New Thiophosphorimides

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Summary The new thiophosphorimides $P_4(NMe)_6S_n$, with $n = 1$—3, have structures related to those of the series of oxides P_4O_7, P_4O_8, and P_4O_9; scrambling of the peripheral sulphur atoms gave equilibrated mixtures in which the inner $P_4(NMe)_6$ core is retained.

WE report on the preparation, structure, and interconversion of new thiophosphorimides of molecular formula $P_4(NMe)_6S_n$, where $n = 1$—3. These crystalline compounds (m.p. 95, 125, and 174 °C, respectively) were obtained by the direct reaction of the stoicheiometric amounts of elemental sulphur on phosphorus tri-*N*-methylimide, $P_4(NMe)_6$.[1,2] Elemental, ^{31}P and ^{1}H n.m.r., and m.s. analysis are consistent with the above formulation and with the compounds having cage structures in which the original tetrahedral $P_4(NMe)_6$ core is preserved. These compounds are therefore structurally related to the known series of oxides, P_4O_7, P_4O_8, and P_4O_9.[3] The fact that the $P_4(NMe)_6$ core remains unaltered was further substantiated by the complete removal of sulphur, using triphenylphosphine, to give $P_4(NMe)_6$.

Mixtures of thiophosphorimides belonging to the above series, corresponding to various overall composition ratios, $S/P_4(NMe)_6$, were also obtained by the following methods: (i) addition of sulphur to $P_4(NMe)_6$; (ii) heating of a benzene or chloroform solution of a pure, isolated species from the series $P_4(NMe)_6S_n$, with $n = 1$—3; (iii) admixing and heating of two or more of the five species $P_4(NMe)_6S_n$ with $n = 0$—4; (iv) exchange-addition of sulphur from triphenylphosphine sulphide to $P_4(NMe)_6$ (v) exchange-abstraction of sulphur from $P_4(NMe)_6S_4$[2] by triphenyl- or tri-n-butylphosphine.

^{31}P n.m.r. was a convenient tool for determining the molecular composition of these mixtures in benzene or chloroform solutions. Upon heating, the compositions of these solutions varied until an equilibrium distribution was reached after *ca.* 8 weeks at 80° or 1 week at 145 °. The equilibrium compositions were found to depend, at a given temperature, only on the overall $S/P_4(NMe)_6$ ratio and not on any particular preparative procedure, solvent, or dilution No P–S–P or P–P links were ever observed to form at these temperatures and no species other than those belonging to the series $P_4(NMe)_6S_n$ ($n = 0$—4) were detected in the equilibrated mixtures. This further proves that the thermodynamic products of the above reactions have their structures related to those of the series of molecular oxides and not, for example, to those of the sulphides of phosphorus.[3]

This unusual redistribution equilibrium phenomena is best described in terms of the following set of three independent constants:[4]

$$K_n = [P_4(NMe)_6S_{n-1}][P_4(NMe)_6S_{n+1}]/[P_4(NMe)_6S_n]^2$$

The measured values of these constants ($K_1 = 0{\cdot}087$; $K_2 = 0{\cdot}77$; $K_3 = 0{\cdot}022$), when compared with those expected for random sorting of the sulphur atoms ($K_1 = K_3 = 0{\cdot}375$; $K_2 = 0{\cdot}445$), stress the dependence of stability upon symmetry in these cage structures.

Analogous behaviour was observed when sulphur was replaced by selenium around the phosphorimide core, whereas no definite soluble compounds could be obtained in our attempts to add oxygen atoms at the periphery of this structure.

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