

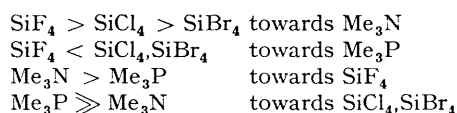
Unique Stable 1:2 Adducts of Silicon Tetrachloride, Silicon Tetrabromide, and the SiCl_3^+ ion with Trimethylphosphine

By G. A. OZIN

(Department of Chemistry, The University, Southampton SO9 5NH)

WE recently reported the preparation of the adduct $\text{AlCl}_3 \cdot 2\text{Me}_3\text{P}$ and predicted that the isoelectronic ion $[\text{SiCl}_3 \cdot 2\text{Me}_3\text{P}]^+$ would be stable.¹ This led us to examine the reaction of silicon tetrahalides with trimethylphosphine. We find that the adducts $\text{SiCl}_4 \cdot 2\text{Me}_3\text{P}$ and $\text{SiBr}_4 \cdot 2\text{Me}_3\text{P}$, have vapour pressures of less than 2 mm. at 25°. In contrast, at 25° and a pressure of 15 cm., no solid adducts form in a gaseous mixture of silicon tetrafluoride and trimethylphosphine at a mole ratio of 1:2. This is in complete contradiction to the behaviour of these tetrahalides with trimethylamine where silicon tetrafluoride forms both a 1:1 and a 1:2 adduct,² with a vapour pressure in each case of *ca.* 4 cm. at 20°; silicon tetrachloride forms a 1:1 adduct only,³ with a vapour pressure of *ca.* 1 mm. at -66°. We found that silicon tetrabromide forms no adduct at -78°. Preliminary X-ray studies⁴ and vibrational spectroscopy suggest that $\text{SiCl}_4 \cdot 2\text{Me}_3\text{P}$ is a *trans*-octahedral species. Further, vibrational spectroscopy

shows that $\text{SiCl}_4 \cdot 2\text{Me}_3\text{P}$ and $\text{SiBr}_4 \cdot 2\text{Me}_3\text{P}$ are only slightly dissociated in benzene at room temperature. The "stability" sequence



appears to be clear cut.

In addition to this unusual behaviour we find that reaction of $[\text{SiCl}_3 \cdot 2\text{Me}_3\text{N}]^+\text{ClO}_4^-$ (in MeCN) with trimethylphosphine yields, on removal of the volatiles, $[\text{SiCl}_3 \cdot 2\text{Me}_3\text{P}]^+\text{ClO}_4^-$. Thus the sequence $\text{Me}_3\text{P} > \text{Me}_3\text{N}$ is found towards SiCl_3^+ .

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¹ I. R. Beattie and G. A. Ozin, *J. Chem. Soc. (A)*, 1968, 2373.

² C. J. Wilkins and D. K. Grant, *J. Chem. Soc.*, 1953, 927. See also J. E. Fergusson, D. K. Grant, R. H. Hickford, and C. J. Wilkins, *J. Chem. Soc.*, 1959, 99.

³ A. Burg, *J. Amer. Chem. Soc.*, 1954, 76, 2674.

⁴ M. Webster, personal communication.