Gas Phase Reactions.[1,2] FPS_2 and FPS

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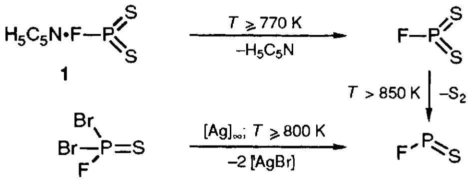
The pyridinium betaine $H_5C_5N{\cdot}FPS_2$ dissociates at 770 K in the gas phase yielding the novel $\sigma^3\lambda^5$-phosphorane FPS_2, which at 900 K splits off S_2 to give FPS as substantiated by comparison with the photoelectron spectrum from its generation by Br_2FPS debromination on silver wool above 800 K.

Small molecules, which violate the outdated 'non-double bond-rule' for main-group elements of third or higher periods, continue to pop up from appropriately designed measurement techniques as, for instance, photoelectron spectroscopy in flowing gases.[3] Those containing both phosphorus and sulfur,[4,5] in particular provide textbook examples such as $Cl{-}P{=}S$[6] and $Cl{-}P({=}S)_2$.[7] Here we present a missing link between the two classes of compounds, $\sigma^2\lambda^3$-phosphanes and $\sigma^3\lambda^5$-phosphoranes (Scheme 1).

The short-pathway thermolysis of the betaine **1** was carried out in an internal electron-bombardment oven of a Leybold Heraeus UPG 200 photoelectron spectrometer[3] by evaporating the solid at 470 K into the reaction zone, the temperature of which was increased in steps of 50 K. The photoelectron spectra recorded (Fig. 1) at 570 K closely resemble that of pyridine (Fig. 1: shaded) and at 770 K show additional bands, *e.g.* at 10.0, 10.5, 11.33 and 13.45 eV. Digital subtraction[1,2] of a prerecorded pyridine spectrum unmasks the ionization



Scheme 1

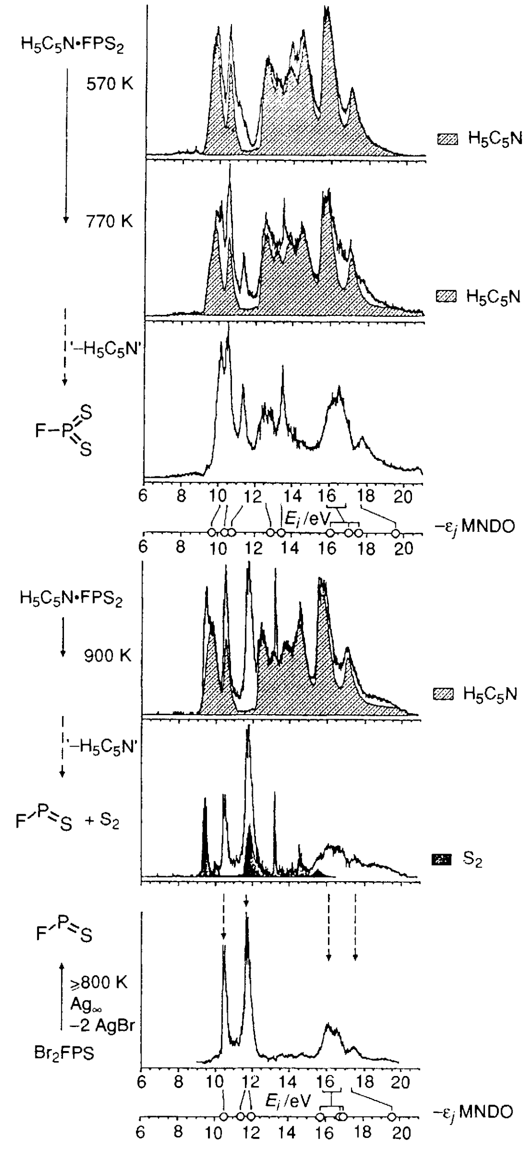


Fig. 1 He I PE spectra of $H_5C_5N{\cdot}FPS_2$ (evaporated at 470 K) at 570 and 770 K, of pyridine (prerecorded, shaded), after its digital subtraction together with Koopmans' assignment for FPS_2, and continued for 900 K with repeated subtraction '$-H_5C_5N$' yielding that of the gaseous mxiture of S_2[8] and FPS. The latter is also recorded after debromination of Br_2FPS on silver wool above 800 K[2] and assigned by another Koopmans' correlation with MNDO eigenvalues (*cf.* text).

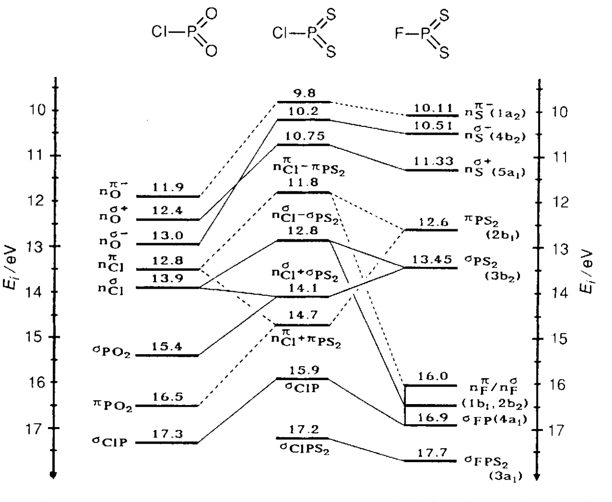


Fig. 2 Comparison of the ionization energies (E_i) for the radical cation states of $ClPO_2$, $ClPS_2$ and FPS_2

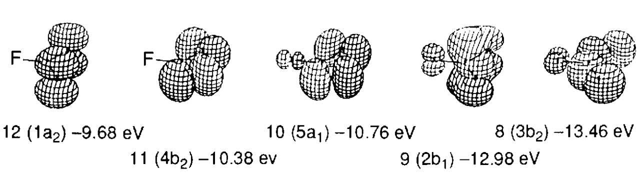


Fig. 3 Orbital diagrams for FPS_2

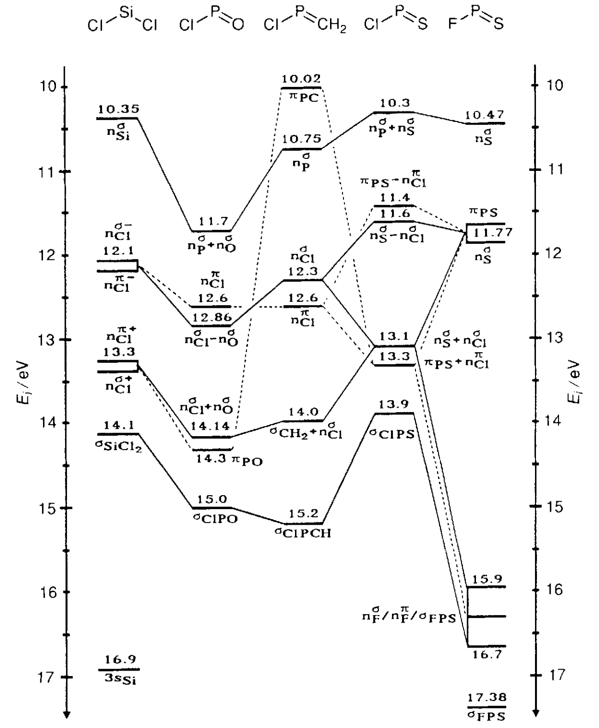


Fig. 4 Comparison of the ionization energies (E_i) for the radical cation states of Cl_2Si (ref. 9), ClPO (ref. 6), $ClPCH_2$ (ref. 10), ClPS (ref. 6) and FPS

pattern of the $\sigma^3\lambda^5$-phosphorane FPS_2 as proven by a radical cation state comparison with the analogous four-centre–24 valence electron molecules $ClPO_2$ and $ClPS_2$ (Fig. 2).[7] The assignments are supported by Koopmans' correlations, $E_{i,n}{}^{V} = -\varepsilon_J{}^{MNDO}$,† with MNDO eigenvalues from geometry-optimized semiempirical SCF calculations (*cf.* refs. 2, 7 and Fig. 1). According to the corresponding orbital diagrams for FPS_2 (Fig. 3), in its five radical cation states of lowest energy, the positive charge is predominantly delocalized over the S and P centres.

On further heating of the evaporated H_5C_5N + FPS_2 mixture in the flow system at 10^{-4} mbar pressure to 900 K, the ionization pattern (Fig. 1) changes again: for instance, bands at 10.11 and 11.33 eV (FPS_2) have vanished and new ones at 9.41 and 13.24 eV (S_2[8]) and at 10.47 and 11.77 eV appear. Renewed digital subtraction of the prerecorded pyridine PE spectrum (Fig. 1: shaded) yields the He I PE bands of another gaseous mixture, in which the component S_2 is immediately recognized by three of its characteristic low-energy peaks at

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† RSC Journals follow IUPAC recommendations with regard to abbreviations. Elsewhere in the literature ionisation energy is often denoted as IE.

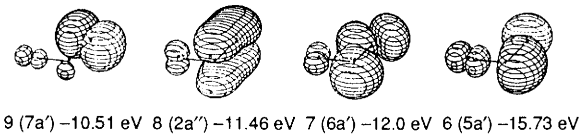

Fig. 5 Orbital diagrams for FPS

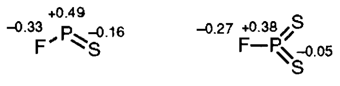

Fig. 6 MNDO calculated charge distributions for FPS and FPS_2

9.41, 13.24 and 14.62 eV.[8] The remaining ones of, at first sight, unknown origin are readily assigned to FPS by comparison with unpublished spectra[2] of the product of Br_2FPS debromination on silver wool[4,5] above 850 K (Fig. 1). Further confirmation is provided by another Koopmans' correlation with MNDO eigenvalues (Fig. 1) and, above all, by the radical cation state comparison with some of the iso(valence)electronic triatomic molecules generated under analogous measurement conditions (Fig. 4).[6,9,10]

FPS differs in structural details from the homologous FNS (d_{FS} 165 pm, d_{SN} 145 pm and $\angle_{FNS}$ 117°),[11] but should be also bent according to both Walsh rules[12,13] and a geometry-optimized MNDO calculation[2] (d_{PF} 154 pm, d_{PS} 180 pm and $\angle_{FPS}$ 111°). The MNDO orbital diagrams (Fig. 5) suggest for the $FPS^{\cdot+}$ ground state as well (*cf.* Fig. 3) a largely sulfur lone pair character. Predominant P and S contributions are predicted for the three $M^{\cdot+}$ states following, $\pi_{PS}(a'')$ and to $\sigma_{FPS}(a')$, of which the latter are separated by more than 4 eV (Fig. 1). Altogether, the MNDO calculated charge distributions for FPS as well as for FPS_2 (Fig. 6) suggest that both molecules should be only moderately polarized, presumably owing to the well-known perfluoro effect,[14] *i.e.* the π back donation from negatively charged F centres.

With regard to the unexpected gas phase formation of a FPS + S_2 mixture from FPS_2 (Fig. 1), dimers $(RPS_2)_2$ containing a four-membered ring are known and can be monomerized thermally.[2,7] On the other hand, N_2S_2 fragments above 900 K into both 2 SN and $N_2 + S_2$, an observation for which energy hypersurface calculations suggest a distorted tetrahedral intermediate.[15]

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