

Ion Chemistry of Phosphirane and Structure of the Phosphirane Molecular Ion

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The mass spectrum and the ion molecule reactions of phosphirane and of mixtures of phosphirane with NH_3 , NH_2D , NHD_2 and ND_3 have been studied by ion cyclotron resonance spectrometry. Almost all important product ions are formed by PH-group transfer reactions, where ethene is generated as the neutral particle. Only two of the more abundant ions, the protonated molecule, $\text{H}_2\text{P}(\text{CH}_2)_2^+$ and the ion $m/e=63$, P_2H^+ , are formed via other reaction pathways. Secondary, tertiary and quarternary product ions with the general formula $\text{R}(\text{PH})_n^+$ (R: phosphirane fragment, $n=1, 2, 3$) have been detected.

The molecular ion is proved to have a cyclic structure. Two possible structures of the product ions with two and three phosphorus atoms are discussed: a structure with an open phosphorus chain, leaving the phosphirane ring intact and a ring extended structure, produced by a ring extension reaction of the PH-group.

Several rate constants of the ion molecule reactions of the phosphirane molecular ion are given.

Introduction

Since ion cyclotron resonance spectrometry¹ has been established, the thermal ion chemistry of a considerable number of chemically important compounds has been studied. However, there are only a few investigations of organic phosphine derivatives: The proton affinities^{2, 3} and the ion chemistry^{3, 4, 5} of the methylphosphines and the ion chemistry of the methylfluorophosphines⁶ have been investigated.

In this work a detailed study of the ion chemistry of phosphirane will be presented including a discussion of the structure of the molecular ion and the product ions resulting from the ion molecule reactions of this three-membered phosphorus heterocycle and of its ion molecule reactions with deuterated ammonia.

Phosphirane has been prepared eight years ago by Wagner et al.⁷ In the meantime microwave⁸ and infrared spectra^{9–11} have been studied and the compound has excited theoretical interest^{12–15}. Recently phenylphosphirane has been utilized as a phenylphosphorus group insertion reagent¹⁶.

Experimental

The standard ICR spectrometer Varian V 5900 (Varian Ass. Palo Alto, California) utilized for the experiments has been described already in the literature¹, therefore only a brief description of the ex-

perimental details will be given. The double inlet system and the flat ICR cell were built up entirely from steel, aluminium and polyimide. All the spectra were recorded at 30 eV electron energy in the mass range $m/e=2-186$, unless otherwise stated. Electron trap currents were typically 10^{-7} A, giving total ion currents between 10^{-11} and 10^{-12} A. Therefore the disturbances by space charges and ion trapping are expected to be small¹⁷. All the ions appearing in the spectra have been subject to double resonance experiments at several pressures and irradiating field strengths. The effects of the changes of rate constants with ion energy and ion ejection phenomena were considered. The results of ion cyclotron double resonance experiments were supported by pressure plots, whenever possible.

Several rate constants of the ion molecule reactions of the molecular ion at 10.5 eV electron energy (uncorrected) have been determined by the approximation method of Goode et al.¹⁸. Because the pressure has been determined directly from the Vac Ion pump current and the residence times of the ions in the source and analyzer regions have been calculated from the setted magnetic and electric field strengths, this method yields only approximate values of the absolute rate constants, which may be wrong by approximately half of their values. Nevertheless the relative rate constants are much less inaccurate, we suppose an accuracy of $\pm 20\%$.

The ions $m/e=62, 93$ and 124 may contain small proportions of P_2^+ , P_3^+ and P_4^+ , respectively from pyrolysis of phosphirane at the hot filament. However the relative abundances of these ions do not change with filament temperature, as it can be observed in the case of ions resulting from pyrolytic processes⁵.

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Phosphirane has been prepared by the reaction of sodium phosphide with 1,2-dichloroethane in liquid ammonia¹⁹ and purified by trap-to-trap condensation in a vacuum manifold until no ammonia has been detectable in the ICR spectrum. To prevent decomposition the compound was stored in vacuo at liquid nitrogen temperature. Commercial ammonia and deuterated ammonia (J. T. Baker Chemicals Co, Phillipsburg, New Jersey; Sharp and Dohme GmbH, München) were dried with metallic sodium and purified by trap-to-trap condensation before use. The mixtures of phosphirane and ammonia were prepared manometrically.

Results and Discussion

ICR Spectrum

The ICR spectrum of phosphirane at a pressure of 5.6×10^{-7} torr is shown in Figure 1. The mass-corrected relative intensities at 30 and 70 eV elec-

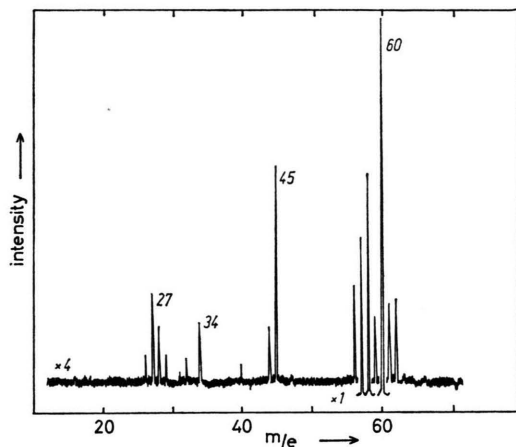


Fig. 1. ICR spectrum of phosphirane at a pressure of 5.6×10^{-7} torr and an electron energy of 30 eV.

tron energy are listed in Table 1 and compared with the two mass spectra available in the literature^{7, 20}. The ICR spectrum compares better with the mass spectrum of Wagner *et al.*⁷ than with that of Chan *et al.*²⁰. However in all cases the molecular ion is the base peak. The ions $m/e = 58$ and 59 are very abundant. It should be noted, that the PCH_3^+ ion, $m/e = 46$, only a minor ion in the spectrum of Wagner and in the ICR spectrum has been found to be an abundant ion by Chan.

If the pressure is raised, new peaks appear in the spectrum. The mass range covered in Fig. 2, showing an ICR spectrum at 5.6×10^{-6} torr, includes all the product ions detected.

Tab. 1. ICR spectra of phosphirane.

Ion comp.	m/e	Relative intensities			
		this work 30 eV	70 eV	Wag- ner ⁷ 80 eV	Chan ²⁰ 70 eV
C_2H_2^+	26	33	135	110	12
C_2H_3^+	27	105	254	305	68
C_2H_4^+	28	71	156	200	272
C_2H_5^+	29	31	—	130	68
C_2H_6^+	30	—	—	—	13
P^+	31	10	128	—	—
PH^+	32	24	120	—	60
PH_2^+	33	—	69	—	64
PH_3^+	34	64	155	132	21
PH_4^+	35	—	—	—	73
PC^+	44	41	86	102	11
PCH_2^+ , HPCH^+	45	166	263	298	89
PCH_3^+ , HPCH_2^+ ^a	46	—	—	—	299
PC_2^+	55	—	—	—	34
HPC_2^+ ^a	56	57	135	170	107
HPC_2H^+ ^a	57	390	607	558	508
HPC_2H_2^+ ^a	58	520	611	622	610
HPC_2H_3^+	59	38	73	—	36
HPC_2H_4^+	60	1000	1000	1000	1000
	61	43	81	—	21
	62	44	107	—	31

^a The composition of these ions has been confirmed by Chan *et al.*²⁰ from their mass spectrometric investigation of deuterated phosphiranes.

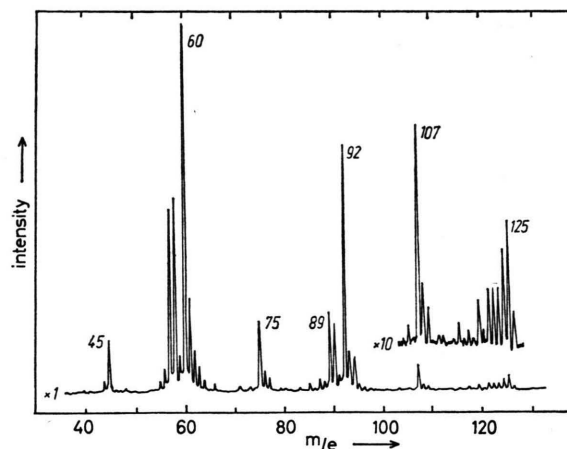


Fig. 2. ICR spectrum of phosphirane at a pressure of 5.6×10^{-6} torr and an electron energy of 30 eV.

The product ions are arranged in groups. Because the more abundant product ions are formed by PH-group transfer reactions, which don't have too different rate constants, each product ion group has a corresponding group of reacting ions, displaced to lower m/e ratios by 32 units, furthermore, both corresponding groups show a very similar distribution of the relative ion intensities.

Pressure Dependence of the Relative Intensities

The pressure dependences of the mass-corrected relative intensities of the more abundant ions are shown in Fig. 3 and those of the less abundant ions in Fig. 4. The dominant proportion of the product ions is formed by four primary ions: $m/e=45$, PCH_2^+ ; $m/e=57$, HPC_2^+ ; $m/e=58$, HPC_2H_2^+ and $m/e=60$, HPC_2H_4^+ . Only the relative intensity of the product ion $m/e=90$ passes through a maximum.

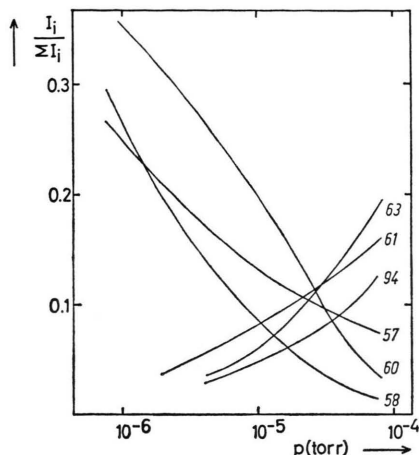


Fig. 3. Mass-corrected relative intensities of the major ions in the ICR spectrum of phosphirane as a function of the total pressure.

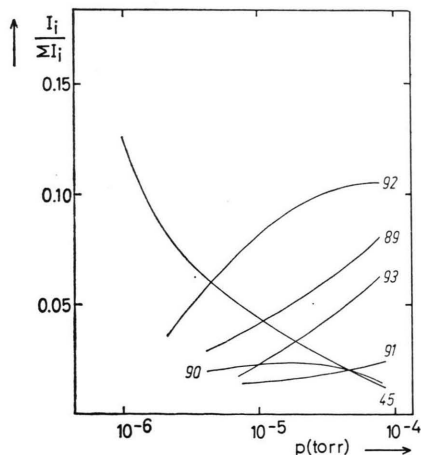


Fig. 4. Mass-corrected relative intensities of the minor ions in the ICR spectrum of phosphirane as a function of the total pressure.

At 10^{-4} torr the product ions are the dominating ion species. However there is no single product ion predominating, the product ion yield is divided

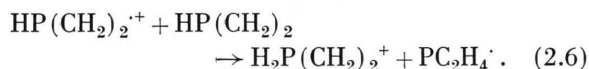
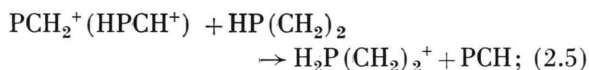
almost equally between several ions. This behaviour is in contrast to that of the methylphosphines^{4,5}, where the protonated molecular ion is the most abundant ion at higher pressures. A second difference between phosphirane and the methylphosphines should also be noted: the relative abundances of the molecular ions of the methylphosphines remain almost constant, raising the pressure, whereas a strong decrease in the case of phosphirane can be observed. Double resonance experiments indicate the lack of charge transfer reactions in the case of phosphirane.

Ion Molecule Reactions

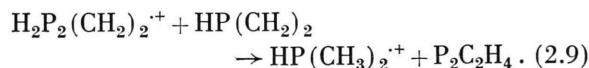
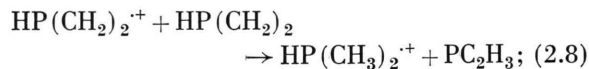
The ion molecule reactions of phosphirane are listed in Table 2. They can be divided into only a few reaction types:

1. reactions leading to diphosphines and triphosphines,
 - a) reactions proceeding via a PH-group transfer,
 - b) other mechanisms;
2. formation of the protonated molecule;
3. collision dissociation reactions;
4. other reactions.

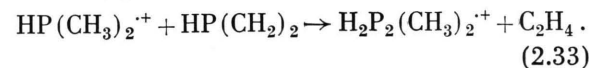
Only one of the more abundant ions, the protonated molecule, is formed by a reaction, which does not proceed via mechanism 1.



The ion $m/e=61$ is thought to be a cyclic quasi phosphonium ion, however ring opening occurs, if a second hydrogen atom is attached:



The ion $m/e=62$ reacts with the neutral phosphirane molecule as does the dimethylphosphine molecular ion²¹ and hence its structure is thought to be $\text{HP}(\text{CH}_3)_2^+$:



A proportion of the primary ions $m/e=55$, 57 and 58 is formed by collision dissociation reactions

Tab. 2. Product ions of the ion molecule reactions of phosphirane.

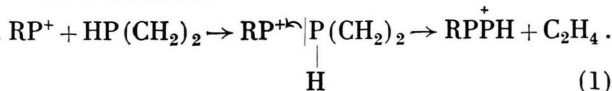
Product ions <i>m/e</i> composition	Reacting ions <i>m/e</i> composition	Reaction type	No.
<i>a) secondary ions</i>			
55 PC ₂ ⁺	57 HPC ₂ H ⁺	3	1
57 HPC ₂ H ⁺	58 HP(CH) ₂ ²⁺	3	2
	60 HP(CH ₂) ₂ ²⁺	3	3
58 HP(CH ₂) ₂ ⁺	60 HP(CH ₂) ₂ ²⁺	3	4
61 H ₂ P(CH ₂) ₂ ⁺	45 PCH ₂ ⁺	2	5
	60 HP(CH ₂) ₂ ²⁺	2	6
62 ^a HP(CH ₃) ₂ ²⁺ (P ₂ ⁺)	56 HPC ₂ ²⁺	4	7
	60 HP(CH ₃) ₂ ²⁺	4	8
	92 H ₂ P ₂ (CH ₂) ₂ ²⁺	4	9
63 HP ₂ ⁺	45 PCH ₂ ⁺	1 b	10
	57 HPC ₂ H ⁺	1 b	11
	60 HP(CH ₂) ₂ ²⁺	1 b	12
64 H ₂ P ₂ ²⁺	60 HP(CH ₂) ₂ ²⁺	1 b	13
65 H ₃ P ₂ ²⁺	33 PH ₂ ⁺	1 a	14
66 H ₄ P ₂ ²⁺	34 PH ₃ ⁺	1 a	15
75 P ₂ CH ⁺ (C ₃ H ₈ P ⁺)	45 PCH ₂ ⁺	1 b	16
	58 HP(CH) ₂ ²⁺	1 b	17
	60 HP(CH ₂) ₂ ²⁺	1 b	18
76 HP ₂ CH ⁺	60 HP(CH ₂) ₂ ²⁺	1 b	19
77 HPCH ₂ ⁺	45 PCH ₂ ⁺	1 a	20
87 HP ₂ C ₂ ⁺	57 HPC ₂ H ⁺	1 b	21
	58 HP(CH) ₂ ²⁺	1 b	22
	60 HP(CH ₂) ₂ ²⁺	1 b	23
88 H ₂ P ₂ C ₂ ²⁺	56 HPC ₂ ²⁺	1 a	24
89 HP ₂ C ₂ H ₂ ⁺	57 HPC ₂ H ⁺	1 a	25
	58 HP(CH) ₂ ²⁺	1 b	26
90 H ₂ P ₂ C ₂ H ₂ ⁺	58 HP(CH) ₂ ²⁺	1 a	27
91 HP ₂ C ₂ H ₄ ⁺	57 HPC ₂ H ⁺	1 b	28
	59 HPC ₂ H ₃ ⁺	1 a	29
92 H ₂ P ₂ C ₂ H ₄ ⁺	60 HP(CH ₂) ₂ ²⁺	1 a	30
<i>b) tertiary and quaternary ions</i>			
93 P ₂ C ₂ H ₇ ⁺ (P ₃ ⁺)	61 H ₂ P(CH ₂) ₂ ⁺	1 a	31
	75 P ₂ CH ⁺	1 b	32
94 H ₂ P ₂ (CH ₃) ₂ ²⁺ (P ₃ H ⁺)	62 HP(CH ₃) ₂ ⁺	1 a	33
107 HP ₂ CH ⁺	75 P ₂ CH ⁺	1 a	34
108 H ₂ P ₃ CH ⁺	76 HP ₂ CH ⁺	1 a	35
	92 H ₂ P ₂ C ₂ H ₄ ⁺	1 b	36
109 H ₂ P ₃ CH ₂ ⁺	77 HP ₂ CH ₂ ⁺	1 a	37
	91 HP ₂ C ₂ H ₄ ⁺	1 b	38
120 H ₃ P ₃ C ₂ ²⁺	88 H ₂ P ₂ C ₂ ²⁺	1 a	39
121 H ₂ P ₃ C ₂ H ₂ ⁺	89 HP ₂ C ₂ H ₂ ⁺	1 a	40
122 H ₃ P ₃ C ₂ H ₂ ⁺	90 H ₂ P ₂ C ₂ H ₂ ⁺	1 a	41
123 H ₂ P ₃ C ₂ H ₄ ⁺	92 H ₂ P ₂ C ₂ H ₄ ⁺	1 b	42
124 H ₃ P ₃ C ₂ H ₄ ⁺	92 H ₂ P ₂ C ₂ H ₄ ⁺	1 a	43
125 H ₃ P ₃ C ₂ H ₅ (P ₄ H ⁺)	89 HP ₂ C ₂ H ₂ ⁺	1 b	44
	93 H ₂ P ₂ C ₂ H ₅ ⁺	1 a	45
126 H ₃ P ₃ (CH ₃) ₂ ²⁺ (P ₄ H ₂ ⁺)	94 H ₂ P ₂ (CH ₃) ₂ ²⁺	1 a	46

^a The dimethylphosphenium ion is formed by reactions of primary and secondary ions.

(2.1) – (2.4). In the course of these reactions H₂ or H₂ + H⁺ are formed as neutral particles.

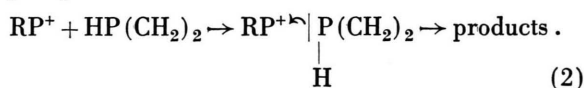
The majority of the product ions is formed by reactions, which have the mechanism 1. The most

probable mechanism of reactions of type 1 a is a nucleophilic attack by the phosphorus atom of the neutral phosphirane molecule at the phosphorus atom of the ion:



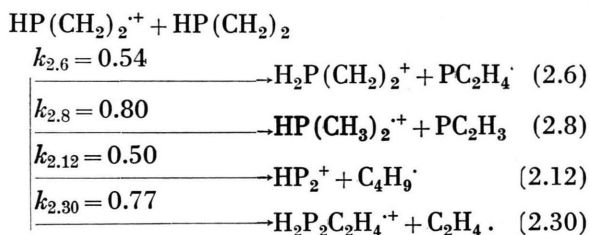
In the course of all these nucleophilic displacements ethene is formed as neutral particle.

The mechanism of the reactions of type 1 b cannot be expressed by a single formula, however the first step will also be an attack of the phosphorus atom of the neutral phosphirane molecule at the phosphorus atom of the ion:



Quantitative Results

The rate constants of the four main ion molecule reactions of the molecular ion of phosphirane are:



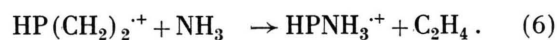
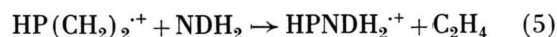
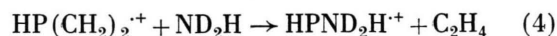
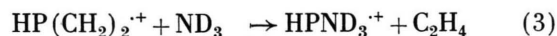
They are given in units of 10⁻¹⁰ cm³ molecule⁻¹ sec⁻¹. The rate constant of the formation reaction (2.6) of the protonated molecule is much smaller than of the open-chained analogue, dimethylphosphine. Its corresponding reaction has a rate constant of 1.4 × 10⁻¹⁰ cm³ molecule⁻¹ sec⁻¹⁵. Formation of the three-membered ring has a strong retarding effect on the rate of this reaction. Further investigations will show, whether the dissociation of a PH- or CH-bond or quaternization of the phosphorus atom is rendered more difficult.

The other three rate constants measured have approximately the same magnitude as the rate constant of reaction (2.6). Not only the ring opening reaction (2.8) but also the reaction (2.12) proceed surprisingly fast. The ion *m/e* = 63, HP₂⁺, which does not react further is the most abundant ion at elevated pressures. Reaction (2.30) is the reaction with the greatest rate constant of the molecular ion, which proceeds according to mechanism 1 a and has a rate

constant approximately by a factor of two larger than the highest rate constants of formation of ions with two phosphorus atoms from the methylphosphines^{4, 5}.

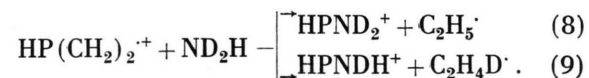
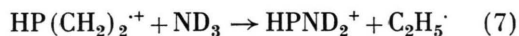
Mixtures of Phosphirane with Deuterated Ammonia, Structure of the Phosphirane Molecular Ion

The phosphirane molecular ion adds a PH-group to ammonia according to reaction type 1 a. At 11 eV electron energy (uncorrected) the following reactions have been observed with ND₃, ND₂H, NDH₂ and NH₃:



This reaction sequence indicates that the formation of the product ions proceeds without scrambling of H and D between the phosphirane molecular ion and ammonia.

Above approximately 15 eV electron energy (uncorrected) a new reaction channel is opened. Additionally an H(D)-atom is dissociated from ammonia:



This second reaction channel is exemplified for the reactions of ND₃ and ND₂H by reactions (7) to (9).

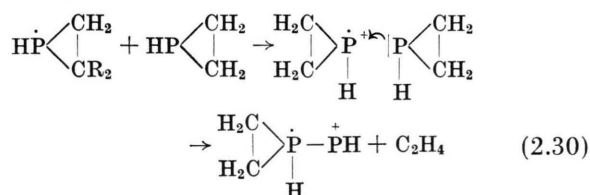
Comparison of the reactions of the phosphirane molecular ion with ammonia and the ion molecule reactions of phosphirane described earlier show that the neutral molecule and the molecular ion undergo the same reactions, namely PH-transfer. Therefore the ring structure of the neutral molecule is proved to be preserved during ionization. The reactions (3) to (9) are paralleled by the reactions of the cyclopropane cation with ammonia, which have been studied by Gross and McLafferty²² who showed that only the cyclopropane molecular ion, which is cyclic, reacts with ammonia and not the propene molecular ion. Predomination of CH₂-group transfer and formation of C₂H₄ neutral molecules in the ion chemistry of the cyclopropane molecular ion contrary to that of the propene molecular ion has also been shown^{21, 23, 24}. A PH-group is also transferred by

phosphirane to the PH₃⁺ ion to form P₂H₄⁺ ions. On the contrary oxirane shows another reaction²⁵: It reacts with PH₄⁺ to form PC₂H₆⁺ ions and H₂O.

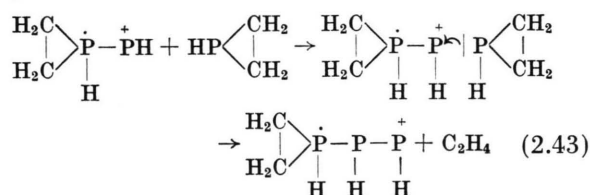
Product Ion Structures

It has already been shown that the cyclic structure of phosphirane remains intact during ionization. Now the structure of ions with two or three phosphorus atoms will be discussed.

According to mechanism 1 a, the product ions formed contain an additional PH-group, and C₂H₄ neutral molecules are generated. One of the most abundant secondary ions with two phosphorus atoms is the ion *m/e* = 92, H₂P₂C₂H₄⁺. If the phosphirane ring remains intact, it must have a phosphorane-phosphinium structure:

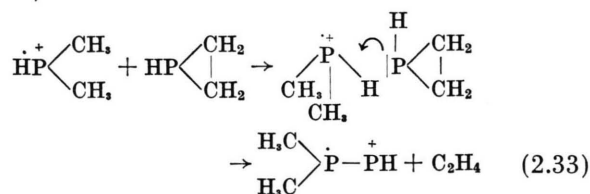


This ion reacts further to a product with three phosphorus atoms:



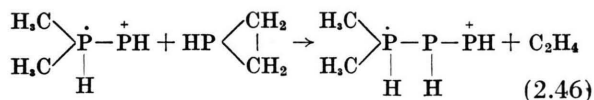
Also the ion *m/e* = 123, H₂P₃(CH₂)₂⁺, is formed by the secondary ion *m/e* = 92, according to mechanism 1 b.

The dimethylphosphonium ion HP(CH₃)₂⁺, formed by reaction (2.7) reacts to give the tertiary ion *m/e* = 94:



This product ion has the same structure as the monomer PCF₃-complex of trimethylphosphine, (CH₃)₃PPCF₃, synthesized by Burg and Mahler²⁶. This complex adds easily one or two molecules of the Lewis acid BH₃²⁷. The ease of the addition of a second PH-unit, which may be regarded as a Lewis

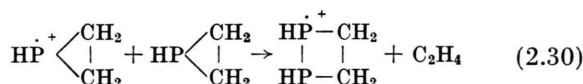
base to the positive charged PH-group of the ion $m/e=94$ can be paralleled to the addition of the Lewis acid BH_3 to the negative PCF_3 -group:



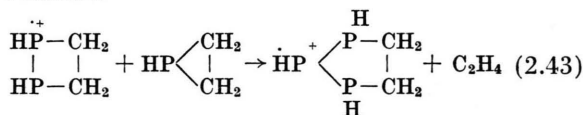
However, an addition of a further PH-group to the quaternary ion $m/e=126$ could not be detected. The formation of linear phosphorus chains is not uncommon. Recently Stelzer and Unger²⁸ described the formation of a molybdenum complex of hexamethyltetraphosphine: *cis*- $\text{Mo}(\text{CO})_4\text{P}_4(\text{CH}_3)_6$.

All the product ions which contain a $\text{P}(\text{CH}_2)_2$ -unit may have structures similar to those of the ions $m/e=92$ and 124, leaving the phosphirane ring intact. However an alternative structure seems to be more probable. Phenylphosphirane inserts a phenylphosphorus group into a dithiene ring¹⁶, ethene is formed in a concerted elimination reaction. There-

fore in the ion chemistry of phosphirane a PH-group insertion reaction with ring expansion is also likely to occur. The formation of the ions $m/e=92$ and 124 may serve as an example:



The ion $m/e=92$ undergoes another ring expansion reaction:



Acknowledgements

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