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

Jean-Jacques Barieux[a] **and Michel C. Démarcq**[b]

[a] *P.C. Ugine Kuhlmann, Centre de Recherche de Lyon, 69310 Pierre-Bénite, France*
[b] *Institut National des Sciences Appliquées, 20, Avenue Albert Einstein, 69621 Villeurbanne, France*

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 ($1—6$ 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_4S_7	P_4S_9	P_4S_n	Unknown	Ph_3P	
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: $[P_4S_9]$ 0.0147 M, $[Ph_3P]$ 0.00754 M; pulse delay 20 s. [b] Probably not all signals are visible. [c] Given by the 'ideal' equation: $2[P_4S_7] + (9 - n)[P_4S_n] = \{[P_4S_7] + [P_4S_9] + [P_4S_n]\} \times 0.00754/0.0147$.

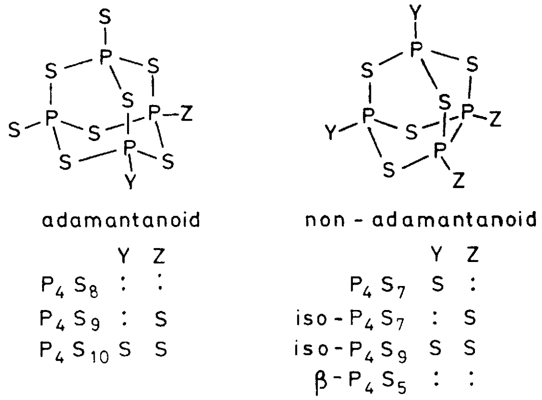

Figure 1. Phosphorus sulphides considered.

and typical of an A_2X_2 system. These lines are indicative of a P_4S_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 P_4S_7/P_4S_n molar ratio was found to increase with the ρ ratio; this indicates that P_4S_n is an intermediate in the reduction of P_4S_9 to P_4S_7; hence $7 \leqslant n \leqslant 9$.

Assuming that, as in every established phosphorus sulphide, each P atom in P_4S_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 P_4S_8, iso-P_4S_9, and iso-P_4S_7 (see Figure 1), all of C_{2v} symmetry and structurally related either to the initial P_4S_9 or to the ultimate product P_4S_7.

The following evidence favours P_4S_8 as the primary product: (a) its derivation from P_4S_9 is straightforward (abstraction of one terminal S atom, with preservation of the cage); further, the *J* values of both compounds are similar (P_4S_9 96 Hz);[4,5] (b) P_4S_9 is quite stable in CS_2 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 Ph_3P, is therefore hardly credible; (c) if iso-P_4S_7 were the intermediate, its life would have to be much shorter, for its isomerization to normal P_4S_7, which is rapid while Ph_3P is present, would have no reason to slow down after the phosphine has been used up.

However, it is not easy to define P_4S_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 P_4S_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 P_4S_8 (most probably adamantanoid) is actually the primary step in the reduction of P_4S_9.

It also appears from Table 1 that the slow secondary decomposition of P_4S_8 gives rise to more P_4S_9 but not to P_4S_7 (or only to a very little). Hence, the whole process can be described by equations (1) and (2). The second-order

$$P_4S_9 \xrightarrow[k_1\ \text{(fast)}]{+\,Ph_3P/-Ph_3PS} P_4S_8 \xrightarrow[k_2\ \text{(fast)}]{+\,Ph_3P/-Ph_3PS} P_4S_7 \qquad (1)$$

adamantanoid stable | adamantanoid unstable | non-adamantanoid stable

$$P_4S_8 \xrightarrow{k_3\ \text{(slow)}} P_4S_9 + \text{unknown products} \qquad (2)$$

kinetic constants k_1 and k_2 were estimated to be approximately equal. By contrast, the desulphuration of P_4S_{10} to P_4S_9 is fairly selective[1,2] (*e.g.* treating P_4S_{10} with 0.875 equiv. of Ph_3P in CS_2 at room temp. gave us P_4S_9 as the only product). On the other hand, since none of the reduction products of P_4S_7[6,7,10,12,13] were detected in the present study, the reactivity order towards Ph_3P should be $P_4S_{10} > P_4S_9 \approx P_4S_8 > P_4S_7$.

The apparent cleanness of the second step of equation (1) suggests that P_4S_7 could result from direct extrusion of the bridge S atom in the P^{III}–S–P^{III} group of P_4S_8, much in the same way as organic P^{III} compounds desulphurize episulphides to alkenes[8] or 9-thiabicyclo[3.3.1]nonane to *cis*-bicyclo[3.3.0]-octane.[9]

Dilution slows down the decomposition of P_4S_8; hence, we suspect it to take place or start by bimolecular sulphur atom transfer between two P_4S_8 molecules (est. k_3 *ca.* 1.4 l mol^{-1} min^{-1} at room temp.).

P_4S_9 is known to dissociate upon melting (at 255—260 °C);[2,11] we found that only P_4S_7 and P_4S_{10} are produced, although P_4S_8 is a probable intermediate, even when the melting time is very short (*ca.* 5 s just above the m.p.).

Received, 20th July 1981; Com. 857

References

1 M. Meisel and H. Grunze, *Z. Anorg. Allg. Chem.*, 1969, **366**, 152.
2 M. Meisel and H. Grunze, *Z. Anorg. Allg. Chem.*, 1970, **373**, 265.
3 W. Zongming, W. Xieqing, and I. Wanzhen, Proc. VIIth Intern. Conf. on Raman Spectroscopy, Ottawa, 1980, p. 132.
4 E. R. Andrew, W. Vennart, G. Bonnard, R. M. Croiset, M. Démarcq, and E. Mathieu, *Chem. Phys. Lett.*, 1976, **43**, 317.
5 C. Brevard and M. C. Démarcq, *Chem. Phys. Lett.*, 1981, **82**, 167.
6 A. M. Griffin and G. M. Sheldrick, *Acta Crystallogr., Sect. B*, 1975, **31**, 2738.
7 G. M. Sheldrick, personal communication.
8 N. P. Neureiter and F. G. Bordwell, *J. Am. Chem. Soc.*, 1959, **81**, 578; D. B. Denney and M. J. Boskin, *ibid.*, 1960, **82**, 4736.
9 E. J. Corey and E. Block, *J. Org. Chem.* 1969, **34**, 1233.
10 J.-J. Barieux and M. C. Démarcq, unpublished results.
11 H. Vincent, *Bull. Soc. Chim. Fr.*, 1972, 4517; H. Vincent and C. Vincent-Forat, *ibid.*, 1973, 499.
12 R. Blachnik and A. Hoppe, *Z. Anorg. Allg. Chem.*, 1979, **457**, 91.
13 W. Bues, M. Somer, and W. Brockner, *Z. Anorg. Allg. Chem.*, 1981, **476**, 153.