Mechanism and Structure in the Ion Chemistry of Tetramethyldiphosphine: An Ion Cyclotron Resonance Spectrometric Study

Karl-Peter Wanczek

Institut für physikalische Chemie der Universität Frankfurt (Main)

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The mass spectrum of tetramethyldiphosphine and the ion chemistries of this compound and of its mixtures with phosphine and dimethylphosphine have been investigated by ion cyclotron resonance spectrometry. Numerous ion molecule reactions have been observed. The rate constants of the two most abundant ions formed by the molecular ion, the tetramethyldiphosphonium ion, $H(CH_3)_2P-P(CH_3)_2^+$ and the hexamethyltriphosphonium ion, $P_3(CH_3)_6^+$, are $k_{2.35} \leqq 0.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and $k_{2.40} = 1.5 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively. The structures of several ions have been determined with the aid of their ion-molecule reactions. The ions $m/e = 79$ and 93 are thought to have the structures $HP-P(CH_3)H^+$ and $HP-P(CH_3)_2^+$. The most probable structures of the ions $m/e = 169$ and 183 are $HP(CH_3)_2-P(CH_3)-P(CH_3)_2^+$ and $(CH_3)_2P-P(CH_3)-P(CH_3)_3^+$. The protonated molecule undergoes several ion-molecule reactions, which proceed via an intermediate, $m/e = 183$, $[(CH_3)_6P_3^+]^*$ which is detected by double resonance experiments.

Introduction

The simplest organo phosphorus compound with a phosphorus-phosphorus bond, tetramethyldiphosphine, shows a chemistry which is characterized by the ease of dissociation of the P-P bond on the one hand and the formation of phosphonium salts with one quarternized phosphorus atom[1] on the other hand. Recent investigations of the ion chemistries of several simple methylphosphines[2–4], the corresponding methylfluorophosphines[5] and of phosphirane[6] show the quasi-phosphonium ions MH^+ (M = neutral molecule), formed by proton or hydrogen transfer reactions to be exceptionally stable. In the case of the methylphosphines and phosphirane, ions with two or more phosphorus atoms are easily formed, too.

Hitherto the ion chemistry of compounds containing a phosphorus-phosphorus bond has not been investigated. In this work an ion cyclotron resonance spectroscopic study of the ion-molecule reactions of tetramethyldiphosphine, and its reactions with phosphine is presented, together with a discussion of the pecularities of this compound with its phosphorus-phosphorus bond.

Experimental

Details of the ICR spectrometer, utilized in this study have been described elsewhere[3, 4]. The realisation of the experiments is much the same as has been described earlier for the monophosphines[3, 4].

All the ions occuring in the spectrum in the mass range $m/e = 2 - 186$ at 30 eV electron energy have been subject to double resonance experiments at several pressures between 10^{-7} and 10^{-4} torr and several irradiating field strengths. Whenever possible the results have been supported by pressure plots.

Tetramethyldiphosphine dissociates continously in the inlet system and in the measuring cell of the spectrometer into dimethylphosphine which could be detected in the ICR spectrum probably together with a second compound, which could not be detected. This dissociation is not influenced by the presence of water vapour, which does not react with tetramethyldiphosphine at room temperature[1, 7]. It was, however, impossible to suppress this dissociation reaction completely.

Two rate constants have been determined by the approximation method of Goode et al.[8] at an electorn energy of 9.1 eV (uncorrected) where only the molecular ions of tetramethyldiphosphine and of the dimethylphosphine impurity appear. For the rate constant of formation of the protonated molecule by a reaction of the molecular ion only an upper limit could be determined, because tetramethyldiphosphine has a much greater proton affinity than dimethylphosphine and is therefore protonated by the latter compound.

The second reaction of the molecular ion of which a rate constant has been determined yields hexamethyltriphosphonium (+1) ions and is not paralleled by a corresponding reaction of the dimethylphosphine impurity. The values of this rate

Reprint requests to Dr. Karl-Peter Wanczek, Institut für Physikalische Chemie der Universität Frankfurt (Main), Robert-Mayer-Straße 11, *D-6000 Frankfurt (Main).*

constant and of the upper limit of the former rate constant may be of approximately 50% accuracy because reaction time and pressure are determined by the approximation methods already discussed elsewhere [4, 8]. Tetramethyldiphosphine was prepared by conventional methods [9]. Separation from impurities can easily be performed by trap-to-trap distillation. The compound was stored in vacuo at liquid nitrogen temperature to avoid any decomposition.

Phosphine was prepared by thermal decomposition of crystalline phosphorus acid at 450 – 470 K in vacuo. Dimethylphosphine was synthesised using conventional methods [9] and purified by trap-to-trap distillation. Mixtures of these compounds with tetramethyldiphosphine were prepared manometrically.

Results and Discussion

ICR Spectrum of Tetramethyldiphosphine

The ICR spectrum of tetramethyldiphosphine at a pressure of 5×10^{-8} torr and an electron energy of 30 eV is shown in Figure 1. The mass-corrected ion abundances have been compared with the two mass spectra available in the literature in Table 1. The mass spectrum by Bogolyubov et al. [10] compares

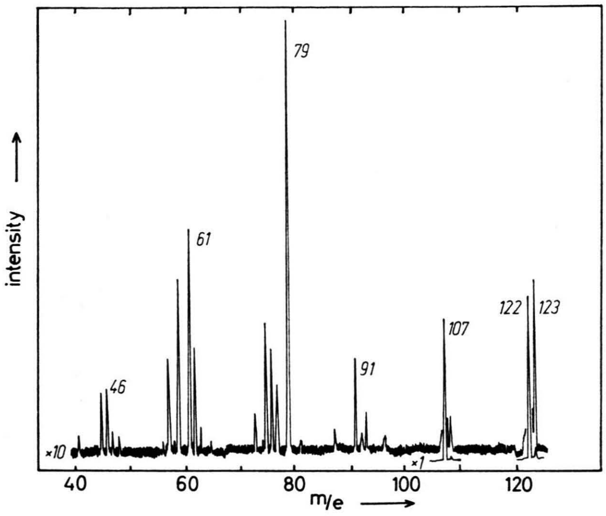


Fig. 1. ICR spectrum of tetramethyldiphosphine at a pressure of 5×10^{-8} torr and an electron energy of 30 eV.

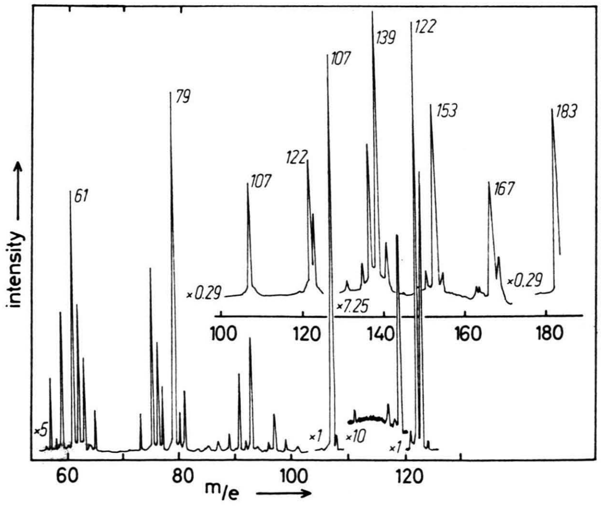


Fig. 2. ICR spectrum of tetramethyldiphosphine at a pressure of 1.5×10^{-5} torr and an electron energy of 30 eV.

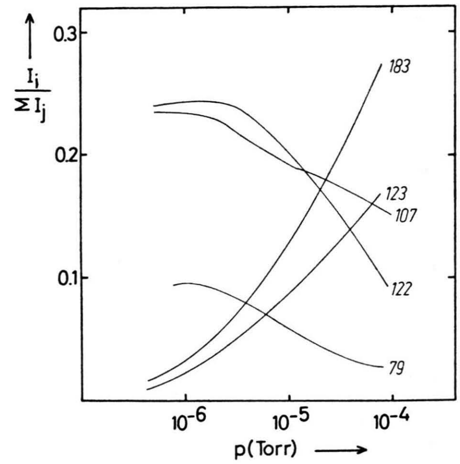


Fig. 3. Mass-corrected relative intensities of the major ions in the ICR spectrum of tetramethyldiphosphine as a function of the total pressure.

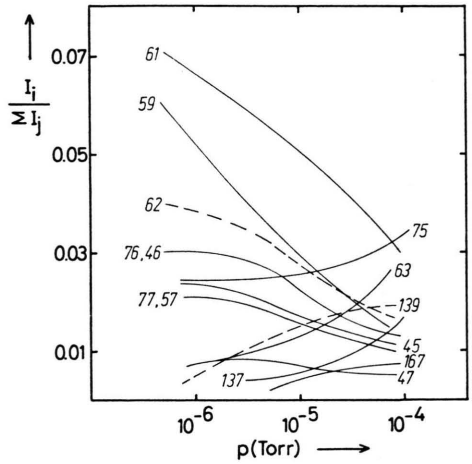


Fig. 4. Mass-corrected relative intensities of the minor ions in the ICR spectrum of tetramethyldiphosphine as a function of the total pressure.

Table 1. ICR spectrum of tetramethyldiphosphine.

Ion comp.	*m/e*	Relative intensities this work 30 eV	 Bogo-lyubov[10] 70 eV	 Seel[11] 70 eV
$C_2H_3^+$	27		25.6	
$C_2H_4^{\cdot +}$	28		25.6	
$C_2H_5^+$	29		35.5	
	41		8.7	
$PCH^{\cdot +}$	44	—	33.1	98
PCH_2^+	45	107	215	417
$PCH_3^{\cdot +}$	46	137	120	1000
$HPCH_3^+$	47	44	45.5	181
$H_2PCH_3^{\cdot +}$	48	22	25.6	
$PC_2H^{\cdot +}$	56	—	16.1	37
$P(CH)_2^+$	57	127	132	190
$PC_2H_3^{\cdot +}$	58	—	32.2	56
$P(CH_2)_2^+$	59	220	219	488
$PC_2H_5^{\cdot +}$	60	—	9.5	28
$P(CH_3)_2^+$	61	268	372	630
$HP(CH_3)_2^{\cdot +}$, $P_2^{\cdot +}$	62	138	161	885
$H_2P(CH_3)_2^+$, P_2H^+	63	39	54.5	
$P_2H_2^{\cdot +}$	64	—	2.5	
$P_2H_3^+$	65	27	16.1	
$PC_3H_6^+$	73	46	38.8	
$PC_3H_7^{\cdot +}$	74		6.6	
P_2CH^+, $(CH_3)_2PCH_2^+$	75	121	110	122
$P_2CH_2^{\cdot +}$, $P(CH_3)_3^{\cdot +}$	76	112	45.5	368
$P_2CH_3^+$	77	71	57.9	
$P_2CH_4^{\cdot +}$	78	—	12.8	
$P_2CH_5^+$	79	414	289	
$CH_3P_2H_4^+$	81	20		
	89		3.3	
$P_2C_2H_5^+$	91	75	48.3	
$P_2(CH_3)_2^{\cdot +}$	92	24	19.4	
$P_2(CH_3)_2H^+$	93	41	42.1	
$P_2(CH_3)_2H_2^{\cdot +}$	94		12.8	
$P_2C_3H_7^+$	105		1.7	
$P_2C_3H_8^{\cdot +}$	106		3.3	
$P_2(CH_3)_3^+$	107	971	1000	258
$P_2(CH_3)_3H^{\cdot +}$	108	26	45.5	
$P_2(CH_3)_3CH_2^+$	121		6.2	
$P_2(CH_3)_4^{\cdot +}$	122	1000	806	276
	123	88	24.8	

fairly well with the ICR spectrum, however, it should be noted that the ion *m/e* = 107, $P_2(CH_3)_3^+$ is the parent peak in the cited spectrum, while the molecular ion is the parent peak in the ICR spectrum. This may be due to the different electron energies, 70 eV in the spectrum by Bogolyubov et al. and 30 eV in this study. The mass spectrum of tetramethyldiphosphine published by Seel et al.[11] is substantially different, the parent peak in this case is the ion *m/e* = 46, $PCH_3^{\cdot +}$. Ions which are to be observed in the mass spectrum of methylphosphine[4] appear with high abundances, the ion *m/e* = 107 and the molecular ion are only of medium abundance. It is therefore suggested that the spectrum by Seel et al. may be due to a mixture of tetramethyldiphosphine and dimethylphosphine, formed by a decomposition reaction of tetramethyldiphosphine similar to that observed in the ICR spectrometer, already discussed in the experimental section.

An ICR spectrum at a pressure of 1.5×10^{-5} torr is shown in Figure 2. Numerous product ions, arranged in groups, can 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 minor ions in Figure 4. Most of the primary ions of tetramethyldiphosphine react with the neutral molecules and a large number of products are formed. However, only two product ions have an abundance of more than 4%: The ion *m/e* = 123, the protonated molecule and the ion *m/e* = 183, $P_3(CH_3)_6^+$, which is the most abundant ion at pressures above 3×10^{-5} torr. The relative abundance of the protonated molecule (Fig. 3) may be somewhat too high, because it is formed from the dimethylphosphine impurity by the reaction:

$$(CH_3)_2PH^{\cdot +} + (CH_3)_4P_2 \rightarrow (CH_3)_4P_2H^+ + (CH_3)_2P^{\cdot} \qquad (1)$$

a reaction which could not be completely suppressed.

Ion-Molecule Reactions

The ion-molecule reactions of tetramethyldiphosphine are listed in Table 2. There are, as in the case of the methylphosphines[3, 4], numerous ion-molecule reactions, but the proportion of product ions for which simple formation reactions can be assumed, is smaller.

If there is more than one possible composition for a product ion only the most probable one is listed in the table, with the exception of the ions *m/e* = 63, which can have the compositions

$$P_2H^+ \text{ or } (CH_3)_2PH^+ \text{ and } m/e = 137, \text{ which can be}$$

$$P_3(CH_3)_2CH_2^+ \text{ or } P_2(CH_3)_5^+.$$

The majority of formation reactions for the product ions can be classified according to the following four reaction types:

a) Transfer of a $P(CH_3)_2$ group, with or without C – H or P – H bond rearrangement,
b) phosphorus atom or PH-group transfer,

Table 2. **Product ions of the ion-molecule reactions of tetramethyldiphosphine.**

Reacting ions		Product ions		Reaction type	No.
m/e	composition	*m/e*	composition		
45	PCH_2^+	75	P_2CH^+	c_1	1
46	$PCH_3^{\cdot +}$	94	$P_2(CH_3)_2H_2^{\cdot +}$		2
		153	$P_3(CH_3)_4^+$	b	3
		(154	$P_3(CH_3)_4H^{\cdot +})$	b	4
59	$P(CH_2)_2^+$	93	$P_2(CH_3)_2H^+$	c	5
		94	$P_2(CH_3)_2H_2^{\cdot +}$		6
		119	$P_2C_4H_9^+$	a, c_1	7
		153	$P_3(CH_3)_4^+$	b	8
61	$P(CH_3)_2^+$	63	$(CH_3)_2PH_2^+$, P_2H^+		9
		121	$(CH_3)_2PPC_2H_5$	a, c_1	10
62	$(CH_3)_2PH^{\cdot +}$	109	$P_2(CH_3)_3H_2^+$	a	11
		(122	$(CH_3)_4P_2^{\cdot +})$	c_1	12
		123	$(CH_3)_4P_2H^+$	d	13
		183	$(CH_3)_6P_3^+$	a	14
75	P_2CH^+?	135	$P_3C_3H_6^+$?	a, c_1	15
76	$P_2CH_2^{\cdot +}$, $P(CH_3)_3^{\cdot +}$	137	$P_3(CH_3)_2CH_2^+$, $P_2(CH_3)_5^+$	a	16
77	$P_2CH_3^+$	139	$P_3(CH_3)_3H^+$	a, c	17
79	$P_2CH_3H_2^+$	93	$HPP(CH_3)_2^+$	a	18
		94	$P_2(CH_3)_2H_2^{\cdot +}$		19
		97	$P_3H_4^+$		20
		139	$P_3(CH_3)_3H^+$	a, c_1	21
		153	$P_3(CH_3)_4^+$	b, c	22
		(154	$P_3(CH_3)_4H^{\cdot +})$	b	23
81	$P_2(CH_3)H_4^+$	97	$P_3H_4^+$		24
91	$P_2CH_3CH_2^+$	151	$P_3(CH_3)_3CH^+$	a, c_1	25
93	$HPP(CH_3)_2^+$	153	$P_3(CH_3)_4^+$	b	26
		(154	$P_3(CH_3)_4H^{\cdot +})$	b	27
107	$CH_3PP(CH_3)_2^+$	123	$(CH_3)_4P_2H^+$	d	28
		167	$P_3(CH_3)_4CH_2^+$	c_1	29
		169	$P_3(CH_3)_5H^+$	c	30
		183	$P_3(CH_3)_6^+$	a	31
108	$H(CH_3)PP(CH_3)_2^+$	157	$P_4C_2H_9^+$		32
122	$(CH_3)_4P_2^{\cdot +}$	81	$P_2(CH_3)H_4^+$		33
		108	$H(CH_3)PP(CH_3)_2^+$		34
		123	$(CH_3)_4P_2H^+$	d	35
		137	$P_2(CH_3)_2CH_2^+$, $P_2(CH_3)_5^+$		36
		141	$P_3(CH_3)_3H_3^+$, $P_4(CH_3)H_2^+$		37
		157	$P_4C_2H_9^+$		38
		(169	$P_3(CH_3)_5H^+)$	c	39
		183	$P_3(CH_3)_6^+$	a	40
123	$(CH_3)_4P_2H^+$	151	$P_3(CH_3)_3CH^+$	c	41
		153	$P_3(CH_3)_4^+$	c	42
		167	$P_3(CH_3)_4CH_2^+$	c	43
		169	$P_3(CH_3)_5H^+$	c	44
183	$P_3(CH_3)_6^+$	167	$P_3(CH_3)_4CH_2^+$		45
		169	$P_3(CH_3)_5H^+$		46

c) formation of a methylphosphine as neutral molecule [in the course of reactions (1), (5) and (43) also alkane molecules are formed],
   c_1) formation of $(CH_3)_2PH$,

d) formation of the protonated molecule.

The transfer of a dimethylphosphino group is a characteristic reaction of tetramethyldiphosphine[9, 12]. It is well known from solution chemistry. The transfer of a P atom or a PH group is observed only for the fragment ions

m/e = 46, $PCH_3^{\cdot +}$; *m/e* = 59, $P(CH_2)_2^+$;
m/e = 79, $P_2CH_3H_2^+$ and *m/e* = 93, $P_2(CH_3)_2H^+$.

It has been observed in the case of the first two ions also in the ion chemistry of trimethylphosphine[3] and of dimethylphosphine[4], in the case of methylphosphine only for the $PCH_3^{\cdot +}$ ion. The formation of neutral phosphine molecules in the course of the ion-molecule reactions has also been observed in the ion chemistry of the methylfluorophosphines[5].

The other reactions, approximately one third of all the ion-molecule reactions detected, have more complicated mechanisms, including rearrangement, formation of P-H-bonds or CH_2 groups in the product ions and of neutral molecules, the number and composition of which cannot be determined in every case.

Ion-Molecule Reactions of the Molecular Ion

The most intense product ion is the ion $m/e = 183$ formed by a $P(CH_3)_2$ transfer reaction of the molecular ion:

$$(CH_3)_2P - P(CH_3)_2^{\cdot +} + (CH_3)_4P_2 \rightarrow P_3(CH_3)_6^+ + (CH_3)_2P^{\cdot} . \qquad (2.40)$$

The rate constant of formation of the hexamethyltriphosphonium (+1) ion is:

$$k_{2.40} = 1.5 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

a high value for a reaction, which doesn't lead to a protonated molecule in the organo phosphorus ion chemistry.

In the first step of this reaction a nucleophilic attack by a phosphorus atom of the neutral molecule at the positive charged phosphorus atom of the ion can be assumed, as has been done for the methylphosphines[3, 4] and phosphirane[6]:

$$\begin{array}{ll} (CH_3)_2P^{\cdot +} - \overline{P}(CH_3)_2 & \\ \quad \circlearrowleft & \rightarrow (CH_3)_2P - P(CH_3) \\ (CH_3)_2\overline{P} - \overline{P}(CH_3)_2 & \quad - P(CH_3)_3^+ + P(CH_3)_2^{\cdot} . \end{array}$$

If the reaction proceeds with a simple dissociation of a $P(CH_3)_2^{\cdot}$ radical without rearrangement, the charge will be at the central phosphorus atom of the ion. However, only the terminal phosphorus atoms of triphosphines have been observed to be quaternized with HBr or CH_3I[13]. Therefore the structure

$$(CH_3)_2P - P(CH_3) - P(CH_3)_3^+$$

is assumed for the ion formed in reaction (2.40), which means a methyl group rearrangement is postulated.

The rate constant of formation of the protonated molecule from the molecular ion

$$(CH_3)_2P - P(CH_3)_2^{\cdot +} + (CH_3)_4P_2 \rightarrow (CH_3)_4P_2H^+ + (CH_3)_2P_2C_2H_5^{\cdot} \qquad (2.35)$$

$$k_{2.35} \leqq 0.1 \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

has a small value, as has been observed for trimethylphosphine[3] which also only has methyl groups bonded to phosphorus.

A reaction of the molecular ion which is thought to proceed similar to the formation of the protonated molecule is the formation of the trimethyldiphosphenium ion $m/e = 108$:

$$(CH_3)P - P(CH_3)_2^{\cdot +} + (CH_3)_4P_2 \rightarrow H(CH_3)P - P(CH_3)_2^{\cdot +} + (P_2C_4H_{11}) . \qquad (2.34)$$

Two reactions of the molecular ion lead to diphosphonium ions with the general formula $P_2R_5^+$. The first yields $P_2CH_7^+$, $m/e = 81$, an ion which is observed also as a primary ion in a complicated reaction including formation of several P-H bonds. This ion is thought to have the structure $P_2CH_3H_4^+$.

The second reaction (2.36) yields the ion $m/e = 137$. This ion may have the compositions $P_2(CH_3)_5^+$ or $P_3(CH_3)_2CH_2^+$. However no decision can be made as to which one is the more probable. This ion is also formed by the primary ion $m/e = 76$. Seel et al.[11] assumed this ion to have the composition $P_2CH_2^{\cdot +}$ but the composition $P(CH_3)_3^{\cdot +}$ must also be considered. Unfortunately no decision could be made between these two possible ion compositions investigating the ^{13}C isotope peaks, because the $P_2CH_3^+$ ion appears at the mass-to-charge ratio 77. The $P(CH_3)_3^{\cdot +}$ ion formed from trimethylphosphine reacts to give the stable $P_2(CH_3)_5^+$ ion[3]. Thus it seems not improbable to assume the composition $P(CH_3)_3^{\cdot +}$ for the primary ion $m/e = 76$ and $P_2(CH_3)_5^+$ for the secondary ion $m/e = 137$. On the other hand the very stable neutral products $(CH_3)_2PH$ and C_2H_6 are generated if $P_3(CH_3)_2CH_2^+$ is formed by the reaction of the tetramethyldiphosphine molecular ion with the neutral molecule according to reaction type c_1.

The ion $m/e = 141$ belongs to the same group of triphosphonium ions $P_3R_6^+$ as the very abundant ion $P_3(CH_3)_6^+$. Its composition is assumed to be $P_3(CH_3)_3H_3^+$. The reactions (2.37) and (2.40) yielding the product ions $P_3(CH_3)_3H_3^+$ and $P_3(CH_3)_6^+$ may be compared with the reactions (2.33) and (2.36) leading to $P_2(CH_3)H_4^+$ and $P_2(CH_3)_5^+$. Apparently in both cases there exists one channel with strong rearrangement and formation of several new P-H bonds and a second more intense reaction channel leading to products without P-H bond formation.

Reactions of Fragment Ions

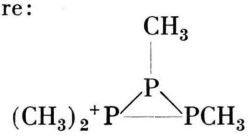
The reactions of the fragment ions are in most cases not as complicated as the reactions of the molecular ion. It is therefore possible to derive the structure of several ions. Only the reactions leading to conclusions in this respect will now be discussed.

An important group of reactions are the phosphorus or PH group transfer reactions, which have been observed for the ions $PCH_3^{\cdot+}$, $P(CH_2)_2^+$, $P_2CH_3H_2^+$ and $P_2(CH_3)_2H^+$. With the exception of the $P(CH_2)_2^+$ ion, which undergoes only a P transfer reaction, P and PH transfer is observed, yielding the products $m/e = 153$ and 154, respectively.

The ion $m/e = 59$ does not only transfer a phosphorus ion (reaction 2.8), a displacement reaction is also observed (reaction 2.7):

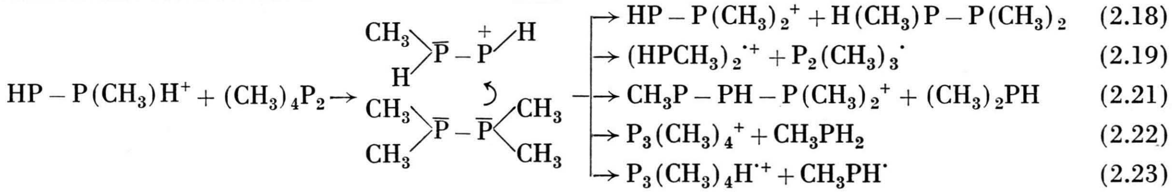
$$(CH_2)_2P^+ + (CH_3)_4P_2 \begin{cases} \rightarrow P_3(CH_3)_4^+ + C_2H_4 & (2.8) \\ \rightarrow (CH_2)_2P-PC_2H_5^+ + (CH_3)_2PH & (2.7) \end{cases}$$

For the ion $m/e = 153$, formed in reaction (2.8), an open-chain structure $(CH_3)_2P-P(CH_3)-PCH_3^+$ or a cyclic structure:



can be considered. However only cyclopolyphosphines with four or more phosphorus atoms in the ring have been synthesized until now[9]. It is therefore suggested that the chain structure will be more probable also for the ion.

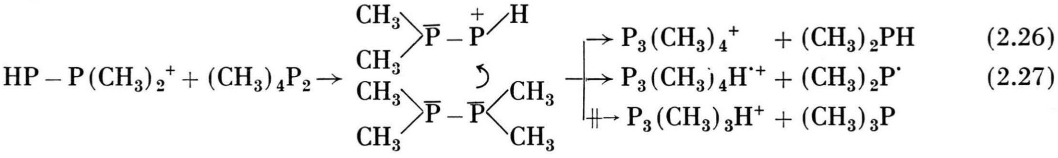
The reactions of the ions $P_2CH_3H_2^+$ and $P_2(CH_3)_2H^+$ yield the ion $m/e = 153$, too, via a formal phosphorus transfer. The following mechanism including H atom or methyl group migration and P-P bond dissociation allows a consistent interpretation of all the reactions of the ion $m/e = 79$ except reaction (2.20):



$$HP-P(CH_3)H^+ + (CH_3)_4P_2 \rightarrow \begin{array}{c} (CH_3)(H)\overline{P}-\overset{+}{P}H \\ \circlearrowleft \\ (CH_3)_2\overline{P}-\overline{P}(CH_3)_2 \end{array} \begin{cases} \rightarrow HP-P(CH_3)_2^+ + H(CH_3)P-P(CH_3)_2 & (2.18) \\ \rightarrow (HPCH_3)_2^{\cdot+} + P_2(CH_3)_3^{\cdot} & (2.19) \\ \rightarrow CH_3P-PH-P(CH_3)_2^+ + (CH_3)_2PH & (2.21) \\ \rightarrow P_3(CH_3)_4^+ + CH_3PH_2 & (2.22) \\ \rightarrow P_3(CH_3)_4H^{\cdot+} + CH_3PH^{\cdot} & (2.23) \end{cases}$$

This interpretation leads also to the conclusion that the ion $m/e = 79$ has the structure $HPP(CH_3)H^+$.

Compared with the ion $m/e = 79$ the ion $m/e = 93$ contains a methyl group instead of a hydrogen atom. The reactions of this ion, yielding only the product ions $m/e = 153$ and 154, can be interpreted according to the following scheme:

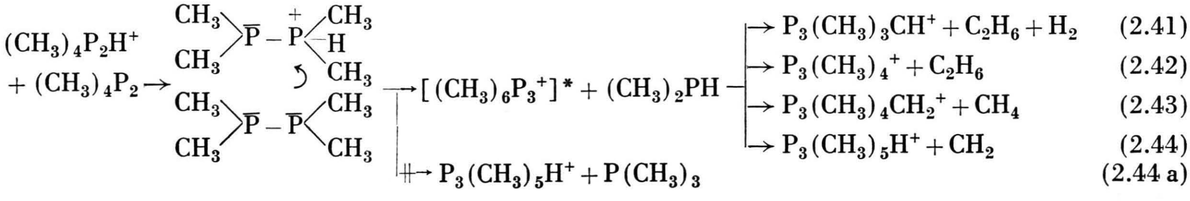


$$HP-P(CH_3)_2^+ + (CH_3)_4P_2 \rightarrow \begin{array}{c} (CH_3)_2\overline{P}-\overset{+}{P}H \\ \circlearrowleft \\ (CH_3)_2\overline{P}-\overline{P}(CH_3)_2 \end{array} \begin{cases} \rightarrow P_3(CH_3)_4^+ + (CH_3)_2PH & (2.26) \\ \rightarrow P_3(CH_3)_4H^{\cdot+} + (CH_3)_2P^{\cdot} & (2.27) \\ \nrightarrow P_3(CH_3)_3H^+ + (CH_3)_3P & \end{cases}$$

The ion $m/e = 139$ is only formed from $P_2CH_3H_2^+$ and not from $P_2(CH_3)_2H^+$, indicating that no methyl group migration to form the neutral trimethylphosphine molecule takes place but only hydrogen atom migration.

Reactions of the Tetramethyldiphosphonium Ion $H(CH_3)_2P-P(CH_3)_2^+$

Several tertiary ions have been detected. They are included in Table 2. Contrary to the monophosphines[3-5] the protonated molecule of tetramethyldiphosphine shows several ion-molecule reactions. These reactions can be interpreted according to the following scheme which resembles that already discussed for the reactions of the ions $P_2(CH_3)H_2^+$ and $P_2(CH_3)_2H^+$. The phosphonium ion is attacked by a nucleophilic phosphorus atom of the neutral molecule as a first reaction step.



$$\begin{array}{l}(CH_3)_4P_2H^+ \\ + (CH_3)_4P_2 \end{array} \rightarrow \begin{array}{c} (CH_3)_2\overline{P}-\overset{+}{P}(CH_3)H \\ \circlearrowleft \\ (CH_3)_2\overline{P}-\overline{P}(CH_3)_2 \end{array} \begin{cases} \rightarrow [(CH_3)_6P_3^+]^* + (CH_3)_2PH \begin{cases} \rightarrow P_3(CH_3)_3CH^+ + C_2H_6 + H_2 & (2.41) \\ \rightarrow P_3(CH_3)_4^+ + C_2H_6 & (2.42) \\ \rightarrow P_3(CH_3)_4CH_2^+ + CH_4 & (2.43) \\ \rightarrow P_3(CH_3)_5H^+ + CH_2 & (2.44) \end{cases} \\ \nrightarrow P_3(CH_3)_5H^+ + P(CH_3)_3 \qquad (2.44\,a) \end{cases}$$

However, this reaction then proceeds via a different route, the intermediate dissociates into $(CH_3)_2PH$ and the ion $[(CH_3)_6P_3^+]^*$. The excited ion $[(CH_3)_6P_3^+]^*$ dissociates again into the product ions and neutral alkane (and hydrogen) molecules. The intermediate $(CH_3)_4P_2(CH_3)_4P_2H^{\cdot+}$ is too short-lived to be detected by double resonance experiments, however, this is the case for the ion $[(CH_3)_6P_2^+]^*$ for the reactions (2.43) and (2.44):

$$[(CH_3)_6P_3^+]^* \begin{cases} \to P_3(CH_3)_4CH_2^+ + CH_4 & (2.45) \\ \to P_3(CH_3)_5H^+ + CH_2 & (2.46) \end{cases}$$

Reaction (2.44) can be interpreted also in terms of a methyl group migration leading to the formation of a neutral trimethylphosphine molecule (reaction 2.44 a). This reactions path is energetically more favourable. However, the reaction is assumed to proceed according to mechanism (2.44), because the dissociation of the intermediate $[(CH_3)_6P_3^+]^*$ can be detected by double resonance experiments; therefore its lifetime must be long enough ($>10^{-4}$ s) so that the $(CH_3)_2PH$ molecule, formed in the first reaction step, can dissociate.

Mixtures of Tetramethyldiphosphine with Phosphine and Dimethylphosphine

Seven new ion-molecule reactions have been detected in an 1:1 mixture of tetramethyldiphosphine and phosphine. Because the proton affinity of $(CH_3)_4P_2$ is much greater than that of phosphine[14], the following proton transfer reaction has been observed:

$$PH_4^+ + (CH_3)_4P_2 \to (CH_3)_4P_2H^+ + PH_3\,. \quad (2)$$

Also the reaction

$$PH_3^{\cdot+} + (CH_3)_4P_2 \to (CH_3)_4P_2H^+ + PH_2^{\cdot} \quad (3)$$

occurs. Furthermore the ion $m/e = 93$ is formed in this mixture by reactions of ions from phosphine:

$$PH^{\cdot+} + (CH_3)_4P_2 \to HP-P(CH_3)_2 + P(CH_3)_2^{\cdot} \quad (4)$$

$$PH_2^+ + (CH_3)_4P_2 \to HP-P(CH_3)_2^+ + HP(CH_3)_2 \quad (5)$$

and by reactions of ions from tetramethyldiphosphine:

$$CH_3PP(CH_3)_2^+ + PH_3 \to HP-P(CH_3)_2^+ + CH_3PH_2 \quad (6)$$

$$(CH_3)_4P_2^{\cdot+} + PH_3 \to HP-P(CH_3)_2^+ + ((CH_3)_2PH_2^{\cdot})\,. \quad (7)$$

These reactions prove the structure $HP-P(CH_3)_2^+$ for the ion $m/e = 93$, which has already been assumed in the discussion of the reactions (2.18), (2.26) and (2.27).

In mixtures of tetramethyldiphosphine with dimethylphosphine the proton transfer reaction

$$(CH_3)_2PH_2^+ + (CH_3)_4P_2 \to (CH_3)_4P_2H^+ + (CH_3)_2PH \quad (8)$$

indicates a greater value of the proton affinity of the diphosphine. Also the reaction (1), which has already been mentioned and the reaction

$$(CH_3)_2P^+ + (CH_3)_4P_2 \to (CH_3)_4P_2H^+ + C_2H_5P \quad (9)$$

yield the tetramethyldiphosphonium ion.

The ion $m/e = 107$, $CH_3PP(CH_3)_2^+$ undergoes an interesting addition reaction with dimethylphosphine:

$$CH_3P-P(CH_3)_2^+ + (CH_3)_2PH \to HP(CH_3)_2-P(CH_3)-P(CH_3)_2^+ \quad (10)$$

indicating the structure $HP(CH_3)_2-P(CH_3)-P(CH_3)_2^+$ for the ion $m/e = 169$. It can therefore be concluded that the CH_2-group in reaction (2.46) is dissociated from a methylgroup at the phosphonium site.

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