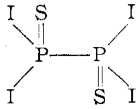
Correspondence

Some Evidence for a New Thioiodide of Phosphorus

Sir:

We wish to report the first structural information on a new[1] unstable thioiodide of phosphorus, $P_2I_4S_2$. The compound is best prepared by prolonged (65 hr.) stirring of a CS_2 solution of the elements in the ratio P:S:2I at room temperature, but it can also be prepared by shaking a CS_2 solution of P_2I_4 with the appropriate quantity of sulfur in a sealed tube until the uptake of sulfur is complete. Both reactions were done in the dark under a dry helium atmosphere, as were subsequent operations such as isolation of the compound, melting point determination, and Nujol mull preparation. Freshly prepared, the compound consists of orange crystals, m.p. 93–94° with decomposition. *Anal.* Calcd. for $P_2I_4S_2$: I, 80.11; S, 10.12. Found (Carius): I, 80.31; S, 10.01. The infrared spectra of Nujol mulls of the freshly prepared compound showed two peaks of approximately equal intensity at 300 and 329 cm.$^{-1}$. We assign the 300 and 329 cm.$^{-1}$ peaks to symmetric and antisymmetric P–I stretching on the basis that the infrared spectrum of P_2I_4, also previously unreported, shows two such peaks at 301 and 329 cm.$^{-1}$ in accord with its C_{2h} molecular symmetry in the solid state.[2] The 725 cm.$^{-1}$ absorption is assigned to P=S stretching by analogy with molecules like $Cl_3P(S)$ and $Br_3P(S)$ which have P=S vibrations[3,4] in the range 718 to 751 cm.$^{-1}$. In conjunction with the analytical data, the infrared spectral evidence indicates the presence of the $P(S)I_2$ group and valence considerations lead to the conclusion that the structure shown below is the most reasonable one.



Supporting evidence comes from the P^{31} n.m.r. spectrum of a CS_2 solution of the freshly prepared thioiodide which shows a singlet at −106 p.p.m. relative to 85% phosphoric acid. This chemical shift is close to the range of −50 to −100 p.p.m. which has been observed for thiophosphoryl compounds,[5,6] and the singlet peak demonstrates that only one type of phosphorus atom is present.

Infrared spectral examination of the thioiodide after storage in the dark in a helium-filled drybox indicated that decomposition had taken place in 2 days or less. After 25 days storage under these conditions the 300 and 329 cm.$^{-1}$ peaks were replaced by a very broad absorption covering the range 294 to 328 cm.$^{-1}$, and new peaks appeared at 228, 243, 387, 404, 413, 428, 441, 465, 481, 522, 545, 669, 678, and 690 cm.$^{-1}$. We have found that PI_3 exhibits a single broad absorption in the range 292 to 328 cm.$^{-1}$, and the remaining peaks have been identified as due to P_4S_7. The infrared spectra of the crystalline phosphorus sulfides, also previously unreported, will be the subject of a future paper. The X-ray powder pattern of the 25-day old material was identical with that of PI_3, and its ultraviolet spectrum in cyclohexane solution showed a band at 5180 Å. characteristic of molecular iodine. The most likely equation representing decomposition is therefore

$$7P_2I_4S_2 \longrightarrow 2P_4S_7 + 6PI_3 + 5I_2$$

The compound is sensitive to ultraviolet and visible light. For instance, irradiation of CS_2 solutions of the thioiodide for 1 hr. with a 20-watt fluorescent daylight lamp caused them to change in color from orange to dark brown (molecular iodine was detected in their ultraviolet spectra), and irradiation of the solid thioiodide for 0.5 hr. caused considerable intensification of the peaks due to decomposition in the infrared spectra.

The thioiodide is hydrolyzed by water with the evolution of H_2S and HI. We are currently investigating this reaction.

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[1] While this work was in progress a short note appeared by M. Baudler, G. Fricke, K. Fichtner, and G. Wetter, *Naturwissenschaften*, **50**, 548 (1963), describing the preparation of this compound, but structural data were not given.

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On the Question of the Hexachlororhenate(III) Ion

Sir:

It has been shown[1-3] that a chlororhenate(III) with empirical formula $CsReCl_4$ actually contains a polynuclear anion, $[Re_3Cl_{12}]^{3-}$, with a cluster of rhenium atoms, whereas Chatt and Rowe[4] have provided indirect but persuasive evidence for the existence

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[2] W. T. Robinson, J. E. Ferguson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

[3] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, **2**, 1166 (1963).

[4] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).