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### On the mechanism of the addition of alkoxy radicals to aryl phosphorus compounds

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Considerable interest has recently been shown in the reactions of arylphosphorous compounds towards alkoxy-radicals [1, 2] and electrons [3, 4]. There is no mechanistic problem for electron addition :

$$ArPL_3 + e^- \rightarrow ArPL_3^{-}, \tag{1}$$

in that the decision to add to the aryl group to give a substituted aromatic anion, or to the phosphorous atom to give a phosphoranyl radical is taken at once, and one or other species if formed directly [4]. We have shown previously [5] that phosphoranyl radical formation is only favoured in the presence of electronegative ligands such as chloride.

Generally, reactions of PL<sub>3</sub> molecules with alkoxy radicals proceed via the phosphoranyl radical :

However, when aromatic ligands are present, the paramagnetic product is a substituted aromatic anion rather than  $(\alpha)$  (equation (3 a)) unless strongly electronegative ligands are present (equation (3 b)). It is possible that this reaction proceeds in two stages *via* a stable phosphoranyl radical  $(\alpha)$  as in (3 a), but a reasonable alternative would be electron transfer during the initial stages of addition, prior to the deformation required for phosphoranyl radical formation (3 b):

$$RO^{\bullet} + *P \stackrel{Ar}{\underset{L}{\longrightarrow}} + \begin{bmatrix} RO^{\bullet} \cdots \stackrel{Ar}{\underset{L}{\longrightarrow}} \end{bmatrix} + \stackrel{a}{\underset{L}{\longrightarrow}} \stackrel{OR}{\underset{P}{\longrightarrow}} \stackrel{L}{\underset{L}{\longrightarrow}} \stackrel{QR}{\underset{L}{\longrightarrow}} \stackrel{L}{\underset{L}{\longrightarrow}} \stackrel{L}{\underset{Ar}{\longrightarrow}} \stackrel{L}{\underset{Rr}{\longrightarrow}} \stackrel{(a)}{\underset{Rr}{\longrightarrow}} (3)$$

The intermediate  $(\alpha)$  has never been detected, so it seemed to be of interest to attempt to demonstrate its formation.

Phenyl dimethylphosphinite {PhP(OMe)<sub>2</sub>} is known to give only the substituted benzene anion with alkoxy radicals [1, 2], so it was selected as a suitable substrate. When solutions in methanol (or CD<sub>3</sub>OD) were exposed to <sup>60</sup>Co  $\gamma$ -rays at 77 K, the only major paramagnetic products detected by e.s.r. spectroscopy were H<sub>2</sub>COH (D<sub>2</sub>COD) and PhP(OMe)<sub>2</sub>+ (see the table). Extra central (g=2) features suggested the formation of the parent anion, with the unpaired electron confined to the benzene ring, and this was supported by the absence of the intense violet colour characteristic of  $e_t^-$  normally obtained from irradiated methanol. On annealing, these anions became protonated giving rise to the characteristic e.s.r. features for cyclohexadienyl radicals. Also, somewhat surprisingly, parallel features characteristic of phosphinyl radicals were detected. These had A  $\parallel$ (<sup>31</sup>P) = 246 G in rigid methanol. This is far smaller than that for P(OMe)<sub>2</sub> in this solvent [6] and, hence, the species must be PhP(OMe) formed by :

$$PhP(OMe)_2 + e^- \rightarrow Ph\dot{P}(OMe) + MeO^-.$$
 (4)

Radical/(solvent)	<sup>31</sup> P Hyperfine coupling constants <sup>+</sup>		
	ľ	Ţ	iso
[PhP(OMe),],+	525	450	475
$PhP(OMe)_{2}^{+/}(CD_{3}OD)$	740	580	633
PhP(OMe),+/(Me,CHOH)	740	580	633
PhP(OMe) <sub>2</sub> (OCHMe <sub>2</sub> )/(Me <sub>2</sub> CHOH)	960	765	830

 $+ G = 10^{-4} T$ ; corrected using the Breit-Rabi equation; **g**-values were close to 2.00. E.s.r. parameters for radicals formed from PhP(OMe)<sub>2</sub>.

We had hoped that MeO radicals, known to be formed in irradiated methanol [7], but not normally detected by e.s.r. spectroscopy, would add to phosphorous to give the phosphoranyl intermediate ( $\alpha$ ). No such species was detected.

If it does add, we must conclude either that  $\boldsymbol{\alpha}$  is unstable, even at 77 K, or that (3 **b**) is the preferred pathway. We have reason to believe, however, that the reaction

$$MeO + CH_3OH \rightarrow CH_3OH + H_2OH$$
(5)

may occur even at 77 K, which would greatly reduce the possibility of detecting reaction (3 a). Also, our unpublished results suggest that isopropanol gives  $Me_2CHO$  radicals on irradiation at 77 K which are trapped at this temperature and do not react efficiently to give  $Me_2COH$  radicals [8]. When this solvent was used, the same features for the cation were initially detected (figure (1 a)) but, on annealing, these were lost (as in the case of methanolic glasses) and new features, shown in the figure (b), developed. The isotropic coupling of c. 830 G is very close to that expected for a phosphoranyl radical with three alkoxy substituents and one phenyl group [9], and the anisotropic coupling is typical for such species. Hence, we suggest that as the glass softens,  $Me_2CHO$ radicals become mobile and addition to phosphorus competes efficiently with hydrogen atom abstraction from solvent molecules. On further annealing



First derivative X-band e.s.r. spectra for a solution of PhP(OMe)<sub>2</sub> in Me<sub>2</sub>CHOH after exposure to <sup>60</sup>Co  $\gamma$ -rays at 77 K : (a) before annealing, showing parallel and perpendicular features assigned to PhP(OMe)<sub>2</sub><sup>+</sup> cations ( $\beta$ ) and parallel features assigned to PhPOMe radicals ( $\gamma$ ); (b) after annealing, showing features assigned to PhP(OMe)<sub>2</sub>OCHMe<sub>2</sub> radicals ( $\alpha$ ).

these features were also lost. Intense central features for Me<sub>2</sub>COH radicals unfortunately precluded the clear detection of the expected benzene anions, but weak outer features characteristic of cyclohexadienyl radicals suggested their presence. This does not establish the second half of reaction (2) since we suspect that some  $\overline{Ph}$ —P(OMe)<sub>2</sub> anions are also present as in the methanolic solutions. However, since the overall process is clearly established [1, 2], and we have now detected the phosphoranyl intermediate, we feel that mechanism (3 a) is confirmed.

Other experiments failed to shed further light on these reactions. Irradiation of the pure substrate gave ' dimers ' formed from the parent cations [10] :

$$Ph Ph Ph \\ \searrow + \swarrow$$

$$PhP(OMe)_{2} + PhP(OMe)_{2} \rightarrow MeO - P - P - OMe, \qquad (6)$$

$$OMe OMe$$

together with central features thought to be the substituted benzene anions. Photolysis of rigid solutions of di-*t*-butylperoxide in methanol containing PhP(OMe)<sub>2</sub> gave only Me<sub>3</sub>C and methyl radicals as clear paramagnetic products. This confirms our previous findings that such photolyses, ideal in the liquid phase for generating RO radicals, are unsatisfactory in glasses.

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