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Mass Spectral Fragmentation Patterns of Trichloroimidophosphoranes, Cl_3PNX, and of Hexachlorodiazadiphosphetidines, $(Cl_3PNX)_2$

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Fragmentation patterns under electron impact of fifteen trichloroimidophosphoranes, Cl_3PNX, and of six hexachlorodiazadiphosphetidines, $(Cl_3PNX)_2$ are reported and discussed. The group X is variously: alkyl, alkoxyl, aryl, arylcarbonyl, arylsulphonyl, $CONPCl_3$, SO_2NPCl_3 or SO_3H.

Introduction

In connection with other work, we had occasion to prepare a number of imidophosphoranes $(XNPY_3)_m$ where m is 1 or 2, in particular those having Y = Cl. Although very many of these derivatives are known, the only physical properties reported[1] for most of them are parameters such as melting point, refractive index or density. With the exception of the ^1H and ^{31}P n.m.r. spectra reported[2,3] for compounds having X = alkyl, essentially no molecular spectroscopic data have been reported for this large class of compound. For many of these compounds, especially for those having X = aryl and Y = halogen, there is uncertainty even as to the value of m.[1] Accordingly we report now the results of a mass spectrometric study of some 21 of these compounds.

Experimental

Compounds having Y = Cl were prepared by reaction of PCl_5 with XNH_2 (if solid), or otherwise with XNH_3Cl, usually in refluxing carbon tetrachloride solution.[4] If X = Ar or $ArSO_2$, then heating XNH_2 and PCl_5 in the absence of a solvent is also satisfactory: however if X = alkyl, reaction in the absence of a solvent generally leads[3] not to $XNPCl_3$ but to XCl and $(NPCl_2)_n$ (n = 3 or 4). For reasons unknown, we were unable to prepare derivatives of the following amines: cyclohexylamine, *o*-phenylenediamine, sulphanilamide, *o*- and *m*-methoxyanilines. Purification was effected by recrystallisation from carbon tetrachloride or light petroleum. No impurities were revealed by ^1H or ^{31}P n.m.r. spectroscopy, or by the mass spectra.

Mass spectra were determined at 70eV using an A.E.I. MS902 instrument: accurate mass measurements were not generally necessary, since the number of chlorine atoms in a particular ion was readily recognised from the isotopic pattern, and this greatly facilitated the recognition and identification of ions.

Results and Discussion

Trichloroimidophosphoranes, Cl_3PNR

For the molecular ion of a monomeric trichloroimidophosphorane of type Cl_3PNR^+, there are several possible decomposition routes: (i) loss of successive neutral chlorine atoms (Route A); (ii) loss of the neutral nitrene NR (Route B); (iii) loss of neutral PCl_3 (Route C); (iv) fragmentation of the group NR while still attached to Cl_3P.

$$Cl_3PNR^+ \xrightarrow{-Cl\cdot} Cl_2PNR^+ \xrightarrow{-Cl\cdot} ClPNR^+ \xrightarrow{-Cl\cdot} PNR^+ \quad (A)$$

$$Cl_3PNR^+ \xrightarrow{-NR} Cl_3P^+ \quad (B)$$

$$Cl_3NR^+ \xrightarrow{-PCl_3} NR^+ \quad (C)$$

$$Cl_3PNR^+ \xrightarrow{-R'} Cl_3PNR''^+ \quad (D)$$

The simplest compounds of type Cl_3PE are Cl_3PO and Cl_3PS, whose mass spectra are summarised in Table I (as in all tables in this paper, mass numbers are quoted only for ions $(^{35}Cl)_nX$, but relative abundances refer to all isotopic ions of composition Cl_nX).

TABLE I. Mass Spectra of Cl_3PO and Cl_3PS.

Ion	E = O	E = S
Cl_3PE^+	37	23
Cl_2PE^+	100	100
$ClPE^+$	5.9	5.7
PE^+	40	17
Cl_3P^+	1.5	3.8
Cl_2P^+	2.9	13
ClP^+	12	11

TABLE II. Mass Spectra of Cl_3PNSO_2X.

Ion	X = OH		X = C_6H_5		X = $C_6H_4CH_3$-p	
	m/e	RI	m/e	RI	m/e	RI
M^+	231	4.2	291	6.7	305	11.2
$(M-X)^+$	214	100	214	8.3	214	8.0
$(M-SO_2)^+$	169	0	227	7.5	241	4.0
$(M-X-O)^+$	198	1.4	198	58	198	92
XN^+	–	–	91	20	105	10
X^+	–	–	77	100	91	100
Cl_3PN^+	150	19.4	150	3.1	150	7.5
Cl_3P^+	136	4.6	136	18	136	2.5
Cl_2PN^+	115	44	115	1.5	115	1.4
Cl_2P^+	101	44	101	71	101	6.3
$ClPN^+$	80	35	80	8.1	80	0
ClP^+	66	24	66	27	66	4.7

For both compounds, the base peak of the spectrum is the quasi-phosphonium ion $Cl_2P{=}X^+$ (X = O, S), with the decomposition of the molecular ion largely following Route A with but a little Route B.

Compounds Cl_3PNSO_2X

In Table II are set out the mass spectra of three compounds of type Cl_3PNSO_2X, having X = OH, C_6H_5, and $C_6H_4CH_3$-p. When X = OH, the base peak of the spectrum is $(M-X)^+$, while for the other two species, the base peak is X^+. No decomposition *via* Route A is observed, the principal fragmentations being *via* Route D: in the aromatic species prominent Route D ions are Cl_3PNSO^+ (RI = 58% of base peak for X = C_6H_5 and 92% for X = $C_6H_4CH_3$), isoelectronic with the neutral thionylimides R_3MNSO (M = C,Si). Loss of SO_2 is observed in the aromatic species as found also in sulphones[5] and sulphonamides[6], together with the ions $XN^+ = (M-Cl_3P-SO_2)^+$. A further Route D ion is Cl_3PN^+, which breaks down primarily *via* Route A, in a similar manner to Cl_3PO^+.

TABLE III. Mass Spectra of $Cl_3PNC_6H_4X$ (X = p-CH_3 and p-CH_3O).

Ion	X = p-CH_3		X = p-CH_3O	
	m/e	RI	m/e	RI
M^+	241	70	257	81
$(M-Cl)^+$	206	7.7	222	19
$(M-2Cl)^+$	171	22	187	29
$(M-3Cl)^+$	136	43	152	50
$(M-CH_3)^+$	–	–	242	100
$(M-CH_3-Cl)^+$	–	–	207	0
$(M-CH_3-2Cl)^+$	–	–	172	17
$(M-CH_3-3Cl)^+$	–	–	137	12
$(M-CH_3-CO)^+$	–	–	214	9.5
$XC_6H_4N^+$	105	100	121	60
$XC_6H_4^+$	91	22	107	7.1
$C_6H_4N^+$	90	6.7	90	19
Cl_3P^+	136	3.2	136	9.4
Cl_2P^+	101	11	101	43
ClP^+	66	6.0	66	18
Cl_3[a]		44.9		51.5
Cl_2		11.5		16.0
Cl_1		17.2		16.5
Cl_0		26.4		16.0

$$^{a}Cl_n = \frac{\text{Ion current carried by ions containing } P + n\,Cl}{\text{Total ion current carried by all P-containing ions}} \times 100.$$

Compounds $Cl_3PNC_6H_4X$

The mass spectra of five compounds of this type have been determined: the spectra of those having X = p-CH_3 and p-CH_3O are set out in Table III, and of those with X = o-NO_2, m-NO_2 and p-NO_2 in Table IV. The spectrum of $Cl_3PNC_6H_4CH_3$ presents an interesting contrast with that of its sulphonyl analogue: Route A is now a major decomposition pathway, and the relative abundances of $NC_6H_4CH_3^+$ and $C_6H_4CH_3^+$ are essentially reversed in the two cases. Notional insertion of a single oxygen atom to yield $Cl_3PNC_6H_4OCH_3$ again gives substantial decomposition of the molecular ion by Route A, but the base peak of the spectrum is now $(M-CH_3)^+$ (structure I)


(I)

from which further loss of CO occurs, to give an ion whose structure is possibly that of the P-pyrrolotrichlorophosphonium ion (II)

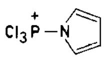

(II)

TABLE IV. Mass Spectra of Three Isomeric $Cl_3PNC_6H_4NO_2$.

		X = *o*-NO_2	X = *m*-NO_2	X = *p*-NO_2
	m/e	RI	RI	
M^+	272	36	10	39
$(M–Cl)^+$	237	2.8	1.9	5.5
$(M–2Cl)^+$	202	0	0	0.8
$(M–3Cl)^+$	167	0	1.6	3.8
$(M–O)^+$	256	0.6	9.0	1.3
$(M–NO)^+$	242	1.6	0	14
$(M–NO_2)^+$	226	0.4	3.9	2.6
$(M–NO–CO)^+$	214	7.0	0.7	2.8
$(M–NO_2–Cl)^+$	191	1.4	1.6	2.5
$(M–NO_2–2Cl)^+$	156	4.4	2.4	4.3
$(M–PCl)^+$	206	11	0	0
$(M–PCl–O)^+$	190	6.4	0	0
$ONC_6H_4N^+$	106	6.4	2.6	6.9
$C_6H_4N^+$	90	100	100	100
$OPCl_3{}^+$	152	30	23	3.4
$OPCl_2{}^+$	117	24	24	10
$OPCl^+$	82	1.7	1.7	0.6
OP^+	47	8.0	5.8	3.2
$PCl_3{}^+$	136	4.4	1.3	4.0
$PCl_2{}^+$	101	30	9.0	13
PCl^+	66	5.0	7.7	2.1
Cl_3		45.8	46.0	59.4
Cl_2		43.3	35.0	27.5
Cl_1		6.4	11.8	6.9
Cl_0		4.5	7.1	6.2

Formation of the pyridinium cation, as observed in the mass spectrum of the parent *p*-methoxyaniline (*p*-anisidine)[7], is precluded by the absence of mobile hydrogen atoms initially bound to nitrogen.

The spectra of the three nitro-substituted derivatives, $Cl_3PNC_6H_4NO_2$ are broadly similar, the base peak of each spectrum being $C_6H_4N^+$: decomposition occurs *via* routes A, B and D to roughly equal extents. Although the majority of the ions produced by Route D decompositions are analogous to ions observed in the spectra of the parent amines, it is of interest that the abundance of Cl_3PO^+ is highest in the *ortho* isomer, decreasing *ortho*>*meta*>*para*. Although unsupported by observation of a metastable peak, it is possible that this ion arises directly from the molecular ion: the "counter-ion" $(M–Cl_3PO)^+$ is observed to a lesser extent in all three isomers.

A most unusual rearrangement, observed only in the *ortho* isomer, and supported by a metastable peak is the extrusion of phosphorus from $(M–Cl)^+$ to give $(M–PCl)^+$ whose subsequent loss of oxygen is also metastable-supported:

$$({}^{35}Cl)_2PNC_6H_4NO_2{}^+ \xrightarrow{\text{m.s. } 179.1} ({}^{35}Cl)_2NC_6H_4,NO_2^+$$

$$\xrightarrow{\text{m.s. } 175.2} ({}^{35}Cl)_2NC_6H_4NO^+$$

We note that in all these aromatic species, $(M–3Cl)^+$ ions, possibly having the quasi-ammonium structure III,

$$XC_6H_4–\overset{+}{N}{\equiv}P \qquad \text{(III)}$$

are very abundant if X is an electron source (CH_3 or CH_3O), but occur hardly at all if X is an electron sink (NO_2).

Finally, we find no evidence from these mass spectra to support the contention[1] that compounds Cl_3PNAr are dimeric, at least in the vapour phase.

Compounds Cl_3PNCOX

The reaction of PCl_5 with carboxylic acid amides to yield, ultimately, nitriles, has been long known, and many intermediates have been suggested,[8] including one in which a 1 : 1 complex is formed, followed by the elimination of Cl_3PO, followed by loss of HCl. We find that refluxing a mixture of benzamide and PCl_5 in carbon tetrachloride gives copious evolution of hydrogen chloride: the mass spectrum of the product remaining after removal of the solvent contains ions due, not only to Cl_3PO^+, $C_6H_5CN^+$ and their decomposition products but also the ion $Cl_3PNCOC_6H_5^+$ and its decomposition products (Table V). Similarly in the spectrum of the product derived from PCl_5 and acetamide, the ions $Cl_nPNCOCH_3^+$ (n = 1, 2 or 3) are observed.

TABLE V. Mass Spectrum of $Cl_3PNCOC_6H_5$.

Ion	m/e	RI
M^+	255	0.7
$(M-Cl)^+$	220	21
$(M-2Cl)^+$	185	1.4
Cl_3PNC^+	162	0.4
Cl_3PO^+	150	17
Cl_2PO^+	117	67
$ClPO^+$	80	4.9
Cl_3P^+	136	0
Cl_2P^+	101	1.2
ClP^+	66	32
$C_6H_5CN^+$	103	100
$C_6H_4^+$	76	69

Compounds Cl_3PNR (R = alkyl)

For compounds in which the alkyl group is unbranched at the α-carbon, dimerisation to diazadiphosphetidines containing a four-membered NPNP ring occurs. When R is branched at the α-carbon, the compounds are monomeric, and the mass spectra of compounds having R = $(CH_3)_3C$, $CH_3(C_2H_5)CH$, and $(CH_3)_2CH$ are summarised in Table VI. On the basis of n.m.r. spectroscopy, Gutmann and his colleagues concluded[2] that the compound having R = $(CH_3)_2CH$ is dimeric: they quoted no numerical data, but based their conclusion on the number of lines observed for the unique C*H* resonance which they reported as nine. This number of lines is incomprehensible for either monomeric or dimeric $(CH_3)_2CH$ $NPCl_3$. We find the unique C*H* resonance, in CCl_4 solution, to be a doublet of septets having δ = 3.83 p.p.m., $^3J(HCNP)$ = 38 Hz, $^3J(HCCH)$ = 7Hz. Both the splitting pattern, and the value of $^3J(HCNP)$ (usually *ca.* 29Hz in dimeric species,[2,3] but 38Hz also[9] in monomeric $CH_3(C_2H_5)CHNPCl_3$) confirm the conclusion drawn here from the mass spectrum that $(CH_3)_2CHNPCl_3$ is indeed monomeric.

The principal decomposition pathway for the molecular ions of these compounds is *via* Route D: surprisingly few common ions containing a C_3NP skeleton are observed, there being no $(M-2Cl)^+$, $(M-3Cl)^+$ or Cl_3PN^+ ions in any of the spectra. However in the spectra of the two butyl derivatives the doubly charged ions $(H_3C_2NPCl_3)^{+2}$, possibly having structure IV are observed (7.3% of base peak when R = $(CH_3)_3C$, and 1.0% when R = $CH_3(C_2H_5)CH$).

TABLE VI. Mass Spectra of Cl_3PNR (R = $(CH_3)_3C$, $CH_3(C_2H_5)CH$ and $(CH_3)_2CH$).

Ion	R = $(CH_3)_3C$		R = $CH_3(C_2H_5)CH$		R = $(CH_3)_2CH$	
	m/e	RI	m/e	RI	m/e	RI
M^+	207	2.7	207	3.0	193	0
$(M-CH_3)^+$	192	87	192	4.7	178	6.1
$(M-C_2H_5)^+$	–	–	178	63	–	–
$(M-Cl)^+$	172	10	172	7.3	158	25
$C_3H_9NPCl_2^+$	160	0	160	100	160	0
$C_4H_9^+$	57	36	57	16	–	–
$C_4H_8^+$	56	83	56	17	–	–
$C_2H_8N^+$	46	100	46	0	46	0
$C_3H_7^+$	43	0	43	0	43	34
$C_3H_6^+$	42	28	42	50	42	100
$C_3H_5^+$	41	39	41	41	41	52
$C_3H_3^+$	39	19	39	18	39	38
PCl_3^+	136	8.9	136	6.5	136	3.4
PCl_2^+	101	20	101	25	101	25
PCl^+	66	18	66	12	66	23

TABLE VII. Mass Spectrum of $(Cl_3PN)_2SO_2$.

Ion	m/e	RI
$O_2SN_2P_2Cl_6^+$	364	0
$OSN_2P_2Cl_6^+$	348	3.4
$OSN_2P_2Cl_5^+$	313	6.9
$ONP_2Cl_5^+$	267	4.6
$ONP_2Cl_4^+$	232	92
$ONP_2Cl_3^+$	197	16
$ONP_2Cl_2^+$	162	34
ONP_2Cl^+	127	4.6
ONP_2^+	92	61
$O_2SNPCl_3^+$	214	68
$O_2SNPCl_2^+$	179	3.5
$NP_2Cl_2^+$	146	11
NP_2Cl^+	111	11
$NPCl^+$	76	23
$NPCl_3^+$	150	28
$NPCl_2^+$	115	17
$NPCl^+$	80	86
PCl_3^+	136	9.2
PCl_2^+	101	100
PCl^+	66	91

$$H_3C{-}C{\equiv}\overset{+}{N}{-}\overset{+}{P}Cl_3 \leftrightarrow H_3C{-}\overset{+}{C}{=}N{-}\overset{+}{P}Cl_3 \qquad \text{(IV)}$$

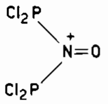
When R = $(CH_3)_3C$ and $(CH_3)_2CH$, the base peak of the spectrum is a decomposition product of RN: when R = $CH_3(C_2H_5)CH$, however, the base peak of the spectrum has composition $C_3H_9NPCl_2^+$. This ion is most plausibly assigned structure V, the adduct of a propylamine with PCl_2^+.

$$C_3H_7{-}\overset{+}{N}H_2{-}PCl_2 \qquad \text{(V)}$$

Although the formation of $C_nH_{2n+3}N^+$ ions is common[10] in the mass spectra of uncomplexed amines, these ions are usually of fairly low abundance.

$(Cl_3PN)_2SO_2$

This compound is the derivative of sulphamide, and its mass spectrum is set out in Table VII. The molecular ion is absent from the spectrum, the two heaviest ions being $OSN_2P_2Cl_6^+$ $(M{-}O)^+$ and $OSN_2P_2Cl_5^+$ $(M{-}O{-}Cl)^+$: no further ions of the series $OSN_2P_2Cl_n^+$ are observed. In the series $ONP_2Cl_n^+$, all ions except that having n = 6 are observed. Further partial series of ions are $O_2SNPCl_n^+$ (n = 3 and 2), $NP_2Cl_n^+$ (n = 2, 1, 0), and $NPCl_n^+$ (n = 3, 2, 1), in addition to PCl_n^+ (n = 3, 2, 1). Surprisingly no doubly charged ions are observed. The base peak of the spectrum is PCl_2^+, and the next most abundant ion is $ONP_2Cl_4^+$, possibly having structure VI, that of the bis(dichlorophosphino)nitroxyl cation,



(VI)

$(Cl_3PN)_2CO$

$(Cl_3PN)_2CO$ is derived from the reaction of phosphorus pentachloride and urea, and its mass spectrum is presented in Table VIII. Just as the spectrum of $(Cl_3PN)_2SO_2$ is dominated by the series $ONP_2Cl_n^+$, initiated by loss of NSO so the spectrum of $(Cl_3PN)_2$ CO is dominated by an ion series initiated by loss of CO, $N_2P_2Cl_n^+$. The most prominent ions are those of the series $OPCl_n^+$, probably arising by the fragmentation

$$Cl_3PNCONPCl_3^+ \rightarrow Cl_3PNCN + OPCl_3^+$$

followed by loss of successive chloride atoms. This would be analogous to the process found in the species Cl_3PNCOR[3] and Cl_3PNCOR^+. The ion $CN_2PCl_3^+$ may have structure VII, arising from the process

$$Cl_3PNCONPCl_3^+ \rightarrow Cl_3PO + CN_2PCl_3^+$$

$$Cl_3PNCN^+ \qquad \text{(VII)}$$

Hexachlorodiazadiphosphetidines, $(Cl_3PNR)_2$

The mass spectra of five N,N-dialkyldiazadiphosphetidines have been recorded, for compounds having R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9 and $C_6H_5CH_2$. As with other compounds containing two Cl_3PN groups, the ions in the mass spectra can be grouped, according

TABLE VIII. Mass Spectrum of $(Cl_3PN)_2CO$.

Ion	m/e	RI
$OCN_2P_2Cl_6^+$	328	4.3
$OCN_2P_2Cl_5^+$	293	2.3
$N_2P_2Cl_6^+$	300	2.6
$N_2P_2Cl_5^+$	265	2.8
$N_2P_2Cl_4^+$	230	25
$N_2P_2Cl_3^+$	195	1.8
$N_2P_2Cl_2^+$	160	1.4
$CN_2PCl_3^+$	174	1.1
$NP_2Cl_3^+$	181	1.7
$NP_2Cl_2^+$	146	1.5
$OPCl_3^+$	152	49
$OPCl_2^+$	117	100
$OPCl^+$	82	9.2
OP^+	47	47
PCl_3^+	136	14
PCl_2^+	101	49
PCl^+	66	18

TABLE IX. Ion Series Occurring in the Mass Spectra of $(Cl_3PNR)_2$.

Series	R = CH_3	C_2H_5	n-C_3H_7	n-C_4H_9	$C_6H_5CH_2$
$(RN)_2P_2Cl_n^+$	+	+	+	+	+
$(RN)P_2NCl_n^+$	–	–	+	–	+
$(RN)P_2Cl_n^+$	–	+	–	–	–
$P_2N_2Cl_n^+$	–	–	–	–	+
$P_2NCl_n^+$	+	–	+	+	+
$(RN)_2PCl_n^+$	+	–	–	–	–
$(RN)PCl_n^+$	+	+	+	+	+
$PN_2Cl_n^+$	+	+	+	+	–

to the number of R groups, and of N or P atoms, into series, the members of an ion series differing only in their numbers of Cl atoms. The ions series represented in the spectra of the compounds studied are set out in Table IX. Some ion series occur in all the compounds studied, others in only one or two: no obvious pattern can be discerned.

TABLE X. Mass Spectrum of $(Cl_3PNCH_2C_6H_5)_2$.

Series	Ion	m/e	RI
$(RN)_2P_2Cl_n^+$	$R_2N_2P_2Cl_6^+$	482	0
	$R_2N_2P_2Cl_5^+$	447	4.7
	$R_2N_2P_2Cl_4^+$	412	0.2
	$R_2N_2P_2Cl_3^+$	377	3.9
	$R_2N_2P_2Cl_2^+$	342	1.0
	$R_2N_2P_2Cl^+$	307	1.0
	$R_2N_2P_2^+$	272	0
$(RN)P_2NCl_n^+$	$RN_2P_2Cl_6^+$	391	0
	$RN_2P_2Cl_5^+$	356	1.6
	$RN_2P_2Cl_4^+$	321	1.2
	$RN_2P_2Cl_3^+$	286	0
	$RN_2P_2Cl_2^+$	251	2.9
	$RN_2P_2Cl^+$	216	0
	$RN_2P_2^+$	181	3.6
$P_2N_2Cl_n^+$	$N_2P_2Cl_3^+$	195	5.3
$P_2NCl_n^+$	$NP_2Cl_4^+$	216	2.7
$(RN)PCl_n^+$	$RNPCl_3^+$	241	1.1
	$RNPCl_2^+$	206	3.1
	$RNPCl^+$	171	0
	RNP^+	136	2.3
	PCl_3^+	136	2.8
	PCl_2^+	101	8.5
	$C_7H_6NPCl_3^+$	240	2.2
	$C_7H_6NPCl^+$	170	3.3
	$C_7H_7Cl^+$	126	89
	$C_7H_7N^+$	105	13
	$C_7H_7^+$	91	100

As an example, the spectrum of the benzyl species is given in full in Table X. The base peak of the spectrum is the ion $C_7H_7^+$ which presumably takes the usual tropylium form[11]; the next most intense is the $C_7H_7Cl^+$ ion, the molecular ion of benzyl chloride. The sample was shown to be free of benzyl chloride before introduction into the mass spectrometer, and although $(Cl_3PNCl_2C_6H_5)_2$ readily forms $C_6H_5CH_2Cl$, $(NPCl_2)_3$ and $(NPCl_2)_4$ on heating[3], the formation of the benzyl chloride by pyrolysis in the sample chamber is felt to be unlikely, since the spectrum shows no evidence whatever for the ions $N_4P_4Cl_8^+$, $N_3P_3Cl_6^+$ or their decomposition products. Consequently the ion $C_7H_7Cl^+$ is regarded as a genuine decomposition product of an ion of higher mass number, although there are no metastable peaks in the spectrum which allow the identification of the process giving rise to $C_7H_7Cl^+$. A plausible metastable at 65.9 corresponding to

$$C_7H_7NPCl_3^+ \rightarrow C_7H_7Cl^+ + NPCl_2$$

is overlain by the strong metastable at 65.7 corresponding to

$$C_7H_7Cl^+ \rightarrow C_7H_7^+ + Cl$$

Five of the ion series mentioned in Table IX are represented in this spectrum, and it is noteworthy that the even-electron ions are generally much more abundant than the odd-electron ions. Ions of the form $X_3N_2P_2^+$, such as $R_2N_2P_2Cl^+$, $RN_2P_2Cl_2^+$ and $N_2P_2Cl_3^+$ may be regarded as eight valence-electron polyhedra, and so most probably[12] have tetrahedral N_2P_2 cages, while ions of the form $XN_2P_2^+$, such as RN_2P_2, are ten valence-electron polyhedra and so have square planar N_2P_2 fragments.

Compositionally analogous to the foregoing N,N-dialkyldiazadiphosphetidines, and presumably having a structure based on the same square planar $(NP)_2$ ring[13] is the N,N-dimethoxy compound $(Cl_3PNOCH_3)_2$, obtained from the reaction of O-methylhydroxylammonium chloride with PCl_5: its mass spectrum is summarised in Table XI. The molecular ion is absent from the spectrum (this is also found to be so in the analogous $(Cl_3PNCH_3)_2$): the two heaviest ions observed

TABLE XI. Mass Spectrum of $(Cl_3PNOCH_3)_2$.

Ion	m/e	RI
$(CH_3O)_2N_2P_2Cl_6^+$	362	0
$(CH_3O)ON_2P_2Cl_6^+$	347	0.3
$(CH_3O)ON_2P_2Cl_5^+$	312	1.5
$ONP_2Cl_5^+$	267	10
$ONP_2Cl_4^+$	232	100
$ONP_2Cl_3^+$	197	10
$ONP_2Cl_2^+$	162	13
ONP_2Cl^+	127	1.5
ONP_2^+	92	8.5
$NP_2Cl_3^+$	181	0.4
$NP_2Cl_2^+$	146	1.8
NP_2Cl^+	111	1.0
NP_2^+	76	1.6
$NPCl_3^+$	150	3.4
$NPCl_2^+$	115	0.8
$NPCl^+$	80	8.3
NP^+	65	0
PCl_3^+	136	3.8
PCl_2^+	101	20
PCl^+	66	8.0

are $(M{-}CH_3)^+$ and $(M{-}CH_3{-}Cl)^+$, and there are no other ions containing methyl groups. With the exception of $(M{-}CH_3)^+$ and $(M{-}CH_3{-}Cl)^+$, the spectrum is very similar to that of $(Cl_3PN)_2SO_2$, both spectra showing strong ion series $ONP_2Cl_n^+$, $NP_2Cl_n^+$, $NPCl_n^+$ and PCl_n^+. The base peak is $ONP_2Cl_4^+$ (structure VI) and in fact the series $ONP_2Cl_n^+$ carries some 74% of the total ion current (*ca.* 32% in $(Cl_3PN)_2SO_2$). The high abundance of $ONP_2Cl_4^+$ suggests that this ion, which if it adopts structure VI will undoubtedly be planar at nitrogen,[14] may be sufficiently stable under ordinary chemical conditions to permit its isolation: this point is currently under investigation.

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