

N.M.R. Evidence for the Existence of P_4S_8

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N.m.r. evidence indicates that the primary product of the desulphuration of P_4S_9 by Ph_3P is P_4S_8 , a new species of limited stability.

P_4S_{10} has been reduced by a variety of P^{III} compounds to P_4S_9 or P_4S_7 ,¹⁻³ but no proof could be obtained of the intermediate formation of P_4S_8 ,² a hitherto unknown phosphorus sulphide. This paper reports a detailed n.m.r. study of the reduction of P_4S_9 by triphenylphosphine.

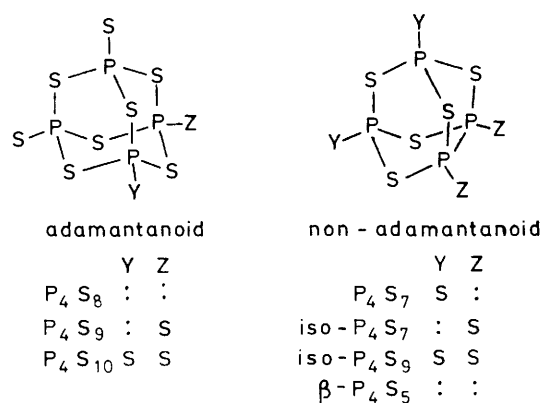
CS_2 solutions of P_4S_9 ($1-6\text{ g l}^{-1}$) were allowed to react at room temp. with Ph_3P (molar ratio, ρ , of Ph_3P/P_4S_9 is 0.4-1.45). Following a temporary initial cloudiness the solutions became clear again and were analysed by Fourier transform ^{31}P n.m.r. spectroscopy (80.76 Hz) after a short time; the following signals were observed (positive δ are downfield from

the external standard H_3PO_4): (a) a broad line, δ 41.9 p.p.m., due to Ph_3PS . Residual Ph_3P (δ -5.9 p.p.m.) is never visible, even when the reaction time is as short as 5 min; hence the desulphuration by Ph_3P is a fast process; (b) the AB_3 multiplet of P_4S_9 between δ 55.9 and 64.4 p.p.m.;⁴ (c) two non-attributed very weak singlets, δ 162 and 167.2 p.p.m. (only for $\rho > 1$), which we shall neglect; (d) two equivalent singlets (unresolved doublets), δ 84.6 and 110.9 p.p.m., belonging to P_4S_7 ,⁵ (on standing, crystals of this sulphide separate from the solution); (e) a pair of triplets, δ 13.4 and 135.4 p.p.m., J 82.8 Hz, belonging to no previously reported phosphorus sulphide

Table 1. Estimation of n from the n.m.r. balance.^a

Accumulation time/min	No. of scans	Integrated P signals (% of total P)					Estimated n value ^c
		P ₄ S ₇	P ₄ S ₉	P ₄ S _{n}	Unknown	Ph ₃ P	
20	59	5.0	54.5	29.5	Non-visible	11.0	7.80
37	110	5.2	58.9	23.5	Visible	12.4	7.54
86	258	5.5	60.2	21.7	Visible	12.6	7.45
124	372	5.2	59.9	18.8	3.6 ^b	12.5	7.28

^a Initial concentrations: [P₄S₉] 0.0147 M, [Ph₃P] 0.00754 M; pulse delay 20 s. ^b Probably not all signals are visible. ^c Given by the 'ideal' equation: $2[P_4S_7] + (9-n)[P_4S_n] = \{[P_4S_7] + [P_4S_9] + [P_4S_n]\} \times 0.00754/0.0147$.

**Figure 1.** Phosphorus sulphides considered.

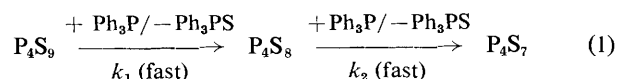
and typical of an A₂X₂ system. These lines are indicative of a P₄S _{n} molecule, bearing two pairs of equivalent P atoms. The stability of this new phosphorus sulphide is limited, even in dilute solution. Its n.m.r. signals fade slowly on standing and disappear completely within a few days at room temp. (or a few weeks at 4 °C), giving new, non identifiable n.m.r. lines. The P₄S₇/P₄S _{n} molar ratio was found to increase with the ρ ratio; this indicates that P₄S _{n} is an intermediate in the reduction of P₄S₉ to P₄S₇; hence $7 \leq n \leq 9$.

Assuming that, as in every established phosphorus sulphide, each P atom in P₄S _{n} can be only tri- or tetra-co-ordinated and is linked, either directly or through one S atom, to each of the three other P atoms, only three formulae are consistent with the n.m.r. spectrum, *viz.* the adamantanoid P₄S₈, iso-P₄S₉, and iso-P₄S₇ (see Figure 1), all of C_{2v} symmetry and structurally related either to the initial P₄S₉ or to the ultimate product P₄S₇.

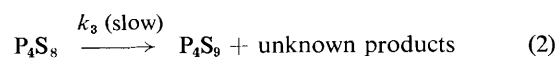
The following evidence favours P₄S₈ as the primary product: (a) its derivation from P₄S₉ is straightforward (abstraction of one terminal S atom, with preservation of the cage); further, the J values of both compounds are similar (P₄S₉ 96 Hz);^{4,5} (b) P₄S₉ is quite stable in CS₂ solutions (no n.m.r. change after 26 days at room temp.); its fast isomerization to a metastable species (*vide supra*), simply upon adding a little Ph₃P, is therefore hardly credible; (c) if iso-P₄S₇ were the intermediate, its life would have to be much shorter, for its isomerization to normal P₄S₇, which is rapid while Ph₃P is present, would have no reason to slow down after the phosphine has been used up.

However, it is not easy to define P₄S _{n} unequivocally because its poor stability precludes its isolation. Instead, we tried to derive n from the integrated n.m.r. spectra. Here again, the instability of P₄S _{n} was an obstacle (long accumulation was not possible). However, as shown in Table 1, the estimated n values clearly converge towards $n = 8$ when the accumulation time becomes shorter. This, to our mind, justifies the conclusion that formation of P₄S₈ (most probably adamantanoid) is actually the primary step in the reduction of P₄S₉.

It also appears from Table 1 that the slow secondary decomposition of P₄S₈ gives rise to more P₄S₉ but not to P₄S₇ (or only to a very little). Hence, the whole process can be described by equations (1) and (2). The second-order



adamantanoid adamantanoid non-adamantanoid
stable unstable stable



kinetic constants k_1 and k_2 were estimated to be approximately equal. By contrast, the desulphuration of P₄S₁₀ to P₄S₉ is fairly selective^{1,2} (*e.g.* treating P₄S₁₀ with 0.875 equiv. of Ph₃P in CS₂ at room temp. gave us P₄S₉ as the only product). On the other hand, since none of the reduction products of P₄S₇^{6,7,10,12,13} were detected in the present study, the reactivity order towards Ph₃P should be P₄S₁₀ > P₄S₉ ≈ P₄S₈ > P₄S₇.

The apparent cleanness of the second step of equation (1) suggests that P₄S₇ could result from direct extrusion of the bridge S atom in the P^{III}-S-P^{III} group of P₄S₈, much in the same way as organic P^{III} compounds desulphurize episulphides to alkenes⁸ or 9-thiabicyclo[3.3.1]nonane to *cis*-bicyclo[3.3.0]octane.⁹

Dilution slows down the decomposition of P₄S₈; hence, we suspect it to take place or start by bimolecular sulphur atom transfer between two P₄S₈ molecules (est. k_3 ca. 1.4 l mol⁻¹ min⁻¹ at room temp.).

P₄S₉ is known to dissociate upon melting (at 255–260 °C);^{2,11} we found that only P₄S₇ and P₄S₁₀ are produced, although P₄S₈ is a probable intermediate, even when the melting time is very short (*ca.* 5 s just above the m.p.).

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