Electrochemical Generation of the Radical Cations $[X_3PPX_3]^{\dot{+}}$

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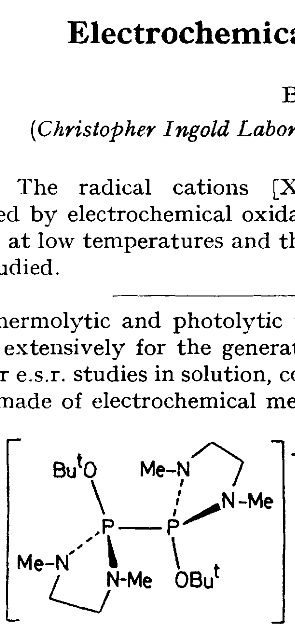
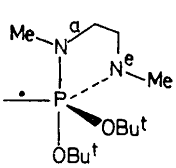
Summary The radical cations $[X_3PPX_3]^{\dot{+}}$ have been generated by electrochemical oxidation of phosphines in solution at low temperatures and their e.s.r. spectra have been studied.

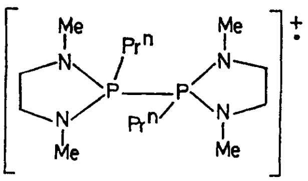
WHILST thermolytic and photolytic techniques have been employed extensively for the generation of transient free-radicals for e.s.r. studies in solution, comparatively little use has been made of electrochemical methods.



(II)



(III)



(IV)

Anisotropic e.s.r. spectra of the radical cations $[X_3P\text{-}PX_3]^{\dot{+}}$ have been detected in the solid state after γ-irradiation of the phosphines, PX_3,[1] but the central features are usually obscured by signals from other paramagnetic species also present. We have obtained clean e.s.r. spectra of such radical cations by *in situ* electrochemical oxidation of phosphines, at low temperatures in aliphatic nitrile solvents, within the cavity of the spectrometer.

$$X_3P \xrightarrow[\text{electrochemical oxidation}]{-e} X_3P^{\dot{+}} \tag{1}$$

$$X_3P^{\dot{+}} + :PX_3 \longrightarrow \underset{\text{(I)}}{[X_3P\text{-}PX_3]^{\dot{+}}} \tag{2}$$

The spectroscopic parameters for (I) are given in the Table, and the spectrum of the species (II), derived by oxidation of 1,3-dimethyl-2-t-butoxy-1,3,2-diazaphospholan, is shown in the Figure.

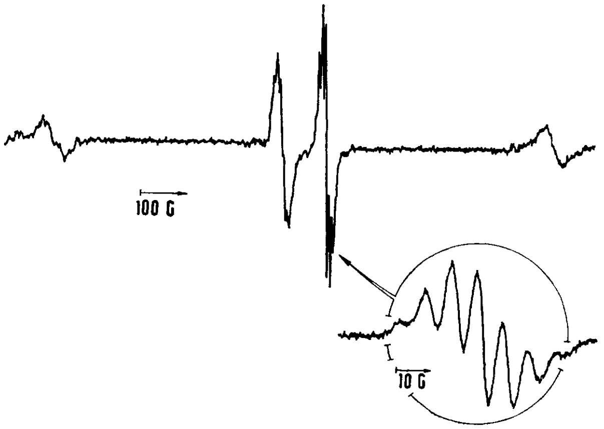


FIGURE. E.s.r. spectrum of (II) at 183 K in Pr^nCN-EtCN (70 : 30 by volume) using $Bu^n{}_4N^+BF_4{}^-$ as carrier electrolyte.

Lyons and Symons[1b] have proposed that the unpaired electron in (I) is contained in a symmetrical σ^*-molecular orbital derived predominantly from phosphorus 3*s* and 3*p*

TABLE

E.s.r. parameters for $[X_3P{-}PX_3]^{+\cdot}$ derived by electrochemical oxidation of the phosphines PX_3

Phosphine[a]	T/K	Hyperfine coupling constants[b]/G $a(P)$[c]	 $a(N)$
$MeNCH_2CH_2N(Me)PPr^n$	200	335	*ca.* 6[d] (4N)
$MeNCH_2CH_2N(Me)PPh$	203	344	7·5 (4N)
$MeNCH_2CH_2N(Me)PBu^t$	190	380	[d]
Et_2POEt	210	482	—
$[OCH_2CH_2OPN(Me)CH_2]_2$[e]	193	536	7·5 (2N)
$OCMe_2CMe_2OPNMe_2$	183	540	Unresolved
$PhP(OEt)_2$	183	540[f]	—
$MeNCH_2CH_2N(Me)POBu^t$	173	544[g]	7·4 (4N)
$PhP(OCH_2CF_3)_2$	163	566	—

[a] Phosphine (*ca.* 0·3 mol l^{-1}) and $Bu_4{}^nN^+BF_4{}^-$ (*ca.* 0·1 mol l^{-1}) in Pr^nCN–EtCN mixture (70:30 by volume); [b] Obtained using the Breit-Rabi equation: all *g*-factors were 2·0020 ± 0·0005; [c] Two equivalent phosphorus nuclei; [d] Nitrogen splitting present, but lines too broad for accurate measurements; [e] It is likely that the P–P bond in the radical cation is formed intramolecularly; [f] Similar line-widths obtained from $C_6D_5P(OEt)_2$; [g] The ethoxy analogue showed a similar spectrum: *a*(P) 535 G, *a*(N) 7·5 G (4N).

atomic orbitals. The phosphorus atoms are equivalent with a pseudo-tetrahedral disposition of bonds, and the $\angle XPX$ in (I) intermediate between those in X_3P: and $X_3P^{+\cdot}$.[1] The apparent identity of the splittings from the four nitrogen nuclei in (II),† even at low temperatures, strongly supports this proposed structure, and contrasts markedly with the very different nitrogen splittings from apical and equatorial ligands in the related phosphoranyl radical (III) [*a*(P) 752 G, *a*(N^a) 19·0 G, *a*(N^e) not resolved].[2]

Using nitrile solvents, the temperature could be lowered sufficiently to allow anisotropic spectra to be detected in a viscous solution or glassy matrix. For example at 117 K the radical cation (IV) gave an anisotropic spectrum from which $A_{\parallel}$ 386 G and $A_{\perp}$ 291 G could be extracted, reflecting orbital populations[1a,b] of 9% and 31% for the 3*s* and 3*p* orbitals, respectively, of each phosphorus atom.

Extension of the use of electrochemical redox reactions for the generation of unstable paramagnetic organometallic species clearly has great potential, and is being explored.

(*Received, 22nd September* 1975; *Com.* 1083.)

† Alternatively, the most stable conformation of (II) may be one with two pairs of equivalent nitrogens. Rotation about the P–P bond may then be rapid on the e.s.r. time scale or the splittings from the two types of ligand may be indistinguishable.

[1] (a) M. C. R. Symons, *Mol. Phys.*, 1972, **24**, 885; (b) A. R. Lyons and M. C. R. Symons, *J.C.S. Faraday II*, 1972, **68**, 1589; (c) B. W. Fullam and M. C. R. Symons, *J.C.S. Dalton*, 1975, 861.

[2] R. W. Dennis and B. P. Roberts, *J.C.S. Perkin II*, 1975, 140.