

ELECTRON SPIN RESONANCE SPECTRA FOR VARIOUS CYCLOHEXADIENYL RADICALS CONTAINING PHOSPHORUS: EVIDENCE FOR STRONG HYPERCONJUGATION INVOLVING C-P σ -BONDS

S.P. Mishra and M.C.R. Symons*

Department of Chemistry, The University, Leicester LE1 7RH.

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In their studies of electrophilic aromatic substitutions, Eaborn and his coworkers¹ explained various kinetic and other observations in terms of a marked stabilisation of the intermediate cation(I) by hyperconjugative electron release from group X, when this contained various heavy atoms directly bonded to the ring. We² have invoked a similar theory to explain the large, nearly isotropic heavy atom hyperfine interactions in radicals of type II, which have been shown to favour the depicted conformation (II).³

Although e.s.r. spectra for radicals of type IV are known, we know of no report relating to radicals of type III, when X contains a heavy atom. In our attempts to prepare such radicals, we have had some success in the case where X is a $-PR_3$ group. Thus, phenylphosphinic acid, $PhPO(OH)_2$, on exposure to ^{60}Co γ -rays at 77 K had an e.s.r. spectrum which showed clear features for the radical $Ph\dot{P}O(OH)$, previously reported by Geoffrey and Lucken,⁴ and a species (a) having $a(^1H_1) \div 40$ G (single proton), $a(^1H_2) \div 10$ G (3 protons) and $A(^{31}P) = 200$ G, all coupling constants being fairly isotropic. In addition, there was a set of lines in the central region comprising a major triplet assignable to radicals having structures IV or V. When $PhPO(OD)_2$ was used, identical results were obtained except that the hydroxyl proton coupling (16 G) manifest in the spectrum of $Ph\dot{P}O(OH)$ was lost.

However, when $PhPO(OD)_2$ was irradiated at 77 K, the quartet assigned to species a was reduced to a broad doublet, thus confirming that the 40 G splitting stems from a 1H coupling. The central set of lines became a major doublet rather than a triplet, thus showing that the proton responsible for ring addition is the one bonded to phosphorus rather than oxygen.

On annealing, the features for species α were lost rapidly. On standing at room temperature, features assigned to the >CHD group of species IV/V, obtained from PhPO(OD)D slowly gave way to those characteristic of a >CH_2 group, and when the di-deuterated material was irradiated at room temperature, only the >CH_2 derivative was formed.

Exposure of PhPO(OH)_2 or $\text{Ph}_2\text{P(OH)}$ to γ -rays at 77 K yielded no features assignable to species of type III, IV or V. PhPO(OH)_2 gave $\text{Ph}\dot{\text{P}}\text{O}_2^-$ and not the expected $\text{Ph}\dot{\text{P}}\text{O(OH)}$ radical. On annealing, species IV/V were formed, and again H-D scrambling was observed with the -OD derivatives.

These observations lead to the following conclusions:

Radical α is the adduct III, with $\text{X} = -\text{PO(OH)H}$ or $-\text{PO(OH)}$ and there is indeed a large hyperconjugative effect involving the phosphorus atom. By comparing the ^3P hyperfine coupling data with those obtained for radicals of type II,² and with the proton coupling for type IV/V adducts, it seems that the ^3P hyperconjugative interaction is comparable in both systems (II and III) and the hyperfine coupling enhancement, interpreted by Whiffen⁵ for the methylene protons, also occurs for phosphorus.

However, adduct (III) seems to be less stable than IV/V, despite this large hyperfine interaction. The efficient H/D exchange observed for IV/V is probably intermolecular, since the deuterium interaction is lost completely. The fact that the hydrogen bonded to phosphorus rather than oxygen is involved is surprising, since the latter is the more acidic. We suggest that this implies an intramolecular proton shift from the phosphorus to the ortho position of the aromatic ring of the parent anion. The fact that the reaction does not occur at 77 K in the absence of a P-H bond supports this scheme.

Exposure of the molecule $\text{Ph}_3\text{P}^+\text{CMe}^-\text{(CO}_2\text{H)}$ to γ -rays at room temperature also gave e.s.r. features clearly indicative of cyclohexadienyl radicals (Fig.). In this case the predominant adduct had structure III, with $A_{\text{ISO}}(^3\text{P}) = 133$ G, $A_{\text{ISO}}(^1\text{H}) = 32$ G and $A_{\text{ISO}}(3 \text{ ring protons}) = 11$ G (average). No clear evidence for other adducts was obtained. The smaller ^3P coupling in this case may support the suggestion that the radical X has a $-\text{PO(OH)}$

rather than a $-\text{PO}(\text{OH})\text{H}$ substituent on the ring, since we have previously found that the hyperfine interaction for groups having lone-pair electrons is greater than those which are fully coordinated.²

References

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Caption to Figure

First derivative X-band e.s.r. spectrum for $\text{Pn}_3\text{P-CMe}(\text{CO}_2\text{H})$ for exposure to ^{60}Co γ -rays showing features assigned to the $-1/2$ (^{31}P) hyperfine component for the corresponding cyclonexadienyl radical (Type III).



