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Gas-Phase Studies of Phosphorus- and Arsenic-Chalcogenide Cage Molecules

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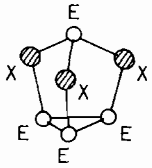
Abstract

Positive and negative ion chemical ionization and electron impact mass spectra of E_4X_3 (E = P, As; X = S, Se) cage molecules were investigated. All the molecules undergo analogous cleavages, which are dominated by even-electron ions. Proton affinities of the tetrapnicogen trichalcogenides were evaluated by the chemical ionization mass spectra (CIMS) of the molecules in the presence of reagents, such as methane, isobutane, acetone, ethylacetate and ammonia, whose proton affinity is known. P_4S_3, P_3AsS_3, $P_2As_2S_3$, PAs_3S_3, P_4Se_3 and As_4Se_3 show similar proton affinities, whilst As_4S_3 exhibits a significantly higher proton affinity. Some correlations are drawn between gas-phase behaviour of these molecules and their reactivity in solution.

Introduction

It has been recently found that the cage molecules of tetrapnicogen chalcogenides P_4S_3, As_4S_3, P_4Se_3 and As_4Se_3 react with various transition metal–ligand moieties, undergoing different reactions. In presence of the trigonal pyramidal $(np_3)M$ [M = Ni, Pd; np_3 = tris(2-diphenylphosphinoethyl)amine] complexes the P_4X_3 (X = S, Se) intact molecules are η^1 coordinated to the metal site through the apical P atom [1, 2]. The P_4S_3 molecule undergoes cleavage of a basal phosphorus–phosphorus bond on reaction with the $(PPh_3)Pt$ moiety [3]. In the reaction with $[(triphos)M]^+$ units [triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane; M = Rh, Ir] cleavage of the E_4X_3 (E = P; X = S, Se. E = As; X = S) molecule occurs with replacement of a basal pnicogen atom by the (triphos)M moiety [4]. More substantial cleavage of the E_4X_3 (E = P, As; X = S, Se) molecules occurs in the reaction with cobalt(II) and nickel(II) tetrafluoroborate in the presence of triphos, which yield the E_2X (E = P; X = S, Se [5]. E = As; X = S [6], Se [7]) or P_3 [8] cyclic units η^3 coordinated to the metal atom.



E = P, As ; X = S, Se

The reactions of cage molecules with d^{10} metal complexes show that pnicogen chalcogenides may interact with the metal units either with the apical or the basal P atoms. The different cleavages of the molecules by Ni(II)–triphos, Co(II)–triphos and M(I)–triphos (M = Rh, Ir) also show that various unusual units, containing pnicogen and chalcogenide atoms, are formed depending on the redox properties of the metal ligand system.

We have investigated the positive electron impact and both positive and negative ion chemical ionization mass spectra of a series of tetrapnicogen trichalcogenides to obtain information on the behaviour of these molecules in the gas phase and to correlate their properties, in the absence of solvents, with their reactivity in solution. To the best of our knowledge only the electron impact mass spectra of P_4S_3 and P_4Se_3 have been previously reported [9].

Experimental

P_4S_3 was purchased from Fluka AG and used after recrystallization from benzene; P_4Se_3 [10], As_4S_3 [11], As_4Se_3 [11] and the mixture of P_3AsS_3, $P_2As_2S_3$ and PAs_3S_3 [12] were prepared according to published procedures.

The mass spectra were run on a double-focusing Kratos MS 80 mass spectrometer of the Laboratory of Gas Chromatography–Mass Spectrometry, Provincia of Turin, University of Turin. Operating conditions were as follows: electron impact mass spectra (EIMS): trap current 100 μA, ionizing energy 70 eV; chemical ionization mass spectra (CIMS):

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TABLE I. Percentage Ion Abundances[a] in the Electron Impact Mass Spectra of E_4X_3 and Metastable Transitions[b] of P_4S_3 and As_4S_3.

Ions	E_4X_3	P_4S_3	As_4S_3	P_4Se_3	As_4Se_3
$[E_4X_3]^+$		100	100	50	41
$[E_3X_2]^+$		27	40	7	7
$[E_3X]^+$		77	13	100	100
$[E_3]^+$		–	2	–	11
$[E_2X]^+$		10	9	18	18
$[E_2]^+$		–	4	–	23
$[EX]^+$		54	23	75	64
$[X]^+$		–	–	23	9
$[E]^+$		–	9	–	26

Transitions	Neutral Fragments	Transitions	Neutral Fragments
$[P_4S_3]^+ \rightarrow [P_3S_2]^+$	PS	$[As_4S_3]^+ \rightarrow [As_3S_2]^+$	AsS
$[P_4S_3]^+ \rightarrow [P_3S]^+$	PS_2	$[As_4S_3]^+ \rightarrow [As_3S]^+$	AsS_2
$[P_3S_2]^+ \rightarrow [P_2S]^+$	PS	$[As_3S_2]^+ \rightarrow [As_2S]^+$	AsS
$[P_3S_2]^+ \rightarrow [PS]^+$	P_2S	$[As_3S_2]^+ \rightarrow [AsS]^+$	As_2S
		$[As_3S_2]^+ \rightarrow [As_3S]^+$	S
		$[As_3S]^+ \rightarrow [As_3]^+$	S
		$[As_3S]^+ \rightarrow [As_2]^+$	AsS
		$[As_2S]^+ \rightarrow [As_2]^+$	S
		$[AsS]^+ \rightarrow [As]^+$	S

[a] Electron impact ionization at 70 eV ionizing energy. [b] B/E linked scan.

emission current 500 μA, primary electron energy 60 eV; accelerating voltage 4 kV, resolution 1000, scan rate 3 s/dec.

The compounds were introduced through a direct insertion probe heated to the minimum temperature necessary to obtain reproducible ion abundances.

The reagent gases methane, isobutane, ammonia and chloromethane, were introduced through an automatic multiple reagent gas inlet system, while acetone and ethyl acetate were introduced through a heated all-glass inlet system at about 0.5 torr.

Results and Discussion

The ionic abundances observed in the EIMS of E_4X_3 (E = P, As; X = S, Se) and the metastable transitions of P_4S_3 and As_4S_3 are reported in Table I. P_4S_3 and As_4S_3 show very similar EIMS and in both spectra the molecular ion is the base peak. The most evident difference is the presence of $[As_n]^+$ (n = 1–3) ions in the spectrum of As_4S_3, which can be ascribed to the ionization energy of As, which is lower than that of P. The corresponding $[P_n]^+$ ions only appear at higher temperature, where the fragmentation pattern also changes due to probable thermal processes.

The metastable transition schemes reported in Table I show that the fragmentation of the two cage molecules occurs through the loss of corresponding neutral fragments. Sulphur can be eliminated only by arsenic-containing ions leading to the $[As_n]^+$ (n = 1–3) species, while $[P_3S]^+$, $[P_2S]^+$ and $[PS]^+$ do not decompose further.

The ion abundances of tetraphosphorus and tetraarsenic triselenide are also reported in Table I. The two compounds exhibit analogous fragmentation pathways, the $[E_3Se]^+$ ion (E = P, As) being the base peak. Metastable transitions of the two molecules are the same as those found for the corresponding compounds containing sulphur. The P_4Se_3 molecule shows the following transition $[P_3Se_2]^+ \rightarrow [P_3Se]^+ + Se$, which has not been observed for P_4S_3.

For all these compounds the main fragmentation pathways generate even-electron ions.

The EI mass spectrum and the metastable transition analysis of the P_3AsS_3, $P_2As_2S_3$ and PAs_3S_3 mixture were also investigated. Due to difficulties in separating the three compounds, which show many common ions, we do not report the ionic abundances of each molecule. All the compounds exhibit very abundant molecular ions, and their fragmentation pathways involve loss of the same neutral fragments as P_4S_3 and As_4S_3.

TABLE II Percentage Abundances of Significant Ions in the Chemical Ionization Mass Spectra, with Methane[a], of E_4X_3

Ions	E_4X_3	P_4S_3	As_4S_3	P_4Se_3	As_4Se_3
$[E_4X_3 + H]^+$		15	100	28	15
$[E_4X_3]^+$		8	80	25	20
$[E_3X_2]^+$		4	31	3	5
$[E_3X]^+$		30	78	100	100
$[E_2X + H]^+$		75	5	5	3
$[E_2X]^+$		30	10	4	9
$[EX]^+$		100	53	18	30

[a] Gas pressure *ca* 0 5 torr

TABLE III Percentage Abundances of Significant Ions in the Chemical Ionization Mass Spectra of P_4S_3 with Different Reagent Gases [a]

Ions	Reagent Gas ΔPA[b]	CH_4 75	$i\text{-}C_4H_{10}$ 7 7	CH_3COCH_3 6 1	$CH_3COOC_2H_5$ 2 7	NH_3 0 0
$[P_4S_3 + 88]^+$		–	–	–	20	–
$[P_4S_3 + 58]^+$		–	–	25	–	–
$[P_4S_3 + 57]^+$		–	12	–	–	–
$[P_4S_3 + 43]^+$		–	25	3	–	–
$[P_4S_3 + 41]^+$		–	20	–	–	–
$[P_4S_3 + 1]^+$		15	100	–	–	–
$[P_4S_3]^+$		8	93	100	100	100
$[P_3S_2 + 58]^+$		–	–	10	–	–
$[P_3S_2]^+$		4	55	35	33	30
$[P_3S + 58]^+$		–	–	35	–	–
$[P_3S]^+$		30	80	95	80	80
$[P_2S + 1]^+$		75	–	–	–	–
$[P_2S]^+$		30	25	13	4	18
$[PS]^+$		100	80	47	15	85

[a] Gas pressure *ca* 0 5 torr [b] Proton affinity relative to ammonia (kcal mol^{-1}), $[NH_4]^+ + B \rightarrow [BH]^+ + NH_3$, methane [15], others [16]

The ionic abundances in the CIMS of P_4S_3, As_4S_3, P_4Se_3 and As_4Se_3 with methane at about 0 5 torr are compared in Table II All the compounds show the protonated molecule $[E_4X_3 + H]^+$, which is always more abundant than $[E_4X_3]^+$ except for As_4Se_3 The fragment relative abundances of the sulphur-containing molecules are quite different, and the base peaks are $[PS]^+$ and $[As_4S_3]^+$ Moreover, As_4S_3 exhibits the most abundant ions in the highest mass region, whilst in the CI mass spectrum of P_4S_3 about 75% of the total ion current is transported by $[P_3S + H]^+$, $[P_2S]^+$ and $[PS]^+$ On the contrary, P_4Se_3 and As_4Se_3 show similar fragmentation patterns and $[E_3Se]^+$ (E = P, As) is the base peak

In Table III the ionic abundances in the CIMS of P_4S_3 with methane, isobutane, acetone, ethylacetate and ammonia at about 0 5 torr are reported The proton affinities of the reagent gases are given as values relative to ammonia (ΔPA), because the actual proton affinity of NH_3, $PA(NH_3)$, is still controversial Even if it has been discussed in detail [13], $PA(NH_3) = 207 \pm 2$ kcal mol^{-1} is only indicated as a "preferred value" [14]

The protonated molecule is formed only when P_4S_3 is in the presence of methane or isobutane Therefore the proton affinity of P_4S_3 is within a quite narrow range, 1 6 kcal mol^{-1} , limited by $\Delta PA(CH_3COCH_3)$ = 6 1 kcal mol^{-1} and $\Delta PA(i\text{-}C_4H_{10})$ = 7 7 kcal mol^{-1}

Moreover the CI mass spectrum of P_4S_3 with CH_4 exhibits more abundant fragment ions than the CIMS run in the presence of the other reagent gases Such behaviour is likely to be a consequence of the difference between the proton affinities of P_4S_3 and CH_4, which is in the range 67 3–68 9 kcal mol^{-1} The exothermicity of the ionization process is known to control the stability of $[M + H]^+$ and the extent of its fragmentation [15]

TABLE IV $[M + H]^+/[M]^+$ Abundances[a] in the Chemical Ionization Mass Spectra of E_4X_3 with Different Reagent Gases[b]

Compounds	Reagent Gases	$i\text{-}C_4H_{10}$	CH_3COCH_3	$CH_3COOC_2H_5$	NH_3
	ΔPA[c]	7 7	6 1	2 7	0 0
P_4S_3		1 0	–	–	–
P_3AsS_3		1 1	–	–	–
$P_2As_2S_3$		1 2	–	–	–
PAs_3S_3		1 4	–	–	–
As_4S_3		3 5	1 7	0 4	–
P_4Se_3		0 9	–	–	–
As_4Se_3		1 1	–	–	–

[a] Where no ratio appears, it means that the protonated molecule $[M + H]^+$ is not observed [b] Gas pressure *ca* 0 5 torr
[c] Proton affinity relative to ammonia (kcal mol^{-1}), $[NH_4]^+ + B \rightarrow [BH]^+ + NH_3$, methane [15], others [16]

In all the CIMS, except in the presence of methane, the base peak is the molecular ion formed by charge exchange or the protonated molecule In the presence of acetone and ethylacetate P_4S_3 exhibits quite abundant adduct ions

The $[M + H]^+/[M]^+$ abundances, in the CIMS of $P_nAs_{4-n}S_3$ (n = 0–4), P_4Se_3 and A_4Se_3, with isobutane, acetone, ethylacetate and ammonia at about 0 5 torr, are reported in Table IV All the cage compounds except As_4S_3 give protonated molecules only in the presence of methane and isobutane and this indicates that their gas-phase proton affinity is between the acetone and isobutane PA values On the contrary, As_4S_3 shows higher basicity, being $\Delta PA(NH_3) < \Delta PA(As_4S_3) < \Delta PA(CH_3COOC_2H_5)$ This means that the proton affinity of As_4S_3, relative to ammonia, is in the range 0 0–2 7 kcal mol^{-1}

In the presence of isobutane the fragmentation of the protonated molecules is strongly reduced, compared with methane, because isobutane and samples exhibit similar proton affinities Therefore we suggest that the $[M + H]^+/[M]^+$ abundances for these cage molecules, in the presence of isobutane, can be correlated to their gas-phase proton affinities In the series $P_nAs_{4-n}S_3$ the $[M + H]^+/[M]^+$ abundances increase with n decreasing from 4 to 0 (Table IV) Moreover As_4S_3 shows decreasing $[M + H]^+/[M]^+$ abundance values when mixed in the source with acetone (ΔPA = 6 6 kcal mol^{-1}) and with ethylacetate (ΔPA = 2 7 kcal mol^{-1}) as the reagent gas under chemical ionization conditions

P_4Se_3 shows $[M + H]^+/[M]^+$ abundance values similar to P_4S_3 and P_3AsS_3, but surprisingly As_4Se_3 also exhibits a value in this range The low volatility of As_4Se_3 requires that the direct insertion probe is heated to a temperature higher than that used for the other compounds examined and this can cause a consequent effect on the ion abundances

In the spectra of $P_nAs_{4-n}S_3$ with methane the abundance ratios between $[M + H]^+$ and $[M]^+$ follow a different trend this is likely to be due to the strong fragmentation which prevents a significant and direct correlation between the proton affinity and the $[M + H]^+/[M]^+$ values under these conditions

The negative ion CIMS of P_4S_3, As_4S_3, P_4Se_3 and As_4Se_3, with methane at about 0 5 torr, were also investigated They display very few ions and most of the total ion current is transported by the molecular ion $[M]^-$ and by $[M + H]^-$ On the contrary, in the presence of chloromethane the negative ion CIMS of P_4Se_3 and As_4Se_3 both show $[M]^-$ and $[M + H]^-$, whilst P_4S_3 and As_4S_3 exhibit only the negative molecular ion

The stability of $[M]^-$ is likely to be achieved by the cleavage of one of the sample bonds and the consequent elimination of the excitation energy The most electronegative chalcogen atoms are suggested to be involved in the addition of the incoming electron to give $[M]^-$ and in the formation of the $[M + H]^-$ species

On the contrary, it is likely that the proton–molecule reactions observed in the positive ion CIMS of E_4X_3 (E = P, As, X = S, Se) are controlled by the pnicogen atoms, even if no direct evidence has been obtained on the addition site of the proton In the $P_nAs_{4-n}S_3$ (n = 0–4) series the gas-phase proton affinity seems to be mainly affected by the nature of the atom in the apical position Continuous and slow increase of the $[M + H]^+/[M]^+$ abundance ratios occurs on going from P_4S_3 to P_3AsS_3, $P_2As_2S_3$ and PAs_3S_3, which are all compounds with the apical position occupied by a phosphorus atom Therefore the substitution of basal phosphorus with arsenic gives very little change, whilst the substitution of the phosphorus in the apical position, as in As_4S_3, causes a relatively large increase in the proton affinity

The hypothesis of the proton addition on a pnicogen atom is in agreement with the results reported on H_2Se and AsH_3 mixture, where the abundance of $[H_3Se]^+$ decreases and $[AsH_4]^+$ increases with pressure [17] An analogous behaviour is typical of a mixture of H_2S and AsH_3 [18]

However the similar ratios between the abundances of the protonated molecule and the molecular ion for

P_4Se_3 and As_4Se_3 indicate that the rationalization proposed for $P_nAs_{4-n}S_3$ (n = 0–4) is not of general application, suggesting that the nature of the chalcogen atom also displays a strong influence Therefore it can be assumed that the gas-phase proton affinity of the E_4X_3 (E = P, As, X = S, Se) cage molecules is affected by the mutual interaction of the pnicogen and chalcogen atoms and by their structures Other compounds which contain phosphorus or arsenic and exhibit simple structures follow an opposite trend PH_3, for example, shows higher gas-phase proton affinity than AsH_3 [18] and PPh_3 [19] behaves in the same way with respect to $AsPh_3$ [20]

Turning to considerations on the chemical reactivity of the cage molecules with d^{10} $M(np_3)$ (M = Ni, Pd) and $Pt(PPh_3)$, systems which have donor properties [21], it may be noted that according to the highest proton affinity of the apical pnicogen their interactions with the metal through either the apical or basal P atoms is determined probably by steric rather than electronic requirements The $Pt(PPh_3)$ moiety, in which the platinum has its coordination sphere occupied only to a small extent by the triphenylphosphine, interacts with the basal P atoms of the cage molecule The $M(np_3)$ complexes, in which the metal atom is surrounded by the skeleton of the ligand and the unique free coordination site to the metal is restricted by the six phenyl groups of the np_3 ligand [22], are forced by steric hindrance to interact with the apical pnicogen of the cage molecules, although the apical donor has the higher proton affinity The weak interaction that occurs between the metal–np_3 unit and the apical donor of the cage molecule [1] is in accordance with the above observations

Finally the different cleavages of the cage molecules by transition metal–ligand moieties afford complexes containing even-electron units, as found in the EIMS In this connection it is worthwhile to point out that the $[E_2X]^+$ (E = P, As, X = S, Se) and $[As_3]^+$ ions found in the mass spectra of the cage molecules probably have triangular structures, found for such units η^3 bonded to cobalt–triphos [5] or nickel–triphos [8] moieties Furthermore the cleavage of cage molecules in presence of metal–triphos (metal = rhodium or iridium) moieties allows us to isolate compounds with E_3X_3 (E = P, X = S, Se E = As, X = S) units that have not been found in mass spectra

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