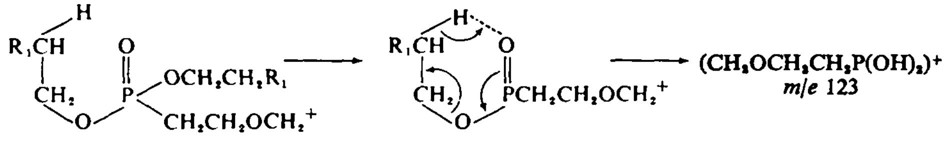
	$(ROCH_2CH_2P(OH)_3)^+$		$(ROCH_2CH_2P(O)(OH))^+$		$(ROCH_2CH_2P(OH)_2)^+$	
	m/e	R.I.	*m/e*	R.I.	*m/e*	R.I.
I	155	3	137	29	138	55
II	169	1	151	4	152	4
III	183	4	165	19	166	58
IV	183	21	165	27	166	57
V	183	10	165	12	166	4
VI	183	1	165	1	166	41
VII	239	—	221	—	222	—
VIII	239	—	221	—	222	—

	$(ROCH_2CH_2P(OR')(OH)_2)^+$		$(ROCH_2CH_2P(O)(OR'))^+$	
	m/e	R.I.	*m/e*	R.I.
I	183	1	165	14
II	197	—	179	5
III	211	—	193	4
IV	211	—	193	2
V	225	3	207	6
VI	239	1	221	1
VII	267	—	249	—
VIII	281	2	263	—

* Contributions from other ions that can appear at the same *m/e* ratio are ignored.

The $(ROCH_2CH_2P(O)(OH))^+$ and $(ROCH_2CH_2P(OH)_2)^+$ ions, which are probably produced by rupture of a single bond of the phosphorus–oxygen linkage and migration of hydrogen atoms, are of low to moderate intensity in I, II, III, IV, V, VI, but not detected in VII and VIII (Table 2). This type of cleavage has been suggested.[3]

The concurrent occurrence of β-cleavage to the ether linkage, scission of the phosphorus–oxygen bond and rearrangement of hydrogens is substantiated by the formation of the $(CH_2OCH_2CH_2P(OH)_2)^+$ ion, *m/e* 123, though the intensity is small to moderate in the spectra of dialkyl β-alkoxyethylphosphonates. This can be explained by the following mechanism. The formation of the ion (XII) is supported by



R_1 H *m/e* 195
R_1 Me *m/e* 223

R_1 H *m/e* 150
R_1 Me *m/e* 164
XII

the appearance of a metastable ion (*m/e* 116) in I, II, III, IV and VII, or (*m/e* 121) in VIII.

Ions formed by the cleavage of the carbon-phosphorus linkage and subsequent migration of hydrogens constitute the major peaks in the spectra of dialkyl β-alkoxyethylphosphonates. These ions are $HP(OR')_2(OH)^+$, $HP(OR')(OH)_2^+$, $HP(OH)_3^+$, etc. and are listed in Table 3, although there may be several different fragments formed by different modes of fragmentation or rearrangement that can appear at the same *m/e* ratio. Similar ions, in which one of the phosphorus–oxygen bonds is severed, are also observed. The occurrence of this type of rearranged ions is also shown in the spectra of dialkyl alkylphosphonates (IX, X and XI) (Table 3).

An ion of mass 125 ($C_3H_9O_3P$) is the base peak in the spectra of I, II, VI and IX, and is among the prominent ions in other ethyl, n-propyl and n-butyl esters, but is less important in the isopropyl ester (V), where the base peak is at *m/e* 109 ($C_2H_6O_3P$). For the n-propyl ester (VIII) an ion (*m/e* 153; $C_6H_{14}O_3P$) is the most abundant. Although no definite account for the genesis of these most prominent ions in the spectra of dialkyl β-alkoxyethylphosphonates is possible at present, they will be formed by the migration of hydrogens. But one probable contribution to the mass 125 in the spectra of dialkyl alkylphosphonates (IX, X and XI) will be the oxonium-type $(CH_3P(OH)_2(OEt))^+$ ion, which can be produced by the hydrogen shift to the $(CH_3P(O)(OH)(OEt))^+$ ion, *m/e* 124.

SUMMARY AND CONCLUSION

The mass spectra of dialkyl β-alkoxyethylphosphonates (I ~ VIII) and dialkyl alkylphosphonates (IX ~ XI) permit a number of inferences to be made. It is clear that the scission of the carbon–phosphorus linkage and the rearrangement of hydrogens are appreciable during electron bombardment of these phosphonates. The former is in direct conflict with the observation by Occolowitz and White[3] on the spectra of diethyl ethylphosphonate and diisopropyl methylphosphonate. Ions thus formed, in which the positive charge remains on the phosphorus-containing fragments, constitute the main peaks.

β-Cleavage of the alkyl group directly bonded to the phosphorus and the shift of hydrogens is the favoured type of fragmentation in dialkyl alkylphosphonates, if the alkyl chain linked to phosphorus consists of three or more carbon atoms. Thus, $(CH_2{=}P(OH)(OR')_2)^+$ ion is afforded as the most prominent or the second abundant ion. Further breakdown of this ion results in the ultimate formation of the oxonium-type $CH_3P(OH)_3^+$ ion.

TABLE 3. IONS IN WHICH THE CARBON–PHOSPHORUS LINKAGE OF DIALKYL β-ALKOXYETHYLPHOSPHONATES AND DIALKYL ALKYLPHOSPHONATES IS CLEAVED*

	$P(O)(OR')_2^+$		$HP(O)(OR')_2^+$		$HP(OH)(OR')_2^+$	
	m/e	R.I.	*m/e*	R.I.	*m/e*	R.I.
I	137	29	138	55	139	21
II	137	46	138	71	139	33
III	137	50	138	77	139	34
IV	137	81	138	70	139	40
V	165	12	166	4	167	25
VI	193	—	194	4	195	—
VII	137	46	138	48	139	40
VIII	165	—	166	1	167	19
IX	137	20	138	50	139	70
X	137	23	138	36	139	60
XI	137	15	138	19	139	51

	$P(O)(OH)(OR')^+$		$HP(O)(OH)(OR')^+$		$HP(OH)_2(OR')^+$	
	m/e	R.I.	*m/e*	R.I.	*m/e*	R.I.
I	109	35	110	26	111	75
II	109	41	110	28	111	80
III	109	96	110	23	111	65
IV	109	100	110	25	111	67
V	123	39	124	32	125	39
VI	137	18	138	5	139	36
VII	109	100	110	16	111	41
VIII	123	16	124	4	125	74
IX	109	34	110	18	111	78
X	109	15	110	9	111	65
XI	109	5	110	5	111	63

	$P(O)(OH)_2^+$		$HP(O)(OH)_2^+$		$HP(OH)_3^+$	
	m/e	R.I.	*m/e*	R.I.	*m/e*	R.I.
I	81	79	82	60	83	29
II	81	88	82	55	83	28
III	81	54	82	34	83	19
IV	81	79	82	39	83	21
V	81	22	82	35	83	8
VI	81	10	82	10	83	50
VII	81	53	82	19	83	18
VIII	81	12	82	21	83	3
IX	81	38	82	36	83	20
X	81	14	82	14	83	14
XI	81	15	82	11	83	16

	$HP(O)(OR')^+$		$HP(OH)(OR')^+$		$HP(O)(OH)^+$	
	m/e	R.I.	*m/e*	R.I.	*m/e*	R.I.
I	93	10	94	2	65	38
II	93	12	94	8	65	47
III	93	8	94	7	65	100
IV	93	12	94	2	65	44
V	107	9	108	3	65	15
VI	121	1	122	—	65	5
VII	93	8	94	4	65	27
VIII	107	4	108	—	65	51
IX	93	23	94	6	65	46
X	93	11	94	4	65	23
XI	93	15	94	4	65	21

* Contributions from other ions that can appear at the same *m/e* ratio are ignored.

The $(CH_2OCH_2CH_2P(O)(OR')_2)^+$ or $ROCH_2^+$ ions, which can be produced by the β-scission to the ether group in dialkyl β-alkoxyethylphosphonates, is of low intensity or not observed at all. The positive charge remains more strongly on the alkyl ion, which is formed by the scission of the carbon–oxygen linkage of the ether, than its counterpart containing the phosphorus group.

Acknowledgement—The author would like to thank Mr. Y. Inamori for the partial measurement of these spectra.