Chemical Communications

NUMBER 7/1968 10 APRIL

Electron Paramagnetic Resonance Studies of Phosphorus-containing Reactive Intermediates

By GERALD F. KOKOSZKA* and F. E. BRINCKMAN

(*National Bureau of Standards, Washington, D.C.* 20234)

IN spite of the postulated importance of a variety phosphorus–halogen-containing radicals as reactive intermediates in many important chemical processes[1,2] direct evidence[3] for even simple species is lacking. Only fluoride radicals have been detected by electron paramagnetic resonance (e.p.r.) and these only in isolation matrices or ionic crystals following subjection to high-energy irradiation.[4–7]

We report† three new phosphorus–chloride radical intermediates (Table) which are observed under milder conditions. Both PCl_2 and PCl_4 were produced from neat PCl_3 with light from a 200 w high-pressure mercury lamp at 77° K ($\lambda_{max} \sim 3600$ Å). A third radical, identified as a methylphosphorus chloride, was produced from $MePCl_2$ under the same conditions.

TABLE

PCl_n *radicals, present work*[a]

Radical	Matrix	g	A_P	A_e
PCl_2	PCl_3	2·018	33	b
PCl_2	PCl_3/PF_3	2·001[c]	269[c]	15[c]
		2·021[d]	28[d]	~0[d]
PCl_4	PCl_3	2·013	1206	62,7
Me_2PCl_2	$MePCl_2$	2·000	1077	b

[a] Values are believed to be accurate to within: $g \pm 0{\cdot}005$; $A_P \pm 5$ gauss; $A_{Cl} \pm 2$ gauss; [b] Unresolved component; [c] Parallel component; [d] Perpendicular component.

Samples of PCl_3 and $MePCl_2$, after purification by standard high-vacuum line techniques, were sealed *in vacuo* in fused quartz tubes. E.p.r. spectra were obtained using an X-band spectrometer (Varian Model 4500) equipped with a cavity containing irradiation slots. A reasonably symmetrical doublet developed in neat PCl_3 immediately on irradiation. Spectra taken as a function of time with continuous irradiation indicated the build-up of spectral intensity followed the law $I_0[1 - \exp(-t/\tau)]$, where I_0 is the final intensity, and τ is an experimental constant. In our case, $\tau \approx 60$ min.

When a mixture of PCl_3 and PF_3 (~10 : 1) was irradiated under comparable conditions, the anisotropic spectrum associated with PCl_2 displayed a seven-line chloride hyperfine structure in the parallel portion (Table). In PCl_3 alone two additional signals were observed on either side of this doublet. These consisted of seven components with relative intensities nearly equal to 1 : 2 : 3 : 4 : 3 : 2 : 1, and additional structure, which, neglecting second order effects,[8] consisted of another set of seven lines. These spectral components are assigned to the PCl_4 radical and our results are also summarized in the Table.

The chlorine hyperfine splitting requires only C_{2v} symmetry. Comparison[9] of A_P with $A_{0(P)}$ implies 33% 3s character in the orbital containing the unpaired electron. This value is approximately consistent with a trigonal bipyramid[6] with

---

† A preliminary account of portions of this work was presented at the 154th National Meeting of the American Chemical Society, Chicago, Illinois, September, 1967.

the unpaired electron in one of the equatorial sp^2 orbitals.

In an undiluted sample, the ratio of the intensities of the PCl_4 to PCl_2 spectra is about 0·15. This suggests that *ca.* 25% of the Cl atoms initially formed from PCl_3 are captured in a secondary process by a neutral PCl_3 to form PCl_4. Visible coloration in irradiated samples suggests formation of free halogen. However, irradiation of PCl_3 diluted in a Xe matrix (PCl_3 : Xe = 1 : 9) again produced a large PCl_2 signal but no evidence for PCl_4. The introduction of diluent atoms thus appears to favour a chlorine combination process at the expense of PCl_4 formation.

From $MePCl_2$, a widely-spaced doublet reminiscent of PCl_4 also appears. Here the phosphorus hyperfine splitting is 10% smaller than that in PCl_4 and the peak-to-peak line width of the individual structureless components is about 100 G. This suggests that at least one of the atoms which gives rise to the larger A_{Cl} in PCl_4 has been replaced by a more electropositive methyl group.[10] Of the possible intermediates Me_2PCl_2 and $MePCl_3$, the latter species, which has been postulated in the direct alkylation of PCl_3,[1] is thought to be less likely on the basis of line-width considerations.

(*Received, January* 26*th*, 1968; *Com.* 100.)

[1] J. I. G. Cadogan, *Adv. Free Radical Chem.*, 1967, **2**, 203.
[2] M. Halman, "Topics in Phosphorus Chemistry", eds., M. Grayson and E. Griffith, Interscience, New York, 1967, vol. 4, p. 49.
[3] N. Basco and K. K. Yee, *Chem. Comm.*, 1967, **1146**.
[4] J. R. Morton, *Canad. J. Phys.*, 1963, **41**, 706.
[5] J. K. S. Kan, J. R. Morton, and H. J. Bernstein, *Canad. J. Chem.*, 1966, **44**, 1957.
[6] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1966, **45**, 1845.
[7] P. W. Atkins and M. C. R. Symons, *J. Chem. Soc.*, 1964, 4363.
[8] R. W. Fessenden, *J. Chem. Phys.*, 1962, **37**, 747.
[9] J. R. Morton, *Chem. Rev.*, 1964, **64**, 453.
[10] P. C. Van der Voorn and R. S. Drago, *J. Amer. Chem. Soc.*, 1966, **88**, 3255.