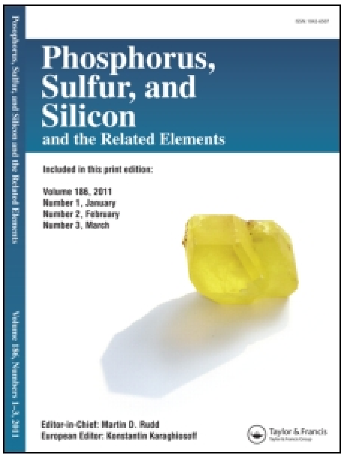

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GASEOUS DIPHOSPHORUS AND TRIPHOSPHORUS SULFIDE: GENERATION AND IDENTIFICATION BY NEUTRALIZATION-REIONIZATION MASS SPECTROMETRY

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GASEOUS DIPHOSPHORUS AND TRIPHOSPHORUS SULFIDE: GENERATION AND IDENTIFICATION BY NEUTRALIZATION-REIONIZATION MASS SPECTROMETRY

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The dissociative ionization by electron impact (70 eV) of tetraphosphorus trisulfide, P_4S_3, yields $[P_3S]^+$ and $[P_2S]^{+0}$ ions whose structures have been investigated by means of Collisional Activation (CA) mass spectra. Using the technique of Neutralization-Reionization mass spectrometry (NRMS) it is shown that both ions can be reduced to the corresponding neutral molecules. Thus, triphosphorus sulfide and diphosphorus sulfide are viable molecules in the rarefied gas phase. The results of *ab initio* MO calculations were used to interpret the experimental findings. Tetrahedral (C_{3v}) and triangular (C_{2v}) structures are proposed for the $[P_3S]^+$ and $[P_2S]^{+0}$ ions respectively.

Key words: Phosphorus sulfides/mass spectrometry; neutralization-reionization; ab initio MO calculations.

In the past, the chemistry of phosphorus sulfides has focused mainly on the solid compounds P_4S_n.[1] Recently, however, there has been a growing interest[2-7] in the structure and reactivity of small phosphorus deficient sulfides both as neutrals and as ions. The latter are kinetically unstable and therefore accessible only by methods which exclude intermolecular interactions. Such "unimolecular conditions" are met in the dilute gas phase of a mass spectrometer. Indeed, intense signals for stable binary PS-ions are frequently observed in the mass spectra of P_4S_n compounds.

A case in point are the $[P_3S]^+$ and $[P_2S]^{+0}$ ions which can conveniently be generated by the dissociative ionization (electron impact: 70 eV) of P_4S_3.[8] We have investigated the structure of these two ions by analysing their Collisional Activation (CA) mass spectra[9] in conjunction with the results of *ab initio* MO calculations. Computational results were also used to interpret the results of a second MS/MS type technique, Neutralization-Reionization mass spectrometry (NRMS),[10] which was used to probe the existence and the structure of the neutral counterparts of these ions. It will be shown that both triphosphorus sulfide, P_3S, and diphosphorus sulfide, P_2S, which has recently been identified in a matrix isolation experiment[6] are stable species in the dilute gas phase.

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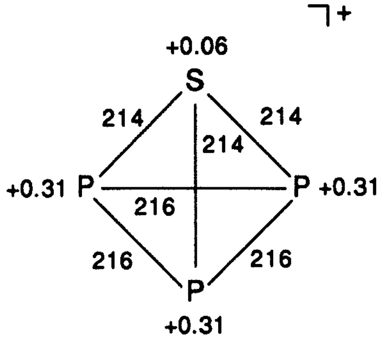
P_3S^+ AND P_3S^0 (TRIPHOSPHORUS SULFIDE)

For the $[P_3S]^+$ system *ab initio* molecular orbital calculations (HF/6-31G* basis set) gave only one minimum (total energy $E_{tot} = -1419.41038$ a. u.) on the potential energy surface. The corresponding structure, which resembles that of the isoelectronic P_4 molecule, is shown below.



(C_{3v})

Surprisingly the positive charge is evenly distributed on the three P atoms. The calculated bond lengths for the P—P bonds and the P—S bonds are 216 pm and 214 pm respectively.†

The CA mass spectrum of $[P_3S]^+$ (Figure 1) is in good agreement with the above mentioned structure. The most intense signals in decreasing order of abundance are $[PS]^+$ (m/z 63; loss of P_2), $[P_2]^{+0}$ (m/z 62; loss of PS), $[P_3]^+$ (m/z 93; loss of S) and $[P_2S]^{+0}$ (m/z 94; loss of P). The presence of the signal at m/z 93 ($[P_3]^+$) supports our assumption that the P_3S ion has the suggested C_{3v} structure. The intense narrow peak at m/z 62.5 ($[P_3S]^{++}$) is due to a "charge-stripping"-(CS-) process.[12] Figure 2a shows the CA mass spectrum of the isotopomer $[P_3{}^{34}S]^+$ (m/z 127) which allows an unambiguous assignment of some of the poorly resolved peaks in the CA mass spectrum of Figure 1.

The NR mass spectrum shown in Figure 2b is also that of the $[P_3{}^{34}S]^+$ isotopomer. Albeit of low intensity, the spectrum does display a "survivor signal" demonstrating that P_3S^0 exists as a neutral molecule. The relative intensity of the fragment ions found in the NR and CA mass spectrum of $[P_3{}^{34}S]^+$ are somewhat different. These differences may originate from contributions to the NR mass spectrum of the collisional induced dissociative ionization of neutral species of lower mass.

Ab initio MO calculations show that the structure of neutral P_3S^0 in its electronic ground state ($E_{tot} = -1419.66257$ a. u.) differs considerably from that of the cation. The S atom in the neutral molecule is bound to only two of the P atoms (bond

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† Semiempirical MO calculations (MNDO) gave much shorter bond lengths: 207 pm and 205 pm for the P—P and P—S bonds respectively.[2] The same trend is found for calculations on P_4: MNDO: 205 ppm; *ab initio*: 217 pm; experimental value: 221 pm.[11] For P_4S_3 the MNDO calculation also yielded bond lengths which are c. 7% shorter than the experimental values.[2]

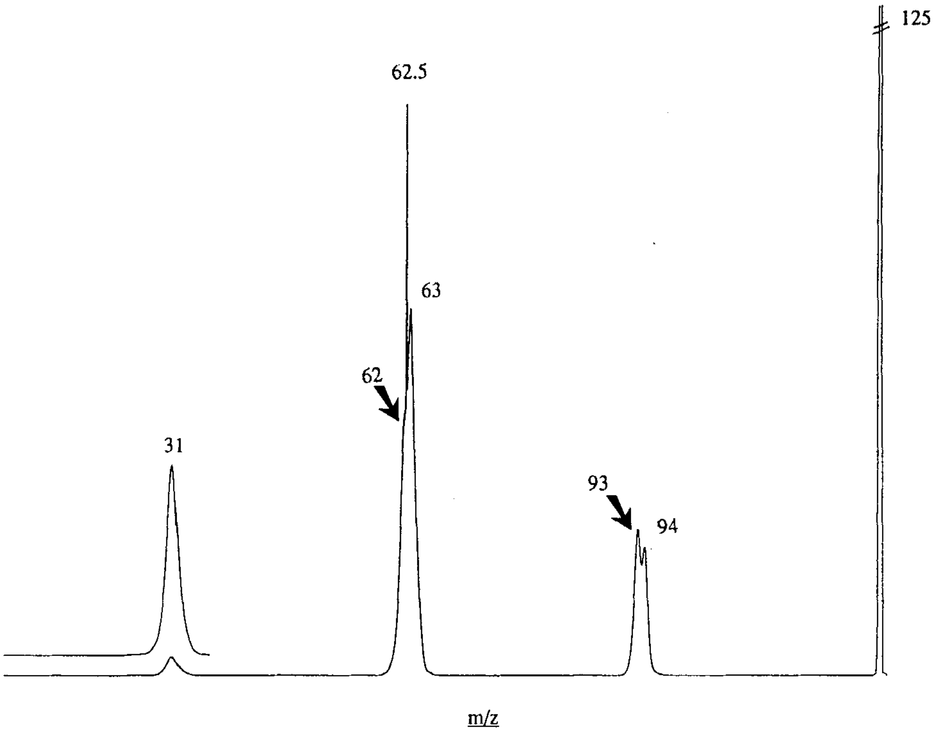
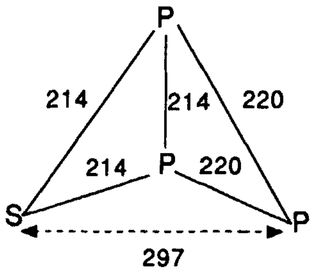


FIGURE 1 CA mass spectrum of $[P_3S]^+$ (m/z 125).

length 214 pm): the distance of S to the remaining P atom (297 pm) is not indicative of PS bonding. Thus, the molecule exists in a "butterfly structure" (C_s) (dihedral angle 103°) depicted below and it can be considered as "thiatriphospha-bicyclobutane."



(C_s)

The bond distance between the P bridgehead atoms is calculated as 214 pm and the bond distance between either of the two P bridgehead atoms to the unbridged P atom is calculated as 220 pm respectively. The calculated spin density indicates that the free electron is localized at the unbridged phosphorus atom. These results

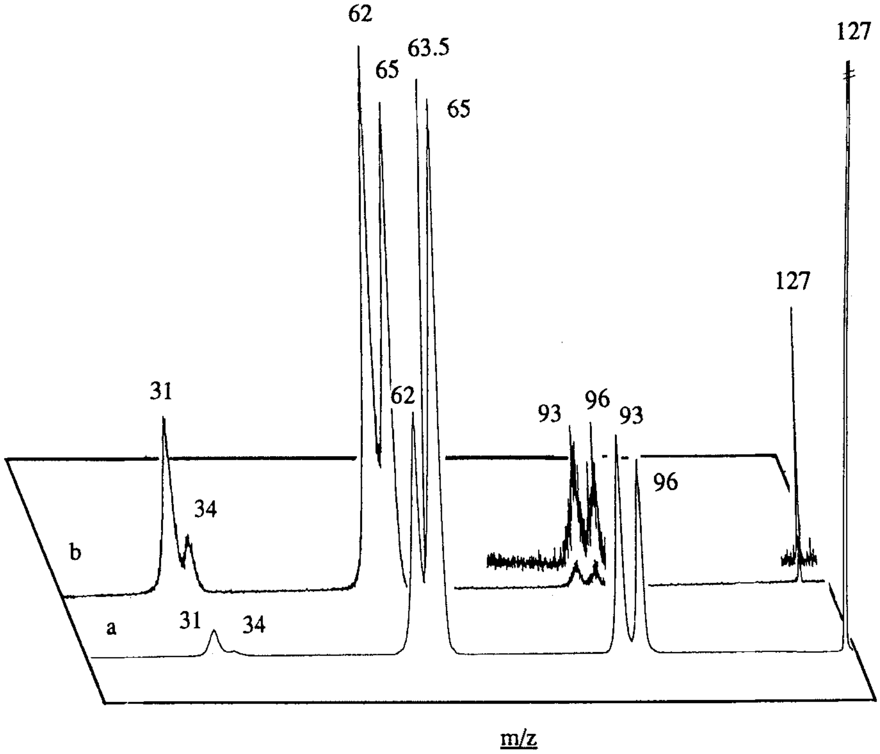


FIGURE 2 CA (a) and NR mass spectrum (b) of $[P_3{}^{34}S]^+$ (m/z 127).

show that substitution of P by S in the P_4 tetrahedron gives rise to a remarkable change in structure.

A similar "butterfly structure" is found in the tetraphospha-bicyclobutane system $(Me_3Si)_2NP_4N(SiMe_3)_2$.[13] In addition, this structure has been proposed for P_4^{2-} ions generated by mass spectrometry[14] and it has been shown by means of ^{31}P-NMR spectroscopy to represent the structure of the HP_4^- ion.[15]

Electron transfer in a NR experiment is a vertical process. This implies that if the ion and the neutral have considerable different geometries the Franck-Condon factors for the formation of the neutral in its ground state will be small. Considering the computational results discussed above, such a situation may well apply to the P_3S^0 system, where most of the neutral species generated in the neutralization process will have the energetically unfavourable tetrahedron structure of the ion. These neutrals are prone to dissociate and this may explain both the relatively weak "survivor signal" in the NR mass spectrum and the intensity differences between the CA and the NR mass spectra mentioned earlier.

P_2S^{+0} AND P_2S (DIPHOSPHORUS SULFIDE)

The CA mass spectrum of $[P_2S]^{+0}$ (m/z 94) (Figure 3a) shows intense signals for $[PS]^+$ (m/z 63), $[P_2]^{+0}$ (m/z 62) and $[P]^+$ (m/z 31). The peak at m/z 47 ($[P_2S]^{++}$)

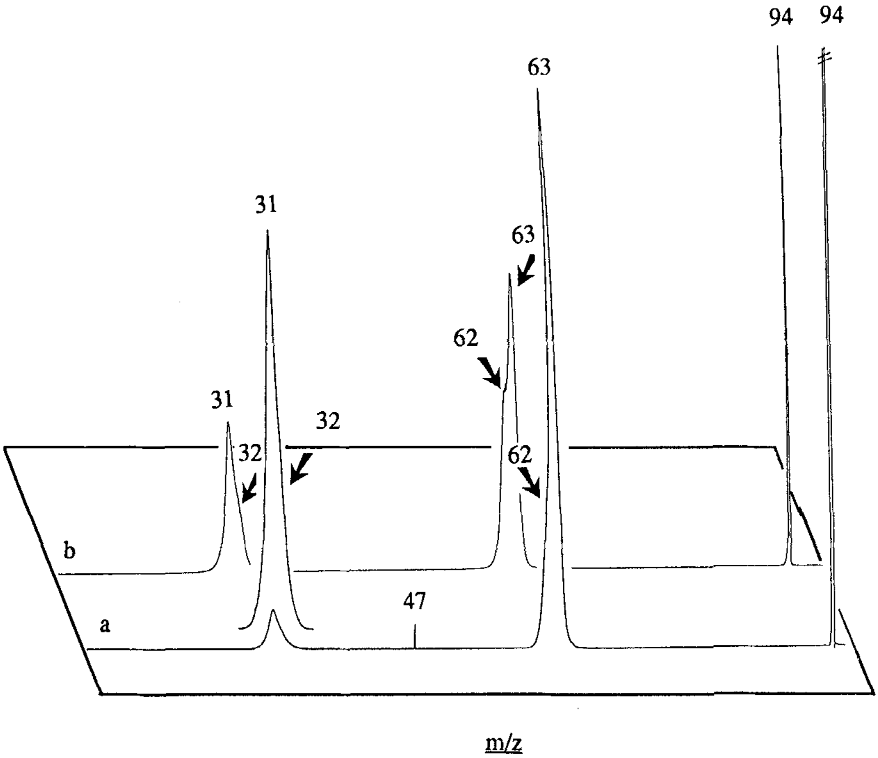
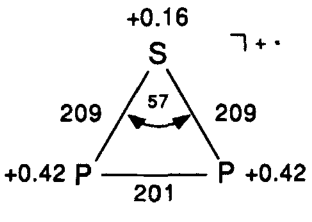


FIGURE 3 CA (a) and NR mass spectrum (b) of $[P_2S]^{+0}$ (m/z 94).

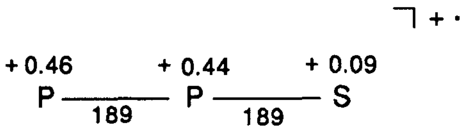
is due to a CS process. Considering that the minimum energy requirement for the dissociation of $[P_2S]^{+0}$ into $[PS]^+$ + P^0 is lower than that for the dissociation into $[P_2]^{+0}$ + S^{16} the presence of the $[P_2]^{+0}$ signal in the CA mass spectrum provides clear evidence that the $[P_2S]^{+0}$ ions have the P—P—S rather than the P—S—P connectivity. *Ab initio* MO calculations (HF/6-31G* basis set) indicate for ions of such a connectivity two minima exist on the potential energy surface. These are represented by the cyclic and the linear structures shown below:



C_{2v}

(E_{tot} = - 1078.64801 a.u.)

I



$C_{\infty v}$

(E_{tot} = - 1078.48294 a.u.)

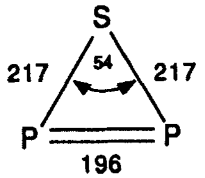
II

The short bond lengths in both species point to a considerable double bond character. However, the cyclic ion I is much more stable than the linear isomer II, by 433 kJ/mol. This makes it very likely that the dissociative ionization of $[P_4S_3]^{+0}$ yields $[P_2S]^{+0}$ radical cations of structure I. Further support for this proposal comes from a comparison of the conventional CA mass spectrum of the P_2S ions with that of the "survivor" P_2S ions resulting from the neutralization-reionization process. The two spectra are closely similar—in particular they show the same m/z 62 $[P_2]^{+0}$/m/z 63 $[PS]^+$ fragment ion intensity ratio—which strongly suggests that we are dealing with P_2S ions of a single structure. As mentioned above, the *ab initio* calculations predict this ion to have the cyclic structure I with short PS (209 pm) and P—P bonds (201 pm) indicating double bond character. The positive charge is evenly spread over the P atoms and the free electron is predominantly found on the S atom.

The structure of the neutral P_2S molecule which is iso(valence)electronic with the linear molecules N_2O[17] and N_2S[18] has been investigated in a recent *ab initio* MO study.[4] This study indicates that a triangular structure akin to I is 30 kJ/mol lower in energy than the linear P—P—S structure II and that the two species are separated by a sizeable barrier of 160 kJ/mol. Our results are in excellent agreement with these findings.[19] Neutral P_2S has recently been identified among the products of a discharge reaction of P_4 and S_8 by *Andrews* et al.[6] These authors, on the basis of infrared spectroscopic investigations, propose the neutral molecule thus generated to have a linear structure but the existence of the ring structure could not be excluded.

Our mass spectrometric investigations show that the m/z 94 ion can easily be neutralized. The NR mass spectrum, see Fig. 3b, shows a strong "survivor signal" and a fragmentation pattern which is very close to that observed in the CA mass spectrum. These observations are consistent with the proposal that neutral species generated from the cyclic ion retains the cyclic structure. The differences between the geometries of the cyclic ion and the cyclic neutral are small and this accounts for the presence of a "survivor signal" of high intensity.

Comparison of the optimized geometry of the cyclic ion with that of the cyclic neutral shows that the P—P bond in the neutral has become shorter (201 pm → 196 pm) whereas the P—S bond length has increased, from 209 to 217 pm. It seems reasonable to assign a double bond between the P atoms in neutral P_2S and to regard it as thiadiphosphirene:



a species which can formally be considered as the product of a [1 + 2]-cycloaddition reaction of diphosphorus P_2 and S.

EXPERIMENTAL

A commercially available sample of P_4S_3 (Fluka) was used for all measurements.

CA mass spectra (collision gas He) were obtained with a Varian MAT 311 A mass spectrometer.

NR spectra and reference CA spectra were obtained with the VG Analytical ZAB-R instrument using cyclopropane for neutralization (80% transmittance, T) and oxygen (70% T) for reionization. The ZAB-R is a BEE type mass spectrometer (B stands for magnetic and E for electric sector) equipped with neutralization reionization collision gas chambers in the second field free region, a quadrupole perpendicular to the neutralization chamber and additional collision gas chambers in the first and the third field free region.[20]

Ab initio molecular orbital calculations were performed by using the Gaussian 88[21] system of programs installed on a Convex C 120 computer. Stationary points on the potential energy surface have been located at the Hartree-Fock (HF) level of theory. Geometry optimization (Berny optimization) and energy calculations have been carried out with the HF/6-31G* basis set, which has polarization basis functions on the non-hydrogen atoms. Bond lengths are given in picometers and bond angles in degrees. The atomic charges were determined using the Mulliken population analysis.

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