

Synthesis of a Perfluoro Compound of Phosphorus and Silicon. Tris(trifluorosilyl)phosphine

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Summary Tris(trifluorosilyl)phosphine, the first perfluoro compound of phosphorus and silicon, has been synthesized in high yield from the mercury-sensitized photolysis of Si_2F_6 with PF_3 .

COMPOUNDS comprised solely of the elements phosphorus, silicon, and fluorine have not been reported previously; indeed, despite the well developed chemistry of fluoroalkyl-phosphines^{1,2} and -phosphoranes,² molecules containing the trifluorosilyl group bonded to phosphorus also appear to be unknown.

Our recent discovery³ that trifluorosilyl radicals can be readily generated *via* mercury-sensitized photolysis of Si_2F_6 has led us to investigate the interaction of these radicals with PF_3 . We report here the synthesis and

characterization of the compound tris(trifluorosilyl)phosphine obtained from the mercury-sensitized photolysis of Si_2F_6 with PF_3 .

In a typical reaction, 30 Torr of Si_2F_6 , 80 Torr of PF_3 , and a small amount of mercury vapour in a 400 ml quartz vessel were irradiated for 90 min at 35 °C with a bank of low-pressure mercury discharge lamps (predominant output at 2537 Å). A small amount of pale yellow translucent film was deposited on the walls of the reaction vessel during the reaction. Volatile products were passed through two traps, the first cooled to -130 and the second to -196 °C, on a glass high vacuum system. The fraction which passed -130 °C and was collected at -196 °C was determined by i.r. analysis to consist solely of SiF_4 and unchanged PF_3 . The fraction held at -130 °C was subjected to n.m.r.

analyses, and was found to contain unchanged Si_2F_6 , $\text{P}(\text{SiF}_3)_3$, and very small amounts of $(\text{SiF}_3)_2\text{PH}$ and Si_2OF_6 . 68% of the hexafluorodisilane had reacted; conversion of Si_2F_6 into $\text{P}(\text{SiF}_3)_3$ was 84%.[†]

Tris(trifluorosilyl)phosphine is a colourless, air-sensitive liquid at room temperature with a strong, acrid odour. Definitive characterization of the molecule is possible on the basis of fluorine and phosphorus n.m.r. spectra, which include both $\text{P}^{28}\text{SiF}_3$ and $\text{F}_3^{29}\text{SiP}^{28}\text{SiF}_3$ species. Coupling constants, chemical shifts, satellite intensities and multiplicities, and heteronuclear decoupling data are all fully consistent with the assigned structure $[\text{P}^{28}\text{SiF}_3]_3$: ^{19}F n.m.r. δ 113.7 p.p.m. {d, $^2J(\text{P-F})$ 1.8 Hz} (upfield from external CFCl_3), ^{31}P n.m.r. δ 324.9 p.p.m. {decet, $^2J(\text{P-F})$ 1.7 Hz} (upfield from external 85% H_3PO_4); $\text{F}_3^{29}\text{SiP}^{28}\text{SiF}_3$: ^{19}F n.m.r. {d of d of septets, $^1J(\text{Si-F})$ 308.0, $^3J(\text{F-F})$ 2.6 Hz}, ^{31}P n.m.r. [$^1J(\text{Si-P})$ 22.5 Hz]. Further characterization of the molecule is afforded by its i.r. and mass spectra. A mass spectrum taken at a low (ca. 12 eV) ionizing voltage contained only the molecular ion at m/e 286 and a fragment ion at m/e 182 corresponding to loss of the very stable neutral SiF_4 from the molecular ion. Similar behaviour has been observed for other polyfluoropolysilanes.⁴

[†] Based on the equation: $3\text{Si}_2\text{F}_6 + \text{PF}_3 \rightarrow 3\text{SiF}_4 + \text{P}(\text{SiF}_3)_3$.

[‡] Characterized by n.m.r. and mass spectra.

[§] Characterized by mass spectra.

¹ A. B. Burg, *Accounts Chem. Res.*, 1969, **2**, 353.

² R. E. Banks, 'Fluorocarbons and Their Derivatives,' 2nd edn., MacDonald, London, 1970.

³ K. G. Sharp and P. A. Sutor, unpublished results.

⁴ K. G. Sharp and J. L. Margrave, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2813.

The i.r. spectrum of the molecule contains characteristic SiF_3 stretching modes at 1001 and 839 cm^{-1} .

$\text{P}(\text{SiF}_3)_3$ is hydrolysed by stoichiometric amounts of water vapour to PH_3 , Si_2OF_6 , and SiF_4 ; however, presence of smaller quantities of water leads to production of the species $(\text{SiF}_3)_2\text{PH}^{\dagger}$ and $\text{SiF}_3\text{PH}_2^{\ddagger}$. Excess of bromine readily cleaves the Si-P bonds at room temperature to give PBr_5 and SiF_3Br . The corresponding reaction with anhydrous hydrogen bromide is rather more complex as SiF_4 is liberated along with SiF_3Br .

Complete separation of $\text{P}(\text{SiF}_3)_3$ from Si_2F_6 is difficult on a vacuum line. The most convenient route to the pure compound is an extended (3–4 h) photolysis of PF_3 with Si_2F_6 , since attack of excited mercury atoms on Si_2F_6 is apparently faster than on the Si-P bonds in the product.

When Si_2F_6 - PF_3 mixtures are photolysed for much shorter periods (10 min), the predominant product is still $\text{P}(\text{SiF}_3)_3$. No clear evidence for the presumed intermediate compounds SiF_3PF_2 and $(\text{SiF}_3)_2\text{PF}$ has yet been obtained in any of the above systems.

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