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MASS SPECTROMETRY OF 1-PHENYL-1,2-DIBROMOPROPYLPHOSPHONIC ACID AND ITS METHYL ESTERS

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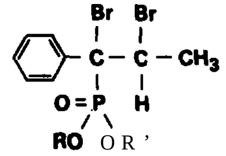
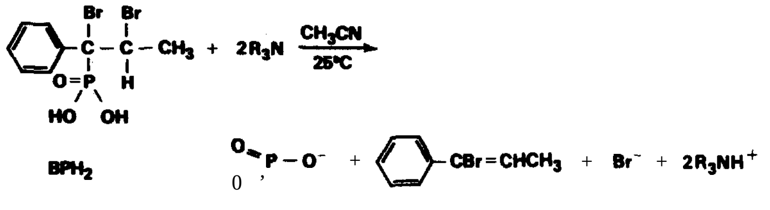
Abstract -- erythro-1-Phenyl-1,2-dibromopropylphosphonic acid-is known to decompose rapidly into the monomeric metaphosphate anion (PO_3), 1-phenyl-1-bromopropene, and bromide ion in **protic** or aprotic solvents in the presence of a hindered tertiary amine. The present study compares the behavior of this **phosphonic** acid in solution and in the gas phase. The gas-phase **thermolysis** of the acid involves mainly the loss of bromine and of the phosphoryl group, -P(O)(OR)(OR') (R = R'= H). The same type of pathway is followed in the ionization/excitation processes ("cationic reactions") that follow from electron impact in mass spectrometry. The thermal and **cationic** reactions of the monomethyl and **dimethyl** esters of the phosphoric acids (R = H, $R'=CH_3$ and R = R'= CH,, respectively, in -P(O)(OR)(OR')) are entirely analogous to those of the free dibasic acid.

We have studied the behavior of erythro-1-phenyl-1,2-dibromopropylphosphonic acid, **BPH_2**, and its mono- and **dimethyl** esters, **MBPH** and DHBP, in the gas phase by the technique of electron-impact mass spectrometry. We have focused attention on both the reactions that precede and those that follow ionization/excitation by electron impact, i.e., on both purely thermal and "**cationic**" reactions. We find that the gas-phase thermal and **cationic** reactions of **BPH_2**, MBPH, and DMBP are all very similar, and result mainly in the loss of bromine atoms and of the phosphoryl group, -P(O)(OR)(OR'), from the molecule or the molecular radical-cation.



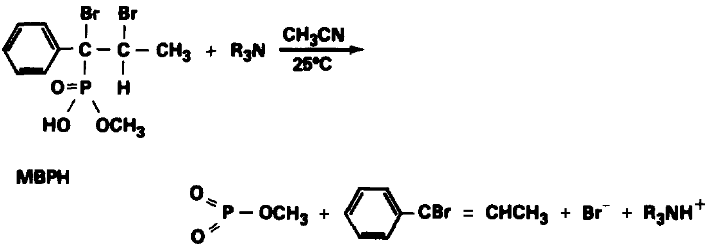
BPH_2 $R = R' = H$
MBPH $R = H, R' = CH_3$
DMBP $R = R' = CH_3$

The present study reveals the inherently different pathways that are available to molecules of the type of the **α,β-dibromoalkylphosphonic** acid, **BPH_2**, and its methyl esters, **MBPH** and DMBP, in the gas phase and in solutions. Previous research has shown that the free acid, **BPH_2**, undergoes rapid loss of the monomeric metaphosphate anion in solution in aprotic solvents according to equation (1) (R_3N = diisopropylethyl amine).' Under the same experimental conditions, the monomethyl ester decomposes into monomeric methyl metaphosphate, according to equation (2).[1] The **dimethyl** ester under similar conditions is stable. Other reactions of **BPH_2**, **MBPH**, and related systems have been described in the literature.[2-9]



BPH_2

(1)



MBPH

(2)

EXPERIMENTAL

Materials. **Z-1-Phenyl-1-propenylphosphonic acid** (Scheme I, 1, R = R' = H), $\delta^{31}P = 8.9$ ppm, $J_{PCCH} = 39$ Hz (in $CDCl_3$; positive chemical shifts are to the low-field side of $H_3PO_4 = 0$), was prepared by the method of Kenyon and Westheimer.[1,4] Bromination of 1 in chloroform at 0° gave erythro-1-phenyl-1,2-dibromopropylphosphonic acid (2, R = R' = H; mp 186-187°C, from CH_3CN). Reaction of the acid with diaxomethane in ether/methanol at 0° provided the dimethyl ester (2, R = R' = CH_3) as an oil. The monomethyl ester (2, R = CH_3, R' = H; mp 158-159°C, from CH_3CN) was obtained when an acetone solution of the diester and LiBr was kept at 25°C for 2 days, followed by acidification of an aqueous solution of the salt.

Mass Spectrometry. Electron-impact mass spectra were measured on a CEC Model 21-110B instrument with electron energy of 70 eV and the source at 250°C. Samples were injected directly into the source via probe, and the spectrum was scanned repeatedly as the probe temperature was gradually raised. In each case volatilization occurred almost solely during one or two such scans. Spectra were recorded in digital form via the AEI DS50S data system at a resolution of 10,000, sufficient to allow unequivocal identification of elemental compositions. Metastable scans, to define decomposition paths, were made by focusing on a selected fragment ion, decoupling the electric-sector voltage from the ion-accelerating voltage, and scanning the latter to increasing values.[10] In view of the propensity of phosphate esters and related species to undergo thermal reactions,[11] we scrutinized the data closely for clues to identify products of such reactions.[11]

RESULTS

Table I shows the spectra of the three bromophosphonates. We have omitted peaks due to hydrocarbon ions smaller than $C_8H_6^{+\cdot}$ and to naturally occurring heavy-isotopic ion contributions other than those containing ^{81}Br as the only heavy isotope. The metastable peaks observed, coupled with ion formulas inferred from high-resolution exact-mass measurements, furnished the data needed to construct decomposition networks, which are displayed in Figures 1, 2 and 3. Reaction steps denoted by solid arrows are supported by ❑ estastable peaks; broken arrows identify steps deemed probable but not so supported. In a few instances, energy resolution was not good enough to allow a clear choice between two possible precursors. Thus, in DMBP, the fragment ions of masses 196/198 and 226 may derive from precursor of mass 305/307 or of 306/308 or both; and in MBPH, the fragment ion of mass 117 may derive from precursor of mass 211 or 212 or both. In each such case, we have included both possibilities in the pertinent figure. Parentheses around an ion formula indicate that no normal peak for that ion was detected; the probable formula in such a case is deduced from the associated daughter-ion formula(s) and the nominal mass difference(s) between parent- and daughter-ion masses.

The spectra can be interpreted in terms of two types of reactions: (i) purely thermal decompositions, and (ii) ionization/dissociation by electron impact on the initial molecules and their thermal decomposition products. The dominant reaction paths, whether solely ionic or a mix of thermal and ionic, are those that effect loss of the phosphoryl groups and bromine. None of the spectra shows a molecular-ion peak. However, the DMBP and MBPH data define fragment-ion compositions and reaction paths that, together, leave little doubt that the bulk of the ion yield arises from the respective parent compounds. Even in BPH,, a ❑ etastable scan of the $C_9H_{10}O_3P^+$ (mass 197) peak identifies as a precursor $C_9H_{11}O_3PBr^+$ (mass 277/279), which most likely arises by

Table I. **Mass** spectra of **1-phenyl-1,2-dibromopropylphosphonic** acid and its methyl esters

Compound		**BPH$_2$**	**MBPH**	DHBP
Composition		$C_9H_{11}O_3PBr_2$	$C_{10}H_{13}O_3PBr_2$	$C_{11}H_{15}O_3PBr_2$
Nominal mol wt^{a}		356/358/360	370/372/374	384/386/388
Initial probe temperature for scan(s) employed, °C		115,240	la3	90
Nominal mass	Ion^{b}	Relative intensity^{c}		
540	$C_{27}H_{27}O_6P_3^{+\cdot}$	1		
406	$C_{20}H_{24}O_5P_3^{+\cdot}$		0.4	
307^{d}	$C_{11}H_{15}O_3PBr^{+}$		7 } e	·18 } f
305^{d}			9	19
294^{d}	$C_{10}H_{14}O_3PBr^{+\cdot}$		11 } g	
292^{d}			10	
293^{d}	$C_{10}H_{13}O_3PBr^{+}$		19 } f	
291^{d}			15	
279	$C_9H_9Br_2^{+}$		2 } h	1 } h
277			4	2
275^{d}			2	1
267	$C_8H_{11}O_3PBr^{+}$		4 } i	
265			1	
266	$C_8H_{10}O_3PBr^{+\cdot}$		1 } i	
264			1	
226	$C_{11}H_{15}O_3P^{+\cdot}$		2^{j}	3^{k}
225	$C_{11}H_{14}O_3P^{+}$		4^{e}	14^{l}
224	$C_{11}H_{13}O_3P^{+\cdot}$			0.2^{m}
213	$C_{10}H_{14}O_3P^{+}$		6^{l}	
212	$C_{10}H_{13}O_3P^{+\cdot}$		17^{k}	0.2^{n}
211	$C_{10}H_{12}O_3P^{+}$		35^{l}	1^{n}
210	$C_{10}H_{11}O_3P^{+\cdot}$		1^{m}	
198	$C_9H_{11}O_3P^{+}$	17^{k}	1^{o}	
197	$C_9H_{10}O_3P^{+}$	20^{l}		
196	$C_9H_9O_3P^{+\cdot}$	19^{m}		
198^{d}	$C_9H_9Br^{+\cdot}$	5 } p	16	10 } p
196		4	13 p	a
197	$C_9H_8Br^{+}$		6 q	2 } q
195			5	1
191	$C_2H_7O_3PBr^{+}$		2 e	7 } r
189			2	7
130	$C_{10}H_{10}^{+\cdot}$		1	1

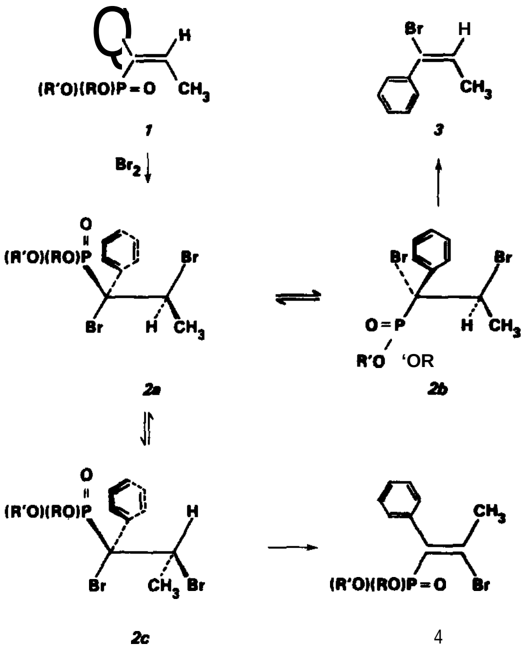
Composition		$C_9H_{11}O_3PBr_2$	$C_{10}H_{13}O_3PBr_2$	$C_{11}H_{15}O_3PBr_2$
Nominal mass	Ion^{b}	Relative intensity^{c}		
129	$C_{10}H_9^{+}$		2	2
117	$C_9H_9^{+}$	46^{s}	88^{s}	100^{s}
116	$C_9H_8^{+\cdot}$	28	36	26
115	$C_9H_7^{+}$	100	100	94
114	$C_9H_6^{+\cdot}$	1	3	1
113	$C_9H_5^{+}$		2	2
109	$C_2H_6O_3P'$		5^{e}	45^{t}
106	$C_7H_6O^{+\cdot}$	1	1	
105	$C_7H_5O^{+}$	5	16	13
104	$C_8H_8^{+\cdot}$	4	1	0.2
103	$C_8H_7^{+}$	6	3	2
102	$C_8H_6^{+\cdot}$	9	10	9
96	$CH_5O_3P^{+\cdot}$		7^{u}	
95	$CH_4O_3P^{+}$		9^{t}	5"
96	$CH_3Br^{+\cdot}$		13	
94			13	
a2	$HBr^{+\cdot}$	43	8	5
80		37	10	5
al	Br^{+}	17	10	3
79		19	9	3
65	$H_2O_2P^{+}$	4	4	1
64	$HO_2P^{+\cdot}$	1	1	0.4
47	OP^{+}	9	10	18

(a) The three values shown for each BP correspond to the three combinations of bromine isotopes. (b) Ion compositions inferred from precise-mass measurements. (c) Value of 100.0 assigned to the most intense peak in each spectrum. In the case of **BPH$_2$**, the spectrum reported here was derived from **summed** intensities over the two scans in which the sample volatilized. *(d)* May include an unresolved contribution from the perfluorokerosene **introduced** to calibrate the mass scale. **(e)** Attributed to **DMBP**. **(f)** **(M - Br)$^{+}$**, where **M** denotes the original molecule. **(g)** **Attributed** to monobromophosphonate molecular ion. (h) **(M - OP(OR)$_2$)$^{+}$**, where R = **H** or **CH$_3$**. (i) Attributed to monobromophosphonate fragment ion. (j) **Attributed to dimethyl** monobromophosphonate fragment ion. **(k)** (M - 2Br)$^{+\cdot}$. **(l)** **(M - Br,HBr)$^{+}$**. **(m)** **(M - 2HBr)$^{+\cdot}$**. **(n)** **Attributed** to **MBPH**. **(o)** **Attributed** to **BPH$_2$**. **(p)** **(M - Br,OP(OR)$_2$)$^{+}$**. **(q)** **(M - HBr,OP(OR)$_2$)$^{+}$**. **(r)** **Suggested structure: (CH$_3$O)$_2$P(Br)OH^{+}**. **(s)** **(M - 2Br,OP(OR)$_2$)$^{+}$**. **(t)** **OP(OR)$_2^{+}$**. **(u)** **HOP(OR)$_2^{+\cdot}$**.

loss of a bromine atom from the **BPH$_2$** molecular ion; hence some **BPH$_2$** apparently volatilized and remained intact long enough to undergo ionization/dissociation by electron impact. The most abundant products in all three spectra are C_9 hydrocarbon ions.

To facilitate description of possible reactions, we show in Scheme I the three staggered conformations, **2a**, **2b** and **2c**, of the **α,β-dihalophosphonates** and the unsaturated compounds, E-I-phenyl-1-bromopropene, **3**, and the Z-1-phenyl-2-bromopropenylphosphonate derivatives, **4**, that would result from elimination reactions *via trans*-coplanar transition states (E2 mechanism). Evidently, the thermal and **cationic** decompositions occurring under the conditions of our experiments need not conform to this concerted mechanism and, hence, product stereochemistry. Molecular models suggest that conformers **2a**, **2b** and **2c** are very crowded, and there seems to be considerable steric hindrance to rotation around the single C-C bond that is needed to interconvert the conformers. It is virtually impossible to rotate the phenyl ring around its C-C bond in the models.

Scheme I



Dimethyl phenyldibromopropylphosphonate. Figure 1 shows a proposed partial decomposition network under electron impact for DMBP and associated thermal reaction products. The data show two well defined primary processes in decomposition of the DMBP molecular ion: loss of a bromine atom and loss of the phosphoryl radical. These same processes, and losses of **HBr** and of the phosphoryl group in conjunction with either a hydrogen or a bromine atom, comprise a large part of the secondary and tertiary reaction steps.

The data reveal also contributions from chemical species other than DMBP. Metastable scans of the $C_{11}H_{15}O_3P^{+\cdot}$ (mass 226) and $C_9H_9Br^{+\cdot}$ (mass 196/198) peaks identify a **common** precursor of mass 3061308, which we picture as the molecular ion of **dimethyl** phenylmonobromopropylphosphonate; the molecule is most probably formed by thermal loss of Br· from DMBP followed by a **hydrogen**-abstraction step. The weak $C_{10}H_{12}O_3P^+$ (mass 211) and $C_{10}H_{13}O_3P^{+\cdot}$ (mass 212) peaks probably indicate a little **MBPH** (see below), possibly present as an impurity from the synthesis. Additional molecular species apparently present in the vapor in the ionization chamber are: (a) $C_2H_6O_3PBr$, mol wt 188/190, presumably dimethoxyphosphoryl bromide, possibly formed by coupling of a bromine atom and a dimethoxyphosphoryl radical; (b) $C_{11}H_{13}O_3P$, mol wt 224, presumably formed by loss of 2BBr from DMBP; and (c) HBr, mol wt 80/82, the **presence** of which supports the suggested reaction path leading to (b) (see below).

The only metaphosphate species indicated in this spectrum is CH_3OPO_2, the neutral product formed with $C_9H_9^+$ (mass 117) from the **MBPH** fragment ion $C_{10}H_{12}O_3P^+$ (mass 211).

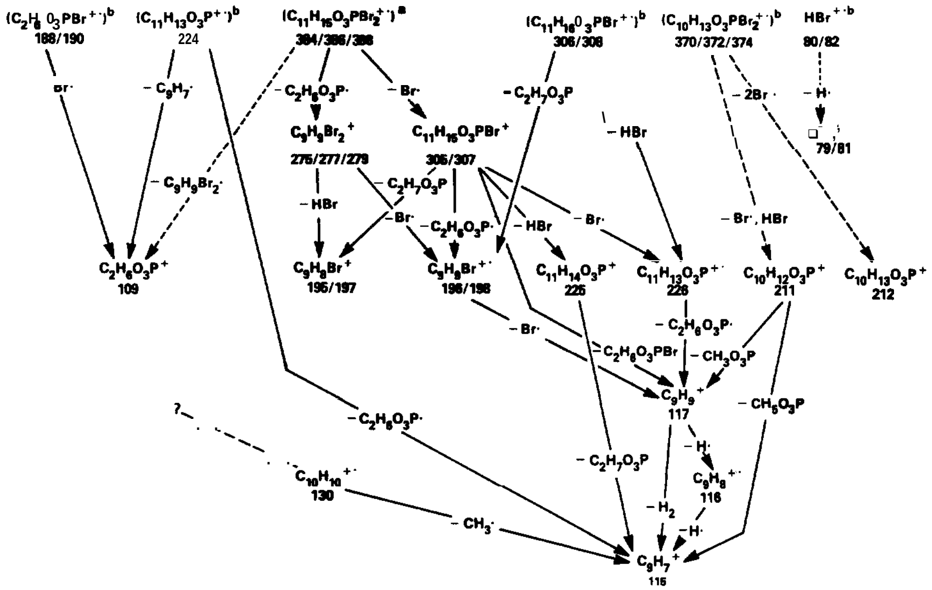


Figure 1. Decomposition of dimethyl phenyldibromopropylphosphonate under electron impact. [a]DMBP molecular ion. [b]Probable molecular ions of other species.

<u>Phenyldibromopropylphosphonic acid</u>. Figure 2 shows a proposed partial decomposition network under electron impact for BPH_2 and associated thermal reaction products.

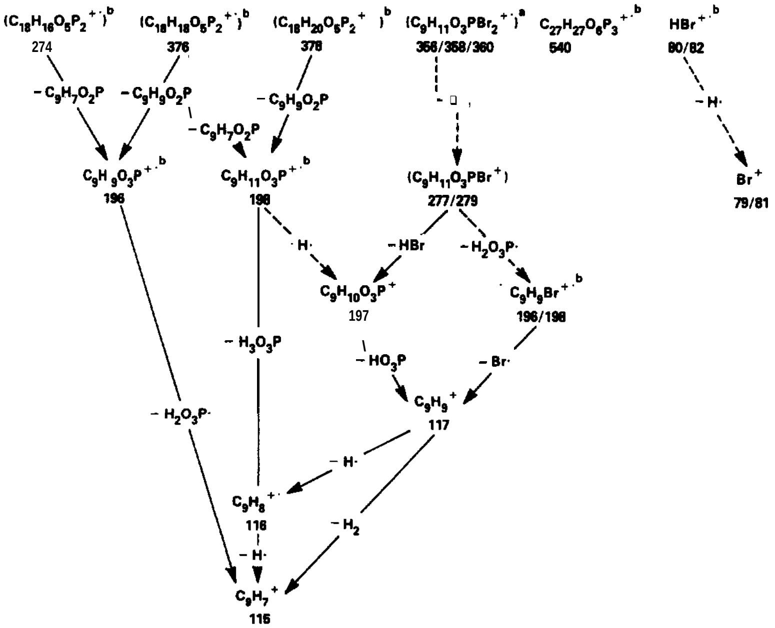
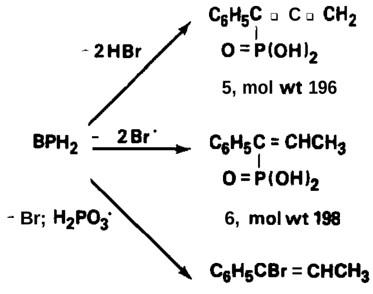


Figure 2. Decomposition of phenyldibromopropylphosphonic acid under electron impact.
[a] BPH_2 molecular ion. [b] Probable molecular ions of other species.

Except for a small peak at mass 540 the spectrum obtained from BPH, shows nothing at mass values beyond the prominent grouping at 196/197/198. Precise-mass measurements on these peaks identify the major contributing ions as containing phosphorus but no bromine, accompanied by ions retaining one bromine atom but free of phosphorus. Formation of the corresponding neutral molecules from BPH, by thermal processes is pictured in equations (3)-(5).

Metastable scans of the peaks of masses 196 and 198 reveal precursors of masses 374, 376, and 378. These masses can be accounted for by loss of H_2O from the three possible combinations of two units each of mass 196 or 198. We therefore assign them to anhydrides -- i.e., pyrophosphonates -- of the phosphorus-containing species of masses 196 and 198, as shown in equations (6)-(8).



(3)

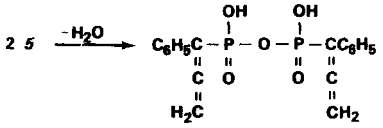
5, mol wt 196

(4)

6, mol wt 198

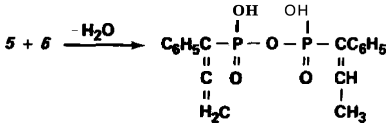
(5)

3. mol wt 196/198



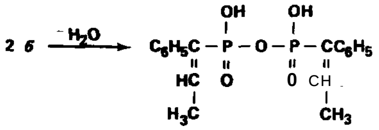
(6)

7, mol wt 374



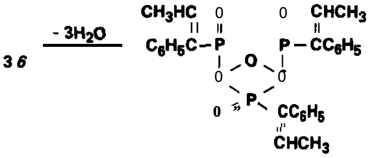
(7)

8, mol wt 376



(8)

9, mol wt 378



(9)

10, mol wt 540

The four metastable peaks observed in these scans are very weak, suggesting that cationic decompositions of 7, 8, and 9 make only a small contribution to the ion yields at 196 and 198. Probably the bulk of $C_9H_9O_3P^{+\cdot}$ (mass 196) and $C_9H_{11}O_3P^{+\cdot}$ (mass 198) are the molecular ions of thermal decomposition products which arise, respectively, by loss of 2HBr and 2Br· from BPH, as shown in equations (3)-(5). Possible mechanisms for these reactions will be suggested in the Discussion section. The $C_9H_9Br^{+\cdot}$ that also appears at masses 196 and 198 may arise by thermal loss of Br· and $(HO)_2PO\cdot$ from BPH, to yield 1-propenyl bromide 3 (Scheme I), followed by ionization. The data do not permit a distinction between this sequence and an alternative one in which Br· and $(HO)_2PO\cdot$ are lost successively from the molecular ion of BPH,.

The compound of mol wt 540 may be the cyclic triphosphonate 10 derived from the I-propenylphosphonic acid 6, as shown in equation (9). Exact-mass measurement supports the composition $C_{27}H_{27}O_6P_3^{+\cdot}$ and hence is consistent with this structure.

Metastable scans of the $HBr^{+\cdot}$ peaks at masses 80/82 reveal no precursors. As in previous work,[11] we take this negative finding as evidence that the ion formed via electron impact on HBr derived from a thermal reaction, such as (3).

In Figure 2, the formation of $C_9H_9O_3P^{+\cdot}$ (mass 196) and $C_9H_{11}O_3P^{+\cdot}$ (mass 198) by decomposition of the molecular ions of the symmetrical allenephosphonic anhydride 7, the mixed allenepropenylphosphonic anhydride 8, and the symmetrical propenylphosphonic anhydride 9 implies loss as neutral products of three-coordinate phosphorus compounds, derived from phosphonates in the same way that metaphosphates are derived from orthophosphates. Similarly, the loss of metaphosphoric acid as a neutral product is implicit in the decomposition step $C_9H_{10}O_3P^+$ (mass 197) → $C_9H_9^+$ (mass 117).

Monomethyl phenyldibromopropylphosphonate. The data on this ester are summarized in Figure 3. As in the case of the phosphoacetoins,[11] the spectrum of the monomethyl ester exhibits the most

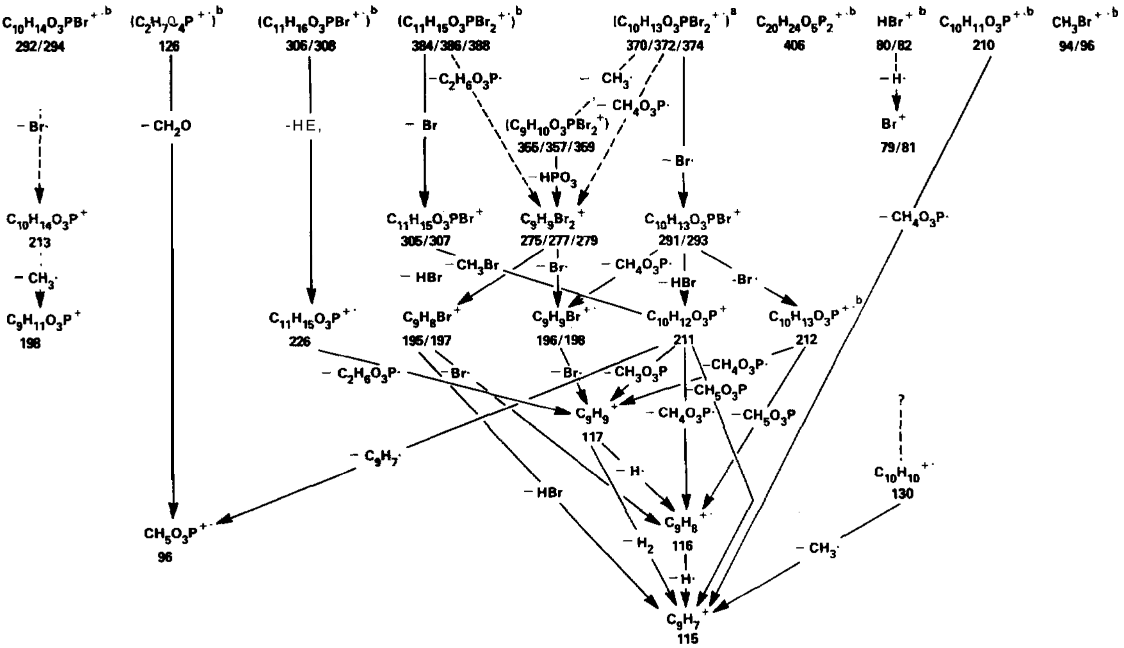
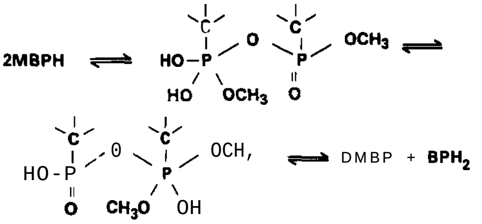


Figure 3. Decomposition of monomethyl phenyldibromopropylphosphonate electron impact.
ᵃ MBPH molecular ion. ᵇ Probable molecular ions of other species.

complex overall chemistry of the three BPs. It shows DMBP, suggesting, by analogy with monomethyl phosphoacetoin, a disproportionation, which may occur <u>via</u> a dimeric intermediate as pictured in equation (10), although we are not able to confirm the accompanying formation of BPH_2. We take $C_{10}H_{14}O_3PBr$, mol wt 292/294, and $C_{11}H_{16}O_3PBr$, mol wt 306/308, to be the monomethyl and dimethyl monobromophosphonates, probably arising, as described above, by loss of a bromine atom from MBPH and DMBP, respectively, followed by hydrogen abstraction. $C_{10}H_{11}O_3P$, mol wt 210, is apparently the homologue of $C_{11}H_{13}O_3P$ and $C_9H_9O_3P$ in the spectra obtained from DMBP and BPH_2, respectively, and is presumably formed by loss of 2HBr from MBPH; this reaction is also the probable source of the HBr observed.



(10)

The elemental composition of the $C_{20}H_{24}O_5P_2^{+\cdot}$ ion, mass 406, is equivalent to that of $2C_{10}H_{13}O_3P^{+\cdot}$, mass 212, less H_2O. Hence it would seem most readily accounted for as the molecular ion of a pyrophosphonate arising by condensation/dehydration of two molecules that in turn form by loss of 2Br· from MBPH. If so, the observed intensity at mass 212 is most likely due in part to the molecular ion of this debromination product and only in part to a fragment ion from a sequence in which loss of the two bromine atoms follows ionization of MBPH, as shown in the figure. The composition $C_2H_7O_4P$, mol wt 126, denotes dimethyl phosphate. If the disproportionation alluded to above proceeds <u>via</u> the suggested MBPH dimer, this dimer would seem to be a potential precursor as well of the dimethyl phosphate. The dimer may also be a precursor of CH_3Br, which, like dimethyl phosphate, we find only in the spectrum of MBPH.

A series of normal mass spectra interspersed as controls among the metastable scans revealed pronounced changes in the spectrum, accompanied by an increase in vapor pressure, at a probe temperature of about 200°C. Intensity at 305/307, attributed to DMBP, remained essentially constant, but that at 291/293, attributed to MBPH, dropped sharply, and new peaks grew in at 274/276/278, with an isotopic intensity profile matching that expected for a dibromo compound. The apparent bromine content and molecular weight are plausibly attributed to 1-phenyl-1,2-dibromopropene, corresponding to thermal loss from MBPH of the phosphoryl radical plus a hydrogen atom, presumably as monomethyl phosphite. In accord with this suggestion, the spectrum obtained from MBPH, unlike those from DMBP and BPH,, contains a peak for $CH_5PO_3^{+\cdot}$ (mass 96), the composition of which corresponds to the molecular ion of monomethyl phosphite.

The network of Figure 3 shows two ionic reaction steps in which metaphosphate species are eliminated as neutral products, namely, the loss of $HOPO_2$ from $C_9H_{10}O_3PBr_2^+$ (mass 355/357/359) to produce $C_9H_9Br_2^+$ (mass 275/277/279), and the loss of CH_3OPO_2 from $C_{10}H_{12}O_3P^+$ (mass 211) to produce $C_9H_9^+$ (mass 117). The latter appears to be a precise counterpart of the loss of $HOPO_2$ from $C_9H_{10}O_3P^+$ (mass 197) to produce $C_9H_9^+$ (mass 117) in the decomposition of BPH_2, as shown in Figure 2.

DISCUSSION

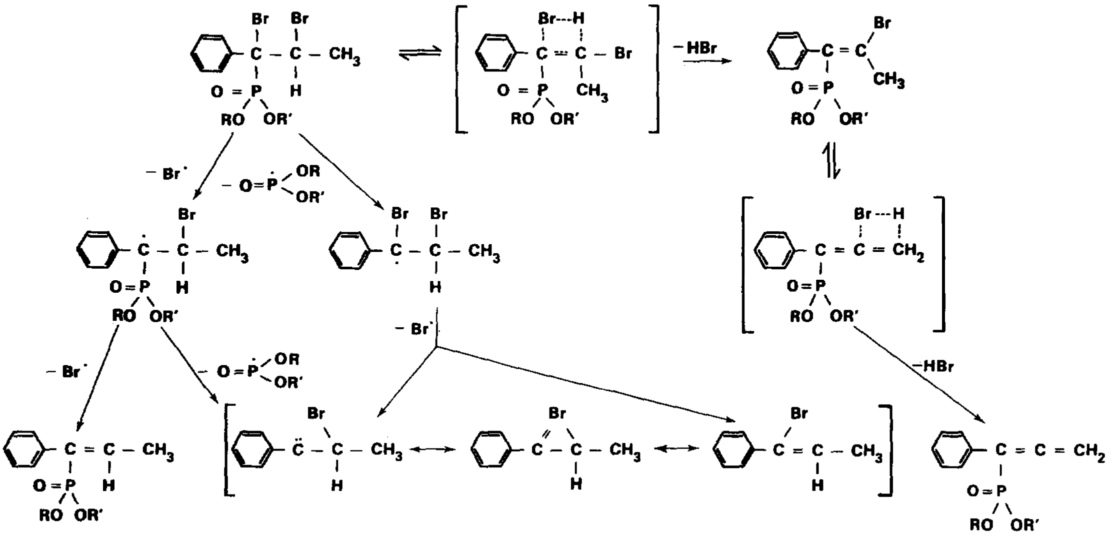
The relative contributions of thermal and cationic reactions range from predominantly thermal in the acid BPH, to predominantly cationic in the neutral ester DMBP. The greater complexity of the spectrum of the monomethyl ester MBPH reflects its intermediate position on this scale. In the bromophosphonates, as well as in the phosphoacetoins,[11] the presence or absence of acidic hydrogens determines the temperature at which the compounds volatilize and also the pathways by which they react at a given temperature.

In terms of their origins, the products of thermal reactions fall into two categories: (a) those formed by reaction sequences or concerted processes initiated by loss of a bromine atom, a phosphoryl radical, HBr, or a phosphite; and (b) those formed in processes that involve dimerization, trimerization, or disproportionation. The dimers in the (b) category may be pyrophosphonates or oxyphosphoranes with 5-coordinate phosphorus. In cationic reaction paths, the main primary steps are loss of a bromine atom and loss of a phosphoryl radical. These are followed, for the most part, by further losses of one or the other of these same species, free or in combination with a hydrogen atom. If we limit-ourselves to consideration of unimolecular events, the thermal and cationic reactions of the BPs parallel each other closely.

We have identified a few reaction steps, both thermal and cationic, that give rise to metaphosphate-type products, but such processes seem to play no more than a small part in the entire reaction networks. In this respect, these reactions differ sharply from reactions of BPH_2 and MBPH in basic solutions. In solution, acidic groups on the BP phosphorus atom are subject to deprotonation to form anions, which then dissociate readily to yield metaphosphate species, as shown in equations (1) and (2). In contrast, the neutral molecules and their corresponding radical-cations whose behavior we have now examined react by pathways dictated by different driving forces.

In the gas-phase thermal reactions the primary bond scission occurs at a carbon-bromine bond or, to a lesser extent, a carbon-phosphorus bond, as shown in Scheme II. In both cases, we assume a

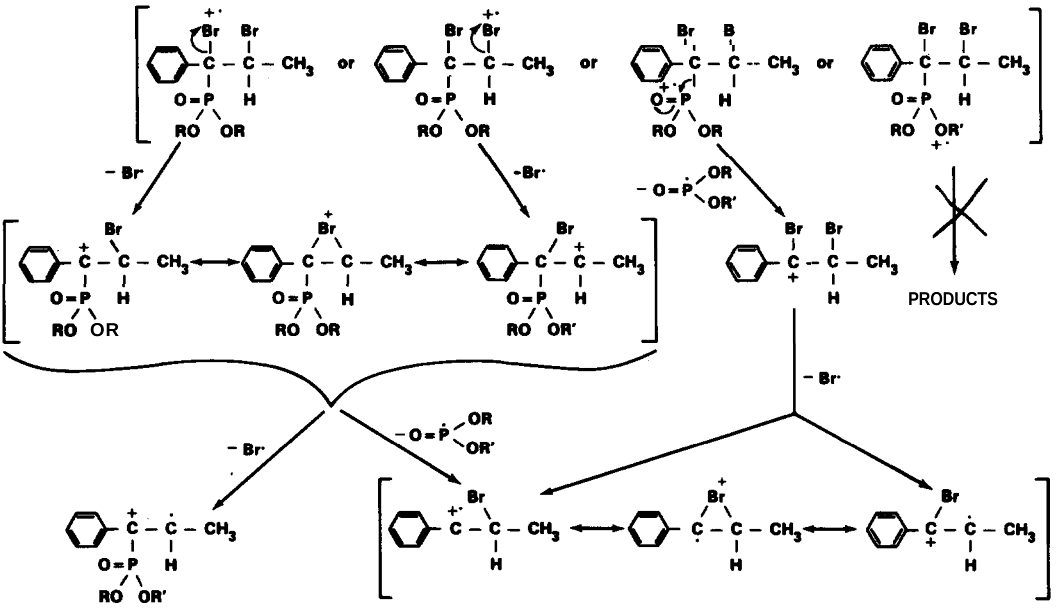
Scheme II. **Thermal Reactions**



homolytic cleavage of the bond with formation of a resonance-stabilized **benzyl** radical. The driving force for the subsequent loss of a second bromine atom or phosphoryl radical seems to be associated with the formation of a styrene derivative or an a-bromocarbene. An interaction between the carbenoid center and the a-bromo substituent, which is represented as a neutral cyclic **three-**centered bronane or **brominane,**[12] may function to stabilize the **carbene** and to facilitate the interconversion between **carbenes** and styrene structures. A second type of thermal reaction, also depicted in Scheme II, is the primary loss of **HBr.** The product is, presumably, E-1-phenyl-2-bromopropylphosphonic acid or the corresponding methyl ester, E-4, an isomer of the olefin, **Z-4,** that would be obtained in a base-catalyzed dehydrobromination in solution **(Scheme I).**

The postulated gas-phase **cationic** reactions are shown in Scheme III. Again, the primary bond scission occurs at a carbon-bromine bond and, to a lesser extent, at the carbon-phosphorus bond.

Scheme III. Cationic Reactions



Now the intermediate is a carbocation represented in its usual cyclic and acyclic resonance structures. These steps are assumed to be heterolytic. The subsequent loss of a second bromine atom or a phosphoryl radical would produce the radical-cations corresponding to the styrene derivatives shown in Scheme II. Scheme III also suggests reasonable sites for charge localization in the BP molecular ion. Charge localization in a nonbonding orbital of either bromine atom is presumed to trigger the loss of that atom. The respective carbon-bromine bond cleavages result in the resonance-stabilized carbocation ↔ bromonium ion, in which the distinction between the two sites considered for the initial ionization has vanished. Charge localization in a non-bonding orbital of the doubly bonded phosphoryl oxygen would set the stage for the formation of the observed bromostyrene radical-cation via successive losses of the phosphoryl radical and a bromine atom. Finally, charge localization is also possible in an alkoxy (or hydroxy) group attached to phosphorus, as also shown in Scheme III. The products to be expected from decomposition of a molecular ion fitting this description would logically involve the cleavage of a phosphorus-oxygen or a carbon-oxygen bond. Such products do not appear in any of the spectra.

In conclusion, the observed loss of a phosphoryl radical in thermal, as well as cationic, decomposition of the **α,β-dibromopropylphosphonates** suggests that such a radical, rather than a monomeric metaphosphate species, may also be the intermediate in the formation of phosphorylated products when **BPH_2** and **MBPH** in solution are heated in a sealed tube.[2]

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