

Mass Spectrum, Mechanism and Structure in the Ion Chemistry of Trimethylmethylenephosphorane

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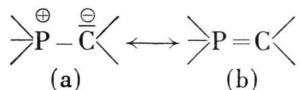
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The gas phase ion chemistry of the simplest known phosphorus ylide, trimethylmethylenephosphorane, has been studied in the mass range $m/e=2-186$ and the pressure range $10^{-7}-10^{-4}$ Torr. The most abundant product ion, $m/e=104$, $(\text{CH}_3)_2\text{C}_2\text{H}_5\text{PCH}_2^+$ is formed by a methylene group transfer reaction of the molecular ion. Almost all of the other product ions formed from the molecular ion can be subsumed under the general formula $(\text{CH}_3)_3\text{PCHPR}_n^+$ ($\text{R}=\text{H}, \text{CH}_3$; $n=1,2,3$). The reactions indicate that the molecular ion has lost its ylide character almost completely. The protonated molecule is formed almost exclusively by a reaction of the fragment ion $m/e=75$. This reaction and the CH_3PH group transfer reaction indicate a cyclic structure $(\text{CH}_3)_3\text{HP}(\text{CH}_2)_2^+$ for this ion. A cyclic structure is also assumed for the ion $m/e=73$, PC_3H_6^+ , which undergoes P and PH transfer reactions. The reactions of the ion $m/e=47$ are consistent with the structure CH_3PH^+ . The ICR and mass spectra are given, some metastable decompositions are discussed.

Introduction

Although trimethylmethylenephosphorane has been known since 1949¹ and a multivarious chemistry of the ylides has since been established², the pure compound was first prepared in 1967 by Schmidbaur and Tronich^{3,4}. Until now several investigations on the NMR⁵⁻⁷, photoelectron⁸ and IR spectra⁹ of trimethylmethylenephosphorane have been published. Also several theoretical studies^{10,11} of simple ylides have appeared in the literature. The reactions of ylides are characterised by electrophilic phosphorus atoms and nucleophilic carbon atoms. Their structure is written in general as a resonance hybrid:



Most of the typical reactions can be rationalised by the structure (a). NMR investigations also indicate a dipolar ylide structure with an sp^2 carbanion and an sp^3 phosphonium center. Sawodny⁹ concludes from his calculations of the force constants that the P–C bond has some double bond character. C–P $\text{d}_{\pi}-\text{p}_{\pi}$ bonding is also concluded from ab initio calculations on the simplest phosphorus ylide carried out by Absar et al.¹⁰.

However, neither a mass spectrum¹² nor an investigation of the ion chemistry of this compound have been published. In this work, the mass spec-

trum, the ion cyclotron resonance (ICR) spectrum and an ICR spectrometric investigation of the ion chemistry of trimethylmethylenephosphorane is presented.

Experimental

The details of the ICR spectrometer and the realisation of the experiments were described elsewhere^{13,14}. The spectra were recorded at an electron energy of 30 eV in the pressure range between 10^{-7} and 10^{-4} Torr. The mass range from $m/e=2$ to 186 was covered. All the ions which appear in the spectrum were subject to double resonance experiments at several pressures and irradiating field strengths. The double resonance results were supported by pressure plots if possible. The ylide could be handled without any decomposition in the spectrometer inlet system and measuring cell. Also no thermal decomposition at the hot filament could be detected.

The trimethylmethylenephosphorane, which was prepared according to the method described by Schmidbaur et al.³ was purified by trap-to-trap distillation and stored in vacuo at liquid nitrogen temperature.

The mass spectra were recorded with a CH 4 mass spectrometer (Varian MAT, Bremen) which was equipped with a room temperature ion source.

Results and Discussion

ICR and Mass Spectra

The ICR spectrum of trimethylmethylenephosphorane is shown in Fig. 1 and listed in Table 1. The

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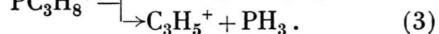
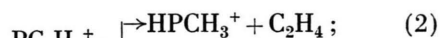
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Tab. 1. ICR and mass spectra of trimethylmethylenephosphorane at an electron energy of 30 eV.

<i>m/e</i>	ion comp.	ICR spectrum <i>p</i> = 4 × 10 ⁻⁷ Torr	mass spectrum
14	CH ₂ ²⁺		31
15	CH ₃ ⁺	31	496
16	CH ₄ ⁺	41	686
27	C ₂ H ₃ ⁺		62
28	C ₂ H ₄ ⁺		62
29	C ₂ H ₅ ⁺		34
32	PH ⁺		18
41	C ₃ H ₅ ⁺	455	467
42	C ₃ H ₆ ⁺		17
43	PC ⁺		10
44	PCH ⁺		48
45	PCH ₂ ⁺	249	155
46	PCH ₃ ⁺	74	42
47	HPCH ₃ ⁺	605	472
48	H ₂ PCH ₃ ⁺		17
49	H ₃ PCH ₃ ⁺		31
57	PC ₂ H ₂ ⁺	138	73
58	PC ₂ H ₃ ⁺	61	38
59	PC ₂ H ₄ ⁺	300	240
60	PC ₂ H ₅ ⁺	24	22
61	P(CH ₃) ₂ ⁺	104	212
62	HP(CH ₃) ₂ ⁺	36	27
71	PC ₃ H ₄ ⁺	63	41
73	PC ₃ H ₆ ⁺	342	257
74	PC ₃ H ₇ ⁺	23	26
75	PC ₃ H ₈ ⁺	772	936
76	(CH ₃) ₃ P ⁺	93	99
77	(CH ₃) ₃ PH ⁺	56	157
89	(CH ₃) ₃ PCH ⁺		16
90	(CH ₃) ₃ PCH ₂ ⁺	1000	1000
91		107	55
92		20	82

molecular ion *m/e* = 90 is the base peak. The ion *m/e* = 76, (CH₃)₃P⁺, is much less abundant than the ion *m/e* = 75, PC₃H₈⁺, indicating that a methyl group is dissociated much easier than a methylene group from the molecular ion in the primary processes, which lead to the formation of the fragment ions. Primary ions which contain P–H bonds and hydrocarbon ions are observed with medium abundances. Such ions have already been observed in the cases of trimethylphosphine¹³ and tetramethyldiphosphine¹⁵. In the spectrum the proportion of such ions increases strongly in the order P(CH₃)₃ < P₂(CH₃)₄ < (CH₃)₃PCH₂. Several fragment ions which are composed only of carbon and hydrogen atoms have also been detected in the mass spectrum of trimethylphosphine. The abundance of the ion *m/e* = 41, C₃H₅⁺, is surprisingly high in the spectrum of (CH₃)₃PCH₂. This ion is formed also in the case of trimethylphosphine by a rearrangement including the methylene group and the two methyl groups of the ion *m/e* = 75, as detected by an investigation of the metastable decompositions¹⁶.

The metastable ions, appearing in the mass spectrum of trimethylmethylenephosphorane show that several primary ion formation processes proceed very similarly in trimethylphosphine and trimethylmethylenephosphorane:



In both cases the molecular ion decomposes to the ion *m/e* = 75 (reaction 1) which decomposes further to the ions *m/e* = 47 (reaction 2) and 41 (reaction 3).

The mass spectrum of trimethylmethylenephosphorane is also listed in Table 1. It is in good qualitative agreement with the ICR spectrum, however, the relative intensities show several differences. Such differences between mass spectra and ICR spectra are not uncommon in the case of organophosphorus compounds^{13–15}. They are to be expected especially in the case of very reactive compounds.

In Fig. 2 an ICR spectrum of (CH₃)₃PCH₂ is shown at a pressure of 1.6 × 10⁻⁵ Torr. The relative intensities of the primary ions have changed and numerous product ions are to be observed.

Pressure Dependences of the Relative Intensities

The pressure dependences of the mass-corrected relative intensities of the major ions are shown in Fig. 3, those of the ions of medium and low abundances are in Fig. 4 and Fig. 5, respectively. It can be seen, that all the primary ions are reactive at pressures above 10⁻⁶ Torr. At pressures higher than 10⁻⁵ Torr the spectrum consists of only a few intense ions, namely the molecular ion which is formed by charge transfer reactions, the protonated molecule which is now the most abundant ion and the ion *m/e* = 104. The other product ions never have abundances greater than 6%. The intensities of the majority of them pass through more or less pronounced maxima as does the molecular ion.

Ion-Molecule Reactions

The ion-molecule reactions of the positive ions of trimethylmethylenephosphorane are listed in Table 2. Only the most probable compositions of the ions resulting from a consideration of their ion-molecule

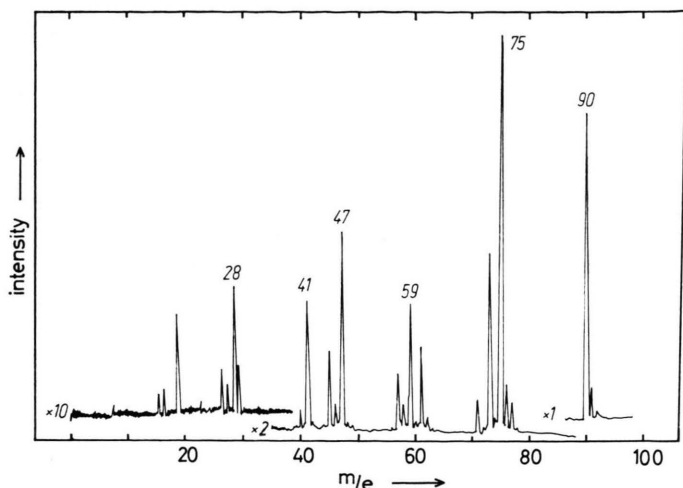


Fig. 1. ICR spectrum of trimethylmethylenephosphorane at an electron energy of 30 eV and a pressure of 5.6×10^{-7} Torr.

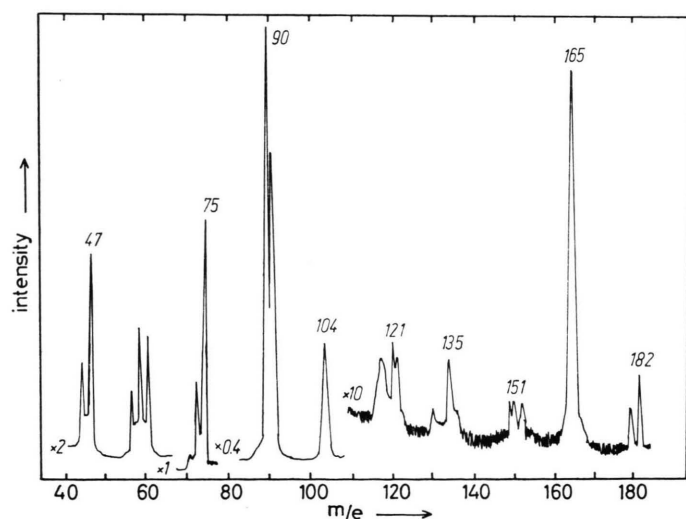


Fig. 2. ICR spectrum of trimethylmethylenephosphorane at an electron energy of 30 eV and a pressure of 1.6×10^{-5} Torr.

reactions are given. It is possible to subsume all the reactions under a few simple principles, already known from ylide chemistry. However, in the gas phase ion chemistry products appear which are often not stable in solution. This fact is very pronounced in the case of the molecular ion and will be discussed later.

All the reactions show that the molecular ion and the fragment ions have lost their ylide character

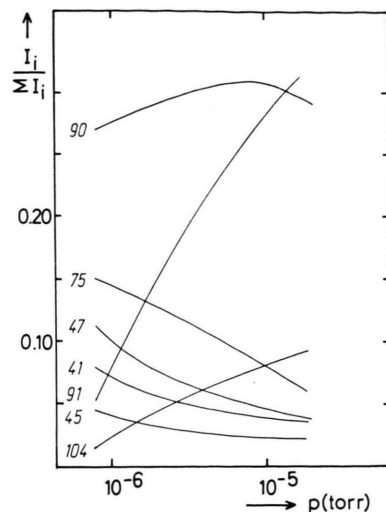


Fig. 3. Mass-corrected relative intensities of the major ions in the ICR spectrum of $(\text{CH}_3)_3\text{PCH}_2$ as a function of the total pressure.

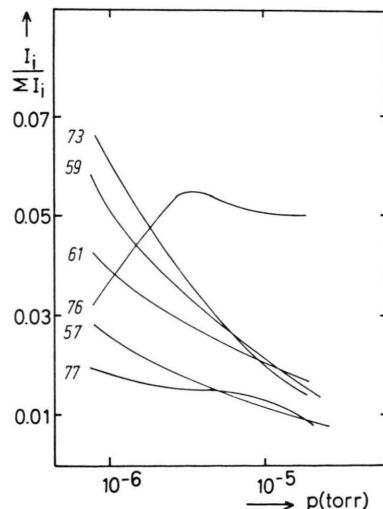
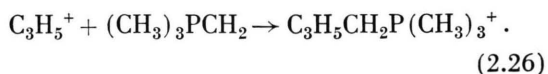


Fig. 4. Mass-corrected relative intensities of the medium abundant ions in the ICR spectrum of $(\text{CH}_3)_3\text{PCH}_2$ as a function of the total pressure.

almost completely and therefore the ion chemistry can be interpreted in terms of reactions of neutral ylide molecules with phosphonium, phosphinium and phosphenium ions.

Also an interesting addition reaction occurs between the neutral ylide and the ion $m/e = 41$, C_3H_5^+ :



Tab. 2. Product ions of the ion-molecule reactions of trimethylmethylenephosphorane.

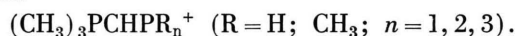
Product ions <i>m/e</i>	ion composition	Reacting ions <i>m/e</i>	ion composition	No.
61	$P(CH_3)_2^+$	47	$HPCH_3^+$	1
76	$P(CH_3)_3^+$	47	$HPCH_3^+$	2
		90	$(CH_3)_3PCH_2^+$	3
		104	$(CH_3)_2(C_2H_5)PCH_2^+$	4
77	$HP(CH_3)_3^+$	47	$HPCH_3^+$	5
87	$PC_4H_8^+$	73	$PC_3H_6^+$	6
		75	$PC_3H_8^+$	7
91	$(CH_3)_4P^+$	47	$HPCH_3^+$	7a
		75	$PC_3H_8^+$	8
		(104)	$(CH_3)_2(C_2H_5)PCH_2^+$	9
92	$P_2C_2H_6^+$ $((CH_3)_4PH^+)$	77	$(CH_3)_3PH^+$	10
103	$PC_5H_{12}^+$	75	$PC_3H_8^+$	11
		91	$(CH_3)_4P^+$	12
104	$(CH_3)_2(C_2H_5)PCH_2^+$	75	$PC_3H_8^+$	13
		90	$(CH_3)_3PCH_2^+$	14
105	$(CH_3)_3(C_2H_5)P^+$	91	$(CH_3)_4P^+$	15
(106)	$P_2C_3H_8^+$	91	$(CH_3)_4P^+$	16
(107)	$P_2C_3H_9^+$	91	$(CH_3)_4P^+$	17
118	$(CH_3)(C_2H_5)_2PCH_2^+$	104	$(CH_3)_2(C_2H_5)PCH_2^+$	18
119	$(CH_3)_2(C_2H_5)_2P^+$	105	$(CH_3)_3(C_2H_5)P^+$	19
121	$(CH_3)_3PCHPH^+$	73	$PC_3H_6^+$	20
		90	$(CH_3)_3PCH_2^+$	21
		(107)	$P_2C_3H_9^+$	22
122	$(CH_3)_3PCHPH_2^+$	73	$PC_3H_6^+$	23
		90	$(CH_3)_3PCH_2^+$	24
123	$(CH_3)_3PCHPH_3^+$	90	$(CH_3)_3PCH_2^+$	25
131	$C_3H_5CH_2P(CH_3)_3^+$	41	$C_3H_5^+$	26
		91	$(CH_3)_4P^+$	27
135	$(CH_3)_3PCHPCH_3^+$	75	$PC_3H_8^+$	28
		90	$(CH_3)_3PCH_2^+$	29
		121	$(CH_3)_3PCHPH^+$	30
136	$(CH_3)_3PCHP(CH_3)H^+$	90	$(CH_3)_3PCH_2^+$	31
137	$(CH_3)_3PCHP(CH_3)H_2^+$	75	$PC_3H_8^+$	32
147	$P_2C_6H_{13}^+$	90	$(CH_3)_3PCH_2^+$	33
149	$(CH_3)_3PCHPC_2H_5^+$?	90	$(CH_3)_3PCH_2^+$	34
150	$(CH_3)_3PCHP(CH_3)_2^+$	(75)	$PC_3H_8^+$	35
		90	$(CH_3)_3PCH_2^+$	36
151	$(CH_3)_3PCHP(CH_3)_2H^+$	90	$(CH_3)_3PCH_2^+$	37
		121	$(CH_3)_3PCHPH^+$	38
165	$(CH_3)_3PCHP(CH_3)_3^+$	75	$PC_3H_8^+$	39
		90	$(CH_3)_3PCH_2^+$	40
180	$((CH_3)_3PCH_2)_2^+$	90	$(CH_3)_3PCH_2^+$	41

This reaction may be compared with the reaction of an ylide with a carbon-carbon double bond, however, the resulting phosphonium ion needs no further stabilisation. A corresponding reaction has also been observed in the case of trimethylphosphine¹³.

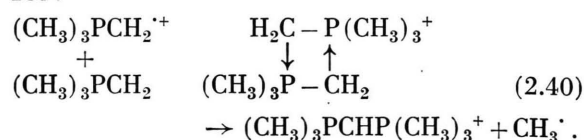
Reactions of the Molecular Ion

The molecular ion is assumed to have a phosphonium radical ion structure according to photoelectron spectrometric results for the neutral trimethylmethylenephosphorane⁸. The molecular ion reacts with the neutral molecule via a four center intermediate forming products which can apart from

three of them, all be described by the general formula



Eight of the nine possible ions are observed, only the ion $m/e = 137$, $(CH_3)_3PCHP(CH_3)H_2^+$ is not formed. The mechanism will now be exemplified for the most abundant of these ions, the trimethyl-trimethylphosphoniummethylenephosphorane, $m/e = 165$:



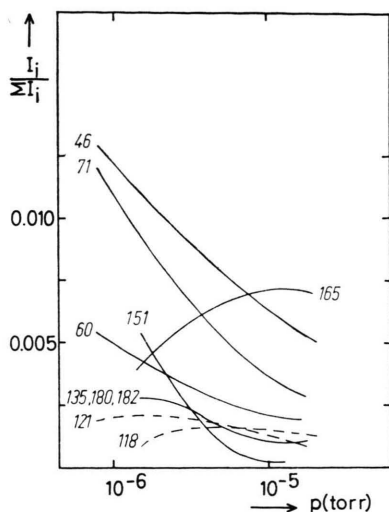
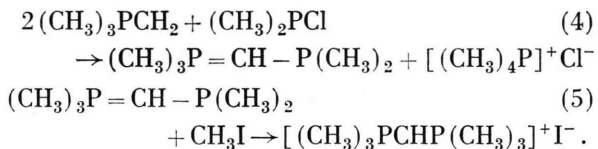
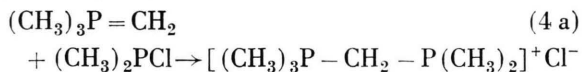


Fig. 5. Mass-corrected relative intensities of the low abundant ions in the ICR spectrum of $(\text{CH}_3)_3\text{PCH}_2$ as a function of the total pressure.

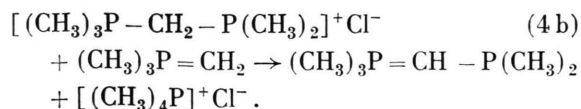
It is assumed, that the phosphonium atom of the molecular ion undergoes an electrophilic attack at the methylene group of the neutral ylide molecule. The intermediate can stabilise itself by dimerisation to the ion $m/e = 180$ (reaction 2.41) or dissociation of a methyl group. This methyl group is formed from the methylene group of the ion and a hydrogen atom of the bridge methylene group. Such hydrogen migrations are not uncommon in ylide chemistry¹⁷. The ion $m/e = 165$ is stable and has already been synthesised by Schmidbaur and Tronich¹⁸ via a transylidation reaction of trimethylmethylenephosphorane and dimethylchlorophosphine followed by a quarternisation of the trimethylphosphinomethylenephosphorane by methyl iodide:



Reaction (4) proceeds in two steps. The first step yields a phosphonium ion:



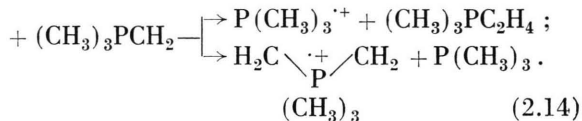
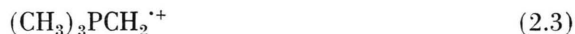
which undergoes a transylidation reaction with a second ylide molecule:



In the ion chemistry the phosphonium ion $m/e = 165$ is formed directly.

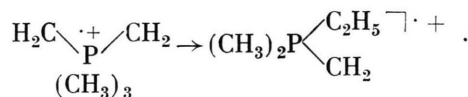
The other ions $(\text{CH}_3)_3\text{PCHPR}_n^+$ are less abundant than the ion $m/e = 165$. During their formation dissociation of several methyl or methylene groups and/or formation of P-H bonds must be assumed. This is not uncommon in the gas phase ion chemistry of organo-phosphorus compounds and has been observed especially in the case of tetramethyldiphosphine¹⁵. However the rearrangements leave the $\text{P}(\text{CH}_3)_3$ group intact originating from the neutral ylide. Until now only a salt of the ion $(\text{CH}_3)_3\text{PCHP}(\text{CH}_3)_3^+$ has been isolated in pure state¹⁸.

One of the three reactions of the molecular ion which do not lead to products with the general formula $(\text{CH}_3)_3\text{PCHPR}_n^+$, namely formation of the dimer molecular ion (reaction 2.41) has already been discussed. The other two reactions yield the very abundant product ion $m/e = 104$ and the minor product ion $m/e = 76$.



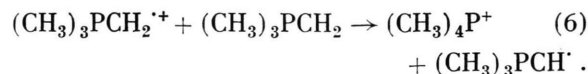
Both reactions lead to products of the same composition, however, the charge is preferably to be found at the particle $m/e = 104$. Reaction (2.14) can be considered as a methylene group transfer, a reaction which is very well known in ylide chemistry¹⁹.

The ion $m/e = 104$ can rearrange, forming again an ylide cation:

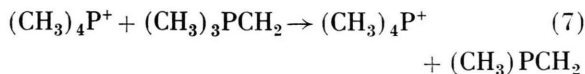


It is known that during ylide formation the alkylidene group is formed selectively at the least alkylated phosphorus atom¹⁷. Therefore a formation of a methylene group is also assumed in the case of this ion.

The protonated molecule is not formed by a reaction of the molecular ion and the neutral molecule. This protonation reaction can be compared with a transylidation:



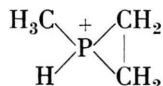
However, the "ylide" formed in reaction (6) does not seem stable enough to favour this transylidation. The transylidation reaction (7)



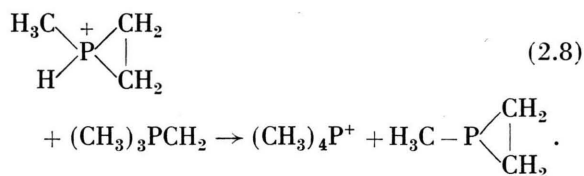
which may occur, cannot be detected with the present ICR equipment.

Reactions of Fragment and Product Ions Containing Phosphorus

The ion $m/e = 75$, which has formally one methyl group less than the molecular ion shows an ion chemistry which is quite different from that of the molecular ion. The main reactions of the ion $m/e = 75$ lead to products which indicate an ion with a cyclic structure and a P–H bond rather than an ion with the structure $(\text{CH}_3)_2\text{PCH}_2^+$



The main reaction of the ion $m/e = 75$ is proton transfer to the neutral molecule:

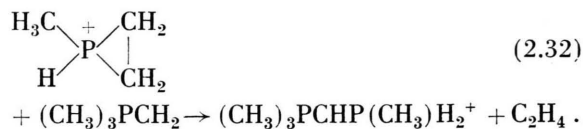


The molecular ion does not react to give the protonated molecule. Therefore a structure of the ion $m/e = 75$ similar to that of the molecular ion must be excluded.

It has been shown that the rate constants of proton transfer reactions have only minor values in the case of ions containing trivalent phosphorus and only P–C bonds^{13–15}. Furthermore the proton affinity decreases strongly if one compares dimethylphosphine with the cyclic phosphirane²⁰. This agrees well with the fact that reaction (2.8) is the main reaction for formation of the protonated molecule.

The ion chemistry of phosphirane shows also the great stability of cyclic ions which contain the PC_2H_4 entity²¹. The most abundant reactions in this ion chemistry are P–H group transfer. Therefore a corresponding transfer reaction should be observed, if the ion $m/e = 75$ is cyclic. Indeed

CH_3PH transfer is detected:



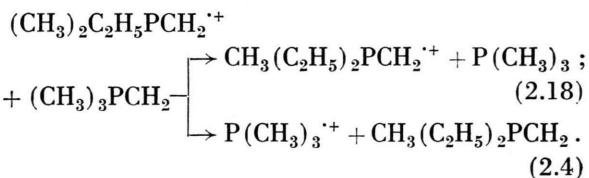
The ion $m/e = 137$ is the single ion with general formula $(\text{CH}_3)_3\text{PCHPR}_n^+$ which is not formed by a reaction of the molecular ion but only from the ion $m/e = 75$. The product of reaction (2.32) is thought to rearrange in a manner similar to that already discussed for these ions.

The reaction leading to the ion $m/e = 165$ is an addition reaction. If this ion has the same structure as the ion $m/e = 165$ formed by the molecular ion, namely $(\text{CH}_3)_3\text{PCHP}(\text{CH}_3)_3^+$, ring opening of the three-membered ring and hydrogen rearrangement must occur. These reactions are not uncommon. However, reaction (2.32) is not indicative for a cyclic structure of the ion $m/e = 75$. Also the further reactions of the ion $m/e = 75$ are not characteristic for a cyclic ion, but also not contradictory. The ions $m/e = 103, 104, 135$ and 165 are also formed by the molecular ion. It may therefore be assumed that part of the ions $m/e = 75$ have the alternative structure $(\text{CH}_3)_2\text{PCH}_2^+$.

Although the tetramethylphosphonium ion is very abundant it is practically unreactive in the pressure range from 10^{-6} to 10^{-4} Torr. It undergoes only five reactions (2.12, 2.15, 2.16, 2.17 and 2.27) with minor yields.

Only minor reactivities have been observed for all the phosphonium ions PR_4^+ ($\text{R} = \text{CH}_3, \text{H}$) in given pressure range^{13, 14}. It should be mentioned, however, that the tetramethyldiphosphonium ion $(\text{CH}_3)_4\text{P}_2\text{H}^+$ is very reactive¹⁵.

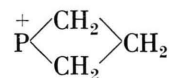
The ion $m/e = 105$ is formed by a methylene group transfer reaction from the $(\text{CH}_3)_4\text{P}^+$ ion as is the ion $m/e = 104$ from the molecular ion. Both ions, $m/e = 104$ and 105 again undergo a CH_2 transfer reaction yielding the products $m/e = 119$, $(\text{CH}_3)_2(\text{C}_2\text{H}_5)_2\text{P}^+$ [from $(\text{CH}_3)_3(\text{C}_2\text{H}_5)\text{P}^+$, reaction 2.19] and $m/e = 118$, $(\text{CH}_3)(\text{C}_2\text{H}_5)_2\text{PCH}_2^+$ [from $(\text{CH}_3)_2(\text{C}_2\text{H}_5)\text{PCH}_2^+$, reaction 2.18]. An alternative form of reaction (2.18) yields $\text{P}(\text{CH}_3)_3^+$:



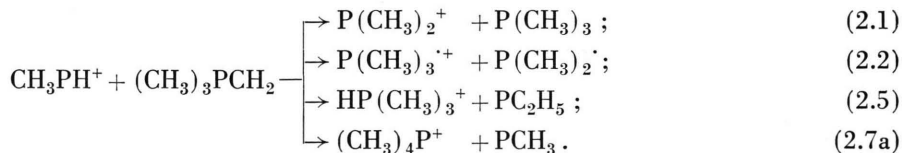
As has been already discussed for the reactions (2.3) and (2.14) in the preceding section, in the reactions (2.4) and (2.18) two products of same composition are also formed differing only in the position of charge.

Two further formal methylene group transfer reactions lead to the ion $m/e=135$ (from $m/e=121$, reaction 2.30) and to the ion $m/e=87$, PC_4H_8^+ (from $m/e=73$, reaction 2.6). The ion PC_3H_6^+ also undergoes two further reactions which can be

regarded as phosphorus transfer (reaction 2.20) and PH transfer (reaction 2.23). Such transfer reactions have been observed almost exclusively in the case of cyclic ions²¹, therefore for the ion $m/e=73$ a cyclic structure must also be assumed:



The four reactions of the ion $m/e=47$ are consistent with the structure CH_3PH^+ .



Reaction (2.1) is a CH_2 transfer. The reactions (2.1) and (2.2) differ only in the position of charge. This has also been observed for the reactions (2.3) and (2.14) and for (2.4) and (2.18) and seems to be typical for reactions in the course of which the $\text{P}(\text{CH}_3)_3$ entity is formed.

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