Although a linear relationship has been shown between chemical shifts and *lowest* excitation energies for octahedral Co(III) complexes,[16] we must note that chemical shifts are not always determined by lowest excited states. In Figure 2, we plot the Mo chemical shifts against the inverse of the lowest optically allowed transition energies observed by Müller et al.[17] Since these excitations do not correspond to the magnetically allowed transitions and since the nature of the excitations is not the d–d* excitation but the intramolecular CT transition,[10] the linearity is not so good as that in Figure 1. Actually, the correlation factors for Figures 1 and 2 in the least-squares fitting are 0.987 and 0.972, respectively.[18]

For MoO_3S^{2-}, we have pointed out[10] that the peak of the lowest excitation is not the first peak at 3.15 eV but the second one at 4.30 eV in the experimental spectra.[17] The SAC–CI calculations have given no peak near 3.15 eV for MoO_3S^{2-}, though they give fairly good agreements with the experimental spectra for the other molybdenum complexes.[10] We have shown[10] that the experimental spectra of MoO_3S^{2-} can be explained as a result of an overlap of the spectra of $MoO_2S_2^{2-}$ onto that of MoO_3S^{2-}. In addition to these results, Figure 2 provides additional evidence supporting the above conclusion; the open circle, corresponding to the observed first peak at 3.15 eV, deviates too much from the rough linear relation that the other complexes show.

The rough linear relation observed in Figure 2 is explained as follows. As studied in detail in ref 10, the lowest optically allowed transitions of the $MoO_{4-n}S_n^{2-}$ and $MoSe_4^{2-}$ complexes are the electron-transfer excitations from the ligands to the d* orbital. Since the occupied ligand levels are rather constant,[1,10] the lowest transitions reflect the level of the d* orbital, which is more sensitive to the ligand substitution. Since this d* orbital is common to the magnetically allowed d–d* transition, a rough parallelism arises between the lowest optically allowed and magnetically allowed transitions.

Summary

In this paper, we have calculated the lowest *magnetically allowed* $d\sigma$–$d\pi^*$ transition energies of the six molybdates $MoO_{4-n}S_n^{2-}$ (n = 0–4) and $MoSe_4^{2-}$ by the SAC–CI theory and discussed the relationship between the Mo chemical shift and the d–d* transition energy.

The nature of the excited states contributing to the chemical shifts should be magnetic dipole allowed, e.g., the excitation to $^1T_1$ states for T_d molecules. The excitation most important to the Mo chemical shift is shown to be $4d\sigma \rightarrow 4d\pi^*$. We have obtained a nice linear relationship by plotting the experimental chemical shifts against the reciprocal of the excitation energies. This confirms the validity of the origin of the ^{95}Mo NMR chemical shifts previously proposed.

Acknowledgment. The calculations were performed by the HITAC M680H and S820/80 computers at the Computer Center of the Institute for Molecular Science. This study was partially supported by Grant-in-Aids for Scientific Research from the Ministry of Education, Science, and Culture of Japan and by the Kurata Foundation.

---

[16] (a) Kidd, R. G.; Goodfellow, R. J. In *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic: London, 1978. (b) Kidd, R. G. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic: London, 1980. (c) Jameson, C. J.; Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987.

[17] (a) Müller, A.; Diemann, E. *Chem. Phys. Lett.* **1971**, *9*, 369. (b) Müller, A.; Diemann, E.; Jostes, R.; Bögge, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 934 and references therein.

[18] The correlation factor in Figure 1 has been calculated by averaging the energies shown in Table I for the complexes MoO_3S^{2-}, $MoO_2S_2^{2-}$, and $MoOS_3^{2-}$.

Contribution from the Organic Chemistry Laboratory, State University of Mons, 7000 Mons, Belgium, and Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, 31077 Toulouse Cedex, France

Electron-Impact and Flash-Vacuum Pyrolysis of Trivalent and Pentavalent Phosphorus Azides: Generation of Original Unsaturated Mono-, Di-, and Tricoordinated Phosphorus Cations

A. Maquestiau,*,† L.-Z. Chen, R. Flammang,† J. P. Majoral,‡ and G. Bertrand‡

Received September 11, 1989

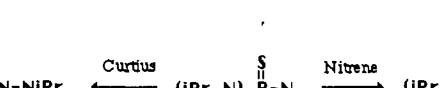
Contrary to most azides, $[(i\text{-}Pr)_2N]_2P(S)N_3$ (**1**) and $[(i\text{-}Pr)_2N]_2PN_3$ (**4**) do not lose nitrogen subsequent to ionization. Instead, the loss of one azide radical appears to be more favorable, reflecting the capability of phosphorus to stabilize a positive charge. Simple cleavage reactions are the privileged decompositions of the molecular ions of $\mathbf{4}^{\bullet+}$, not only within the ion source but also within the field-free regions for metastable $\mathbf{4}^{\bullet+}$. Besides the unconventional dicoordinated divalent ($>P^+$) or tetravalent ($-P^+{\equiv}N$) phosphonium ions formed in these processes, original monocoordinated phosphonium $P^+{=}N-$ ions are also observed. A prominent rearrangement reaction differentiates the behavior of $\mathbf{1}^{\bullet+}$: immonium ions h are produced at low internal energy by loss of a phosphorus-containing radical, pointing out the stabilizing effect of sulfur. A similar conclusion arises from a flash-vacuum pyrolysis (FVP) study of **1** and **4**: formation of $(i\text{-}Pr)_2N{-}P{=}S$ (**6**) is observed at ca. 400–500 °C during the pyrolysis of **1**, while no significant phosphorus-containing product could be unambiguously identified for **4**. In both cases, diisopropylamine (**7**) and *N*-isopropyldimethylimine (**8**) were the main pyrolysis products. These results were derived from tandem mass spectrometry (MS/MS) experiments.

Introduction

Much work has been devoted to organic azides[1] since the discovery of the Curtius reaction in 1890.[2] Thermolytic, photolytic, or acid-promoted rearrangement of aliphatic, aromatic, or heteroaromatic azides afford the corresponding carbon–nitrogen double-bonded compounds. Similarly, it has been shown that the Curtius rearrangement is effective for group 13 (B), group 14 (Si, Ge), and group 15 (P) azides (Scheme I).[3]

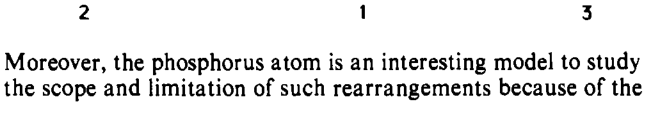
In addition to this behavior, competitive nitrene-type reactions sometimes occur, such as hydrogen abstraction or CH insertion.

Scheme I



$$R_nMN_3 \xrightarrow[\text{or } h\nu \text{ or } H^+]{\Delta} R_{n-1}M{=}N{-}R + N_2$$

Scheme II



$$\underset{\mathbf{2}}{iPr_2N{-}\overset{\overset{S}{\|}}{P}{=}N{-}NiPr_2} \xleftarrow{\text{Curtius}} \underset{\mathbf{1}}{(iPr_2N)_2\overset{\overset{S}{\|}}{P}{-}N_3} \xrightarrow{\text{Nitrene}} \underset{\mathbf{3}}{(iPr_2N)_2\overset{\overset{S}{\|}}{P}{-}NH_2}$$

Moreover, the phosphorus atom is an interesting model to study the scope and limitation of such rearrangements because of the

---

† State University of Mons.

‡ Laboratoire de Chimie de Coordination du CNRS.

0020-1669/90/1329-3097$02.50/0 © 1990 American Chemical Society

Table I. Relative Abundances of the Fragments in the CA Spectra of *m/z* 173 Ions from Precursors **1** and **4**[a]

	m/z										
	[145]	[130]	115	[103]	[88]	73	70	61	58	44	43
$[(i\text{-Pr})_2N]_2P(S)N_3$ (**1**)	15	53	16	271	213	34	38	37	*100*	60	48
$[(i\text{-Pr})_2N]_2PN_3$ (**4**)	51	29	15	501	225	36	36	39	*100*	58	47

[a] Unimolecular processes are indicated within brackets.

Scheme III

$$\underset{4}{(iPr_2N)_2P\text{-}N_3} \xrightarrow{-N_2} \underset{5}{(iPr_2N)_2P\text{-}N}$$

variety of its known and potentially available hybridization states. For example, it has been demonstrated that azidophosphine sulfide **1**[4] affords thionoiminophosphorane **2** with a small amount of nitrene-type product, **3** (Scheme II).

On the other hand, tricoordinated trivalent phosphorus azide **4** produces the corresponding phosphinonitrene **5** without the formation of a Curtius-type rearrangement product as theoretical predictions[5] and experimental results[4,6] have shown. The formation of **5** has been confirmed by ^{31}P NMR[6] and photoelectron spectroscopy[7] (Scheme III).

In contrast to these condensed-phase results, relatively little has been done on (gas-phase) mass spectrometry of heavier main-group element azides. Inversely, the electron-impact-induced fragmentations of aliphatic and aromatic azides have been thoroughly investigated.[8] In most cases, the loss of N_2 is the dominant reaction pathway with rare exceptions due to the loss of the azide radical. For example, in the mass spectra of several triarylmethyl azides, formation of a resonance-stabilized triarylmethyl cation is the driving force for the $^{\bullet}N_3$ loss.[9] Some sulfonyl azides were also found to lose an azide radical.[10] Most other azides appear to decompose under EI by N_2 loss.[8]

All previous work stimulated us to investigate the behavior of phosphorus azides upon electron impact. In this paper, we investigate azidobis(diisopropylamino)phosphine sulfide (**1**) and azidobis(diisopropylamino)phosphine (**4**) by means of the tandem mass spectrometry techniques (MS/MS). We report also on the behavior of these azides upon flash-vacuum pyrolysis under very low pressure conditions.

Results and Discussion

A. Tandem Mass Spectrometry. As a general characteristic of azides, the molecular ions of the phosphine sulfide **1** are not very stable and keep a moderate abundance (14% relative to the *m/z* 100 base peak) in the 70 eV mass spectrum. Significant fragment ion peaks are also found at *m/z* 263, 205, 173, and 58 (Figure 1). Of importance is the absence of N_2 loss; instead, an azide radical loss occurs to give phosphine sulfide ion a (*m/z* 263), which is stabilized by delocalization of the nitrogen nonbonding electrons. The consequence of the partial positive charge developed on the nitrogen is the consecutive elimination of propene, yielding ion c through the sequence *m/z* 221 → 179 → 137 → 95 (Scheme IV). All these peaks are already seen on the CA spectrum of the *m/z* 263 ion, although with a reduced intensity (indicated by an asterisk in Figure 2).

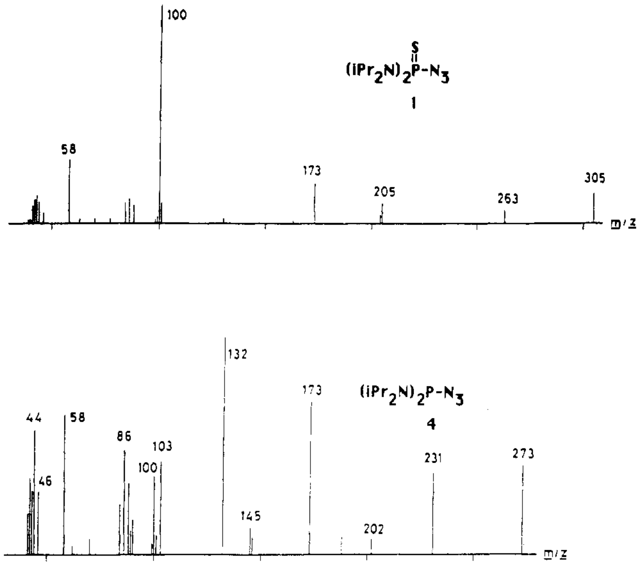


Figure 1. Electron-impact (70 eV) mass spectra of the phosphorus azides **1** and **4**.

The low-energy unimolecular fragmentations (MIKE spectrum) mainly give ions at *m/z* 204 (−101 Da (daltons)) and *m/z* 100; after collisional activation a quite intense fragment ion peak at *m/z* 173 is also produced. The loss of 101 Da involves the elimination of diisopropylamine: the proposed mechanism depicted in Scheme IV starts with an isomerization of the molecular ion into the distonic[11] species d by a γ-hydrogen transfer. The loss of $(i\text{-Pr})_2NH$ may then be concerted with a cyclization process into an azathiaphosphetidine (or phosphaziridine) structure e (or e′). Hydrogen transfer on sulfur cannot a priori be excluded, since it has been recently demonstrated that compounds like $Et_2HPS^{\bullet+}$ lose ethylene to produce the $EtHP\text{-}SH^{\bullet+}$ ion.[12] However, the fact that $(i\text{-Pr})_2NH$ is lost in this reaction and that the CA spectrum of the *m/z* 204 ion presents a base peak at *m/z* 99 ($Me_2C{=}NiPr^+$ ion, which may result from a retrocycloaddition reaction) favors the proposed cyclic structure(s).

The *m/z* 173 ion is considered to be the dicoordinated phosphonium ion g formed by consecutive losses of a diisopropylamino group and a sulfur atom from $M^{\bullet+}$ and involving the intermediate ion f (*m/z* 205). The CA spectrum of the *m/z* 205 ion indeed presents a base peak at *m/z* 173 (Figure 2). The synthesis of this unusual ion g has been previously reported.[13] Other recent works have also shown the existence of phosphenium ions in the condensed phase.[14]

---

(1) Patai, S. *The Chemistry of the Azide Group*; Wiley-Interscience: New York, 1971. Lwowski, W. *Nitrenes*; Wiley-Interscience: New York, 1980. Scriven, E. F. V. *Azides and Nitrenes: Reactivity and Utility*; Academic Press: New York, 1984. Bock, H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 504.

(2) Curtius, T. *Chem. Ber.* **1890**, *23*, 3023.

(3) Bertrand, G.; Majoral, J. P.; Baceiredo, A. *Acc. Chem. Res.* **1986**, *19*, 17.

(4) Baceiredo, A.; Bertrand, G.; Majoral, J. P.; El Anba, F.; Manuel, G. *J. Am. Chem. Soc.* **1985**, *107*, 3945.

(5) Trinquier, G. *J. Am. Chem. Soc.* **1982**, *104*, 6969. Gonbeau, D.; Pfister-Guillouzo, G.; Barrans, J. *Can. J. Chem.* **1983**, *61*, 1371. Ha, T. K.; Nguyen, M. T.; Recelle, P. *Chem. Phys.* **1984**, *87*, 23.

(6) Sicard, G.; Baceiredo, A.; Bertrand, G.; Majoral, J. P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 459. Baceiredo, A.; Bertrand, G.; Sicard, G.; Jaud, J.; Galy, J. *J. Am. Chem. Soc.* **1984**, *106*, 6088.

(7) Gonbeau, D.; Pfister-Guillouzo, G. Private communication.

(8) See for example: Crow, W. P.; Wentrup, C. *Tetrahedron Lett.* **1967**, 4379. Hedaya, E.; Kent, M. E.; McNeill, W. W.; Lossing, F. P.; McAlister, T. *Tetrahedron Lett.* **1968**, 3415. Preston, P. N.; Palmer, M. H.; McKensie, T.; Stevens, M. F. G. *Org. Mass Spectrom.* **1970**, *3*, 863. Wentrup, C. *Tetrahedron* **1970**, *26*, 4969. Ashby, J.; Suschitzk, H. *Tetrahedron Lett.* **1971**, 1315. Fraser, R. T. M. *Org. Mass Spectrom.* **1973**, *7*, 83.

(9) Moriary, R. M.; Klieyman, J. M. *Tetrahedron Lett.* **1966**, 4123.

(10) Campbell, M. M.; Punn, A. D. *Org. Mass Spectrom.* **1972**, *6*, 599.

(11) Hammerum, S. *Mass Spectrom. Rev.* **1988**, *7*, 123.

(12) Kuchen, W.; Kueckelhaus, W.; Kuehlborn, S.; Terlouw, J. J. *Phosphorus Sulfur Relat. Elem.* **1987**, *34*, 169. Heck, H.; Kuchen, W.; Renneberg, H.; Terlouw, J. K. *Phosphorus Sulfur Relat. Elem.* **1988**, *40*, 227.

(13) Marre, M. R.; Sanchez, M.; Wolf, R. *J. Chem. Soc. Chem. Commun.* **1984**, 566.

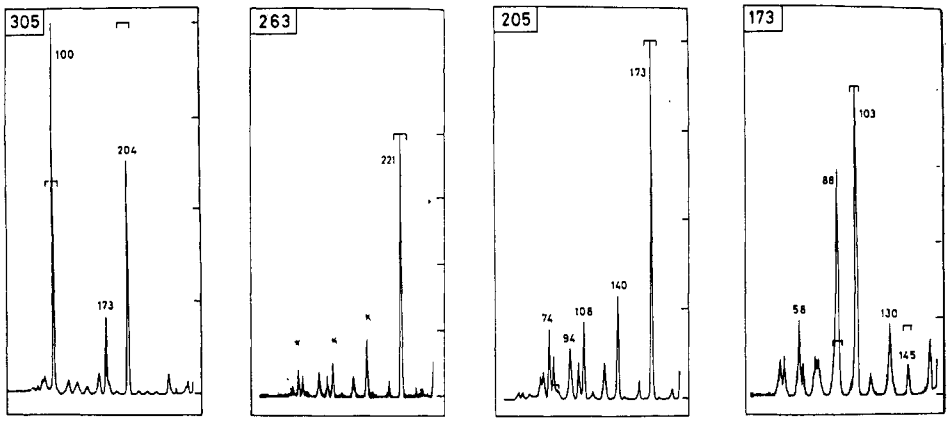


Figure 2. Collisional activation spectra of the m/z 305, 263, 205, and 173 ions produced by the ionization of the phosphorus azide **1**. Relevant unimolecular reactions (relative intensities) are indicated by horizontal brackets.

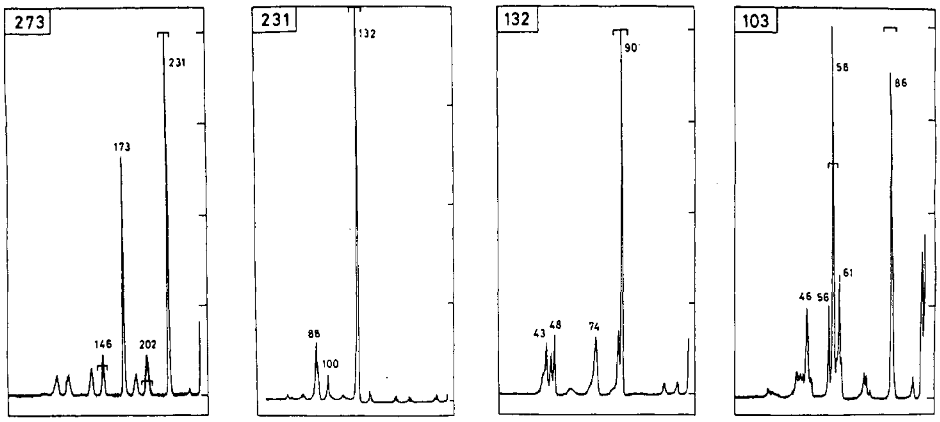


Figure 3. Collisional activation spectra of the m/z 273, 231, 132, and 103 ions produced by the ionization of the phosphorus azide **4**. Relevant unimolecular reactions (relative intensities) are indicated by horizontal brackets.

Table II. Relative Abundances of the Fragments in the CA Spectra of $[C_3H_8N]^+$ m/z 58 Ions

	m/z													
	43	42	[41]	40	39	38	37	[30]	29	28	27	26	[18]	15
t-$BuNH_2$	21	*100*	207	21	38	11	3	14	4	16	11	4	23	9
i-$PrNH_2$	21	*100*	282	19	38	10	4	16	3	15	10	4	31	9
i-Pr_2NH	30	*100*	352	19	36	8	3	35	4	20	11	4	26	10
$[i\text{-}Pr_2N]_2P(S)N_3$	22	*100*	160	20	37	10	3	34	5	19	9	4	12	6
$[i\text{-}Pr_2N]_2PN_3$	37	*100*	275	22	44	11	4	35	10	22	10	3	14	6
$C_2H_5CH(CH_3)NH_2$	46	60	658	23	46	15	8	61	40	*100*	35	18	7	7

The structure of the m/z 100 ion is inferred from its CA spectrum, which shows mainly a propene loss (to m/z 58), and from the actual structure of the m/z 58 ion, demonstrated as being predominantly (vide infra) the immonium ion. The stretching of the N–P bond is thus accompanied by the 1,2-migration of a hydrogen and/or a methyl group, yielding the immonium ions h and/or h′ (Scheme IV).

The low-energy $M^{\bullet+} \rightarrow$ h reaction pathway becomes less important in the case of azidobis(diisopropylamino)phosphine (**4**), which is characterized by intense peaks at m/z 273, 231, 173, and 132 in the high-mass region of its mass spectrum (Figure 1). The loss of nitrogen is here also absent and replaced by a more favorable azide loss, shown by the base peak in the CA spectrum of the molecular ion (Figure 3). The bis(diisopropylamino)phosphonium ions j consecutively lose an imine molecule and propene, as described in Scheme V.

Another important fragmentation of **4**$^{\bullet+}$ is the loss of a diisopropylamino radical to produce the azidophosphonium ion g (m/z 173), which is the same as that formed from **1**$^+$, as proved by their superimposable CA spectra (Table I).

Besides these prominent simple cleavage reactions, secondary decomposition pathways forming ions at m/z 202, 188, 146, 131, 103, 100, and 88 are observed. Some of these reactions imply a nitrogen loss, which is however always concerted with another neutral molecule loss, e.g. $N_2 + C_3H_7^\bullet$ (m/z 202) or $N_2 + C_6H_{13}N$ (m/z 146). This behavior probably reflects the instability of phosphonitrene radical cations.

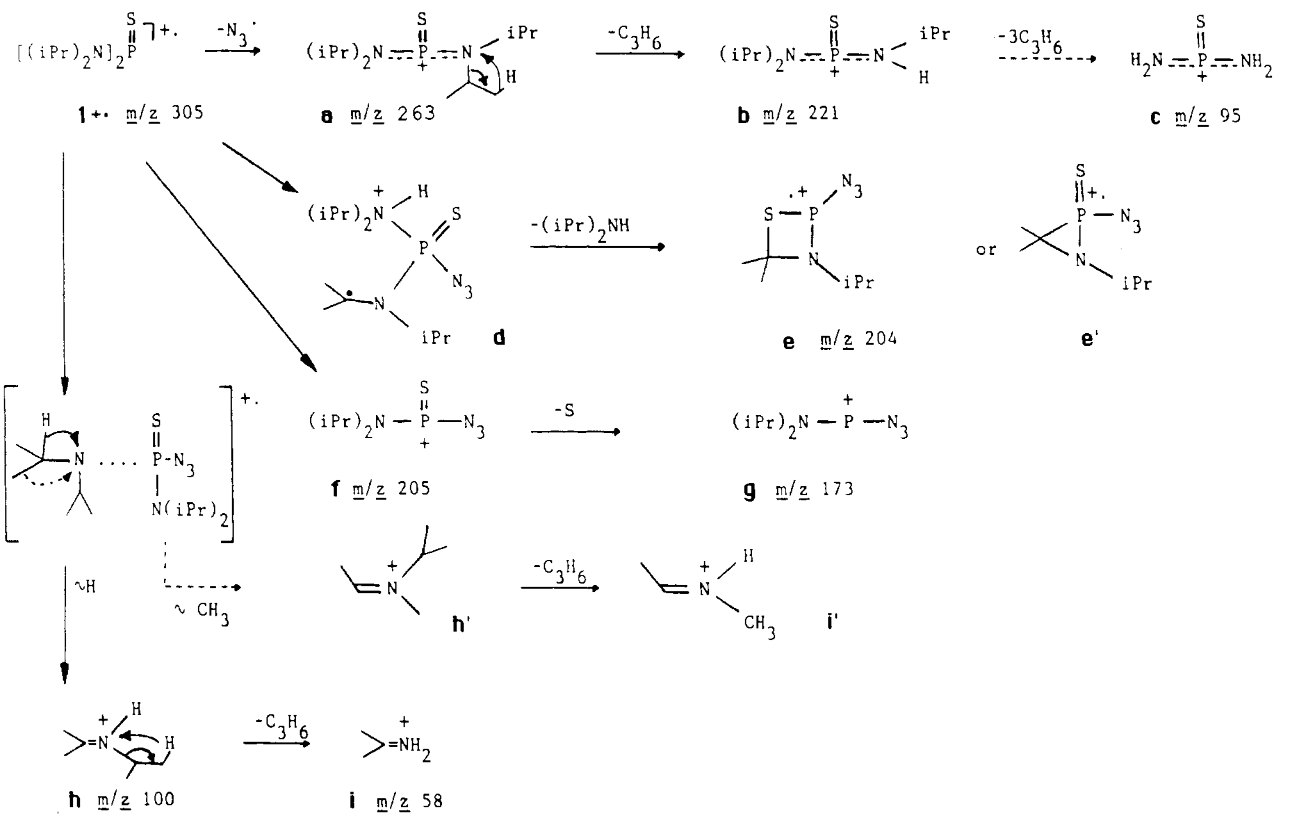
As in the case of **1**$^{\bullet+}$, the m/z 58 ion corresponds also to immonium ion i. It originates mainly through the sequence **4**$^{\bullet+}$ $\rightarrow m/z$ 173 $\rightarrow m/z$ 103 $\rightarrow m/z$ 58, which can be described as in Scheme V: consecutive losses of N_2 and C_3H_6 afford ion m, which undergoes further fragmentation into ion i by $P{\equiv}N$[15] loss associated with a 1,2-hydrogen/alkyl shift. In the case of a concerted 1,2-hydrogen shift, immonium ion i should be produced. The comparison of the CA data of the m/z 58 ion with the appropriate reference ion [$(M-CH_3)^+$ from *tert*-butylamine or $(M-H)^+$ of isopropylamine] reveals however some minor differences (Table II), such as the inversion of the intensity ratio (m/z 30)/(m/z 18), which can be ascribed to the competitive formation of immonium ion i′ by loss of PN concerted with a 1,2-methyl shift. In this sequence, the stretching of the N–P bond increases

---

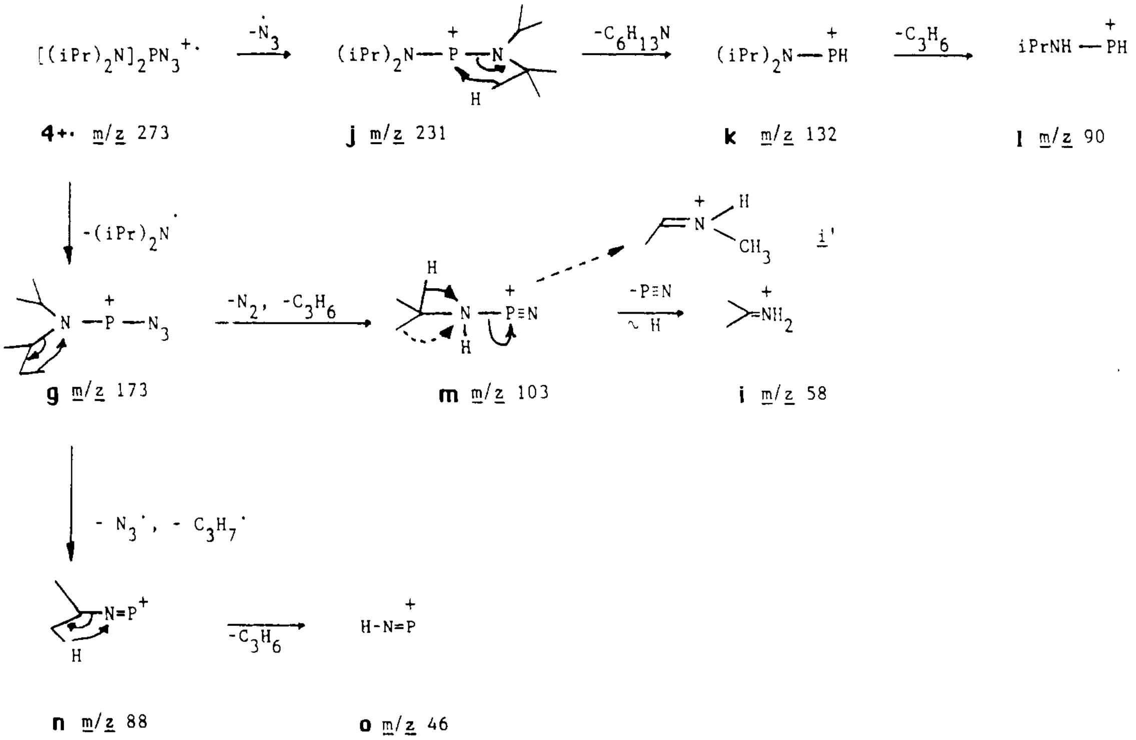
(14) Cowley, A.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367. Mazieres, M. R.; Roques, C.; Majoral, J. P.; Sanchez, M.; Wolf, R. *Tetrahedron* **1987**, *9*, 2109. Roques, C.; Mazieres, M. R.; Majoral, J. P.; Sanchez, M. *Tetrahedron Lett.* **1988**, *4547*.

(15) Atkins, R. M.; Timms, P. L. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 113.

Scheme IV. Principal Fragmentations Induced by Electron Impact Ionization of Phosphine Sulfide **1**



Scheme V. Principal Fragmentations Induced by Electron Impact Ionization of Phosphine **4**



the positive charge on nitrogen and the nascent nitrenium ions undergo an isomerization process into the more stable immonium ions. Difference in energy content between the ions studied cannot be taken into account, as clear differences appear already in the MIKE spectra: the *m/z* 30 peak has a dish-topped shape in the case of *t*-BuNH$_2$, whereas a composite profile is shown for **1** and **4**.

The fragmentation of g is of particular interest, since it involves the transient formation of an unknown dicoordinated tetravalent phosphorus cation $-P^+{\equiv}N$ (m) and the elimination of a σ^1 λ^3-phosphonitrile moiety's P≡N. Note also that considerable rearrangement must take place within the *m/z* 103 metastable ion, as one of the prominent peaks in the CA spectrum corresponds to the loss of ammonia. Another decomposition pathway of the ion g is the concerted loss of N$_3$ and C$_3$H$_7$ radicals (ion n, *m/z* 88) followed by propene loss (o, *m/z* 46). The monocoordinated divalent phosphenium structures n and o are proposed on the basis of high-resolution mass determination (*m/z* 88.037 18 and

Table III. Evolution of the Mass Spectrum of **1** at Various Pyrolysis Temperatures

T, °C	305	263	205	173	163	130	120	101	100	99	98	88	86	84	77	70	63	58	46	44	43	42	41	40	39
200	14	6	9	18	1	2		9	*100*	3	2	8	11	9	2	2	2	29	4	10	13	11	8	1	2
300	14	7	10	19	2	4	2	10	*100*	5	3	8	12	15	2	2	3	29	5	20	14	21	9	1	3
400	8	4	5	10	23	8	21	14	66	22	12	12	50	59	13	5	20	32	11	*100*	46	99	46	6	22
500	<1	<1	<1	<1	9	3	9	9	18	21	8	4	37	59	7	3	11	17	5	84	36	*100*	43	6	21
600					2	<1	2	7	8	19	6	<1	31	59	4	3	6	12	2	71	28	*100*	44	8	21
700								7	4	18	5		28	53	3	3	5	10		65	24	*100*	53	10	24

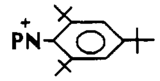
Table IV. Evolution of the Mass Spectrum of **4** at Various Temperatures

T, °C	273	231	202	188	173	146	145	132	103	101	100	99	90	89	88	86	84	70	62	58	46	44	43	42	41
200	41	38	7	8	70	8	12	*100*	43	9	36	5	16	11	33	48	23	7	4	64	29	57	29	35	19
300	7	7	1	1	13	2	6	22	11	11	23	8	7	3	8	71	28	5	1	32	8	*100*	22	48	20
400	<1	<1			1		2	4	<1	9	4	9	7		<1	45	27	3	3	13	2	*100*	17	53	22
500							2	4		9	7	11	7			44	33	5	4	16		*100*	20	67	29
600							1	2		9	5	14	6			43	40	7	5	16		*100*	21	82	39
700							<1	<1		8	5	10	3			38	30	8	3	14		*100*	18	60	30

Table V. Relative Abundances of the Fragments in the CA Spectra of *m/z* 101 Ions Produced from **1**, **4**, and **7**

	T, °C	[86]	70	[58]	56	44	43	41	39	30	27
$[(i\text{-Pr})_2N]_2P(S)N_3$ (**1**)	700	2100	47	108	17	*100*	76	50	8	4	7
$[(i\text{-Pr})_2N]_2PN_3$ (**4**)	700	1835	41	76	15	*100*	73	49	9	3	9
$[(i\text{-Pr})_2]_2NH$ (**7**)	200	2260	36	76	14	*100*	70	47	8	3	10

45.985 06, respectively) and CA spectra. The stability of these monocoordinated phosponium ions in the gas phase is noteworthy. Only one very recent[16] report has described the existence of a PN analogue of diazonium stabilized by a very bulky substituent on nitrogen.



B. Flash-Vacuum Pyrolysis. In these experiments, before entering the ion source of the mass spectrometer, samples passed through a heated quartz tube, allowing real-time analysis of the pyrolysis products to be performed. Table III lists the mass spectra of **1** obtained in a 200–700 °C pyrolysis temperature range and indicates some significant changes: (i) Peaks at *m/z* 305 ($M^{•+}$), 263, and 173 decrease when the temperature rises above 400 °C and almost completely disappear at 500 °C. (ii) At 400 °C, significant peaks appear at *m/z* 163, 130, and 120, but as the temperature is increased further, their intensities decrease and they disappear at 700 °C. (iii) Peaks at *m/z* 101, 99, 96, and 86 also increase to a large extent as the temperature rises to 400 °C. Elevated temperatures have no obvious influence on their relative abundances.

To obtain a detailed and actual outline of the pyrolysis, MS/MS experiments were carried out on these main ions.

***m/z* 163 Ion.** The 142-Da difference between this ion and the molecular ion of **1** is considered to be due to consecutive losses of azido and diisopropylamino radicals. As higher mass ions are not observed at high temperature, this *m/z* 163 ion corresponds to the molecular ion of a new compound for which the diisopropylamino phosphanediyl sulfide structure **6** is proposed (Scheme VI). HRMS indeed confirms the composition (found *m/z* 163.057 73, calculated for $C_6H_{14}NPS$ *m/z* 163.058 46), and the CA spectrum affords structural information through the identification of the fragments at *m/z* 130, 120, 99, and 63 (Figure 4). Most of the fragmentations involve however an isomerization process into a distonic species **6a** before competitively losing SH and C_3H_7 radicals. Besides these fragmentations, the MI and CA spectra also indicate the production of imine ions (*m/z* 99), implying the loss of an unusual (H, P, S) neutral molecule.

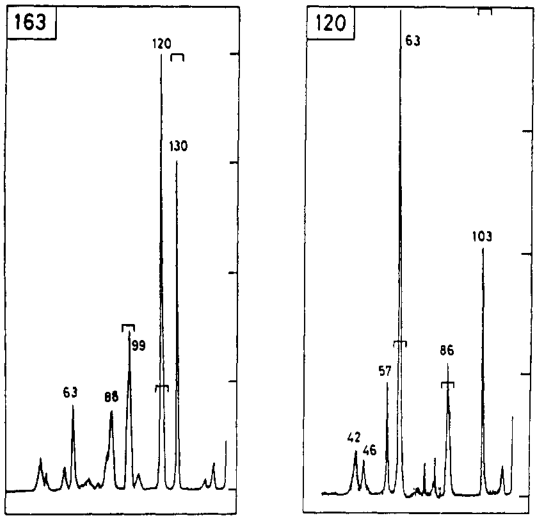


Figure 4. Collisional activation spectra of the *m/z* 163 and 120 ions produced by the ionization of the FVP products of the phosphorus azide **1**. Relevant unimolecular reactions (relative intensities) are indicated by horizontal brackets.

***m/z* 101 and 99 Ions.** HRMS confirms the $C_6H_{15}N$ and $C_6H_{13}N$ compositions for these *m/z* 101 and 99 ions, which also must mainly constitute molecular ions, as they remain present in the mass spectrum even when **6** is consecutively pyrolyzed. CA spectra (Table V) indicate that the *m/z* 101 ion is the molecular ion of diisopropylamine (**7**). The corresponding *N*-isopropyldimethylimine structure $\mathbf{8}^{•+}$ is thus suggested for the *m/z* 99 ions: loss of $CH_3^•$ produces nitrilium ion p, which in turn consecutively loses propene to give protonated acetonitrile. Preliminary chemical ionization experiments using mixtures of isopropyl isocyanide and CH_3I as a methylating reagent indeed produce the *m/z* 84 ion whose CA spectrum shows a base peak at *m/z* 42. The very low intensity of the signal precludes however an accurate determination of the abundance ratios. Fragmentation within the isopropyl group of $\mathbf{8}^{•+}$ appears unlikely, as nitrilium ions have been shown to be usually the more stable $C_nH_{2n}N^+$ isomers[17] (Scheme VI). It thus

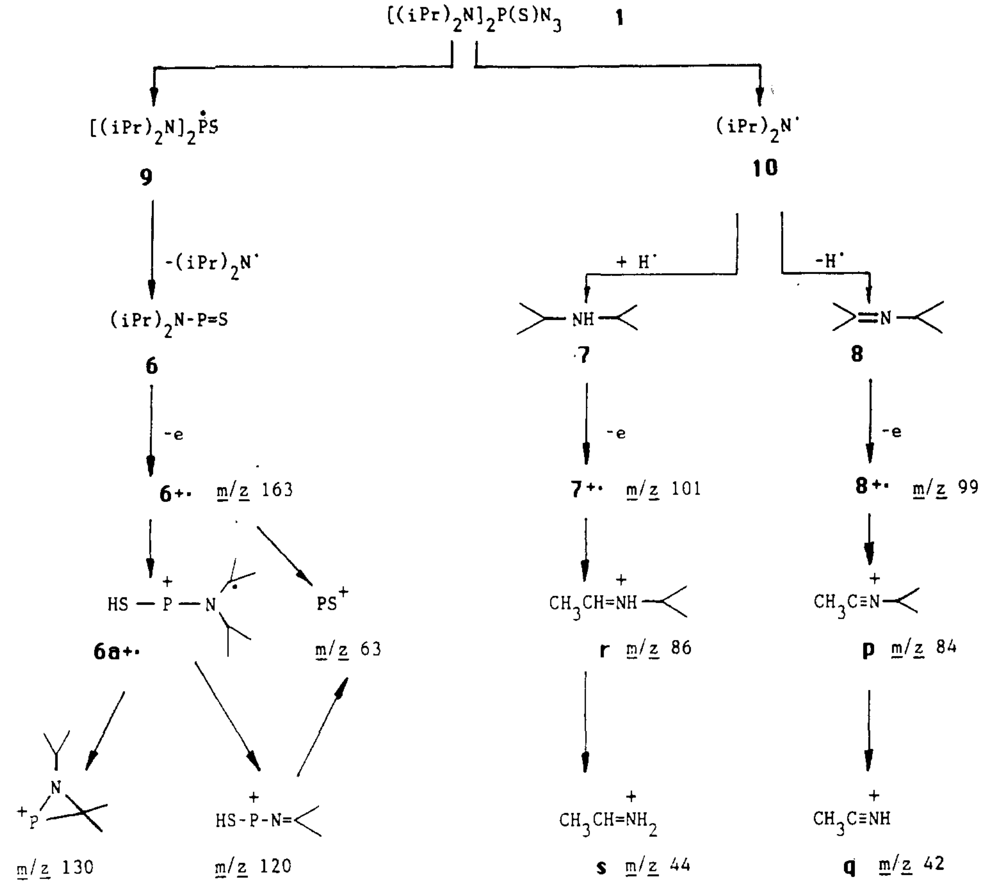
---

[16] Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, 1715.

[17] Bouchoux, G.; Flament, J. P.; Hoppilliard, Y.; Tortajada, J.; Flammang, R.; Maquestiau, A. *J. Am. Chem. Soc.* **1989**, *111*, 5560.

[18] Scherer, O.; Glassel, W. *Chem.-Ztg.* **1975**, *99*, 246.

Scheme VI. FVP/MS/MS Results from Azide 1



appears that P–N bond homolysis of **1** upon FVP produces two kinds of radicals, **9** and **10**; the former loses a diisopropyl radical, generating **6**, and the latter abstracts or loses a hydrogen atom, providing the nitrogen product **7** or **8**.

In contrast to **1**, **4** is thermally less stable and is already pyrolyzed even at 400 °C (Table IV). The ions at *m/z* 101 and 99 are also present after ionization of the pyrolyzate, and the CA spectra prove that they are identical with the ions produced after FVP of **1**. No evidence was however found for the presence of a phosphorus radical partner that must therefore undergo extensive fragmentation before ionization. This behavior is in good agreement with the EI-induced dissociations where the formation of h with the loss of phosphorus radical is only observed for **1** in the field-free region, pointing out the primordial influence of sulfur upon the radical stabilization.

Conclusion

The behavior of **1** and **4** upon EI excitation and FVP conditions has been investigated by using tandem mass spectrometry techniques. Upon EI, **4** mainly loses an azide radical but a competitive N–P bond cleavage also readily occurs. Unusual phosphonium ions[19] $H{-}P^+{-}N(i\text{-}Pr)_2$ and $H{-}P^+{-}N(H){-}i\text{-}Pr$ are produced during these processes. In the case of the sulfur analogue **1**, a new low-energy reaction channel is available, consisting of *N*-isopropyldimethylimine ion h formation with the elimination of a sulfur-stabilized phosphorus radical.

Moreover our results show that monocoordinated phosphonium cations $i\text{-}PrN{=}P^+$ and $H{-}N{=}P^+$, which can be considered as nonstabilized PN analogues of diazoniums, may constitute stable species in the gas phase. The unimolecular elimination of 45 mu from the *m/z* 103 ions of $\mathbf{4}^{\bullet+}$ also points out the possible existence of $P{\equiv}N$ as a stable neutral molecule in the gas phase.

A similar behavior was noted when the samples were submitted to FVP conditions: no detectable phosphorus-containing compound was observed in the case of **4**, while the original dicoordinated thioxophosphanediyl $(i\text{-}Pr)_2N{-}P{=}S$ (**6**) was identified for **1** by the characteristic CA spectrum of its *m/z* 163 molecular ions.

Contrasting with previous photolytic experiments,[5,6,12] no indications were found for the occurrence of nitrene or Curtius-rearrangement products.

Experimental Section

Mass spectra were recorded on a reversed geometry (B/E) Varian Mat 311 A instrument (3 kV, 70 eV, 1 mA) using air as the collision gas in the second field-free region. HRMS measurements were performed by means of the peak-matching technique at a resolution of about 10^4 (50% valley definition). Appropriate isobaric samples were chosen as reference molecules. Samples **1** and **4** were synthesized according to the literature,[18] while **9** and **7** were commercially available.

The gaseous samples were pyrolyzed in an "internal" furnace (incorporated in the source housing) consisting of a ~10-cm quartz tube (i.d. 1 cm) electrically heated, located in such a way that the exit lies at a very short distance from the ionization region. This system allows us to achieve very short contact times with reduced reactor wall collisions between the pyrolysis and ionization steps. Samples were introduced with a conventional direct-insertion probe at the quartz tube entrance.

Some of the data (CA spectra of the *m/z* 58 ions) were obtained with a modified[19] AEI MS 902 triple-sector (E/B/E) mass spectrometer (8 kV, 70 eV, 200 μA) using helium as the collision gas in the third field-free region.

Registry No. **1**, 96455-32-2; **4**, 56183-64-3.

---

[19] Maquestiau, A.; Van Haverbeke, Y.; Flammang, R.; Abrassart, M.; Finet, D. *Bull. Soc. Chim. Belg.* **1978**, *87*, 765.