SHORT PAPER

J. Chem. Research (S),
2000, 342–343

Electron paramagnetic evidence for the $\cdot PF_3$ radical Anion

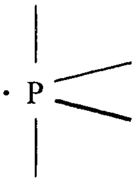
Martyn C.R. Symons

Department of Chemistry, De Montfort University, The Gateway, Leicester LE1 9BH, UK

Although $\bullet PF_2$ radicals have been extensively studied there does not seem to be any spectroscopic evidence for $\bullet PF_3$- radical anions. Here it is proposed that an EPR spectrum previously assigned to $\bullet PF_2$ radicals is almost certainly due to $\bullet PF_3$-centres. The ^{31}P and ^{19}F hyperfine coupling constants for these radicals are expected to be very similar. However, the $\bullet PF_3$-radicals should show an extra coupling to the third ^{19}F nucleus. This is clearly present.

A large number of inorganic radicals and radical anions have now been studied by EPR spectroscopy. This is a powerful tool not only for purposes of identifcation, but also for providing very accurate details of their structures.[1]

However, some years ago, a problem arose over the nature of a radical having a very large hyperfine coupling to ^{31}P and to four equivalent ^{19}F nuclei. This was identified as the radical $\bullet PF_4$.[2] The problem was that normal phosphoranyl radicals have distorted structures, with two strongly coupled axial ligands and two weakly coupled equatorial ligands (**1**). Thus, rapid bond angle inter changes would be required to make the four flourines equivalent. Later a small extra doublet splitting was detected, and the radical was re-identified as $\bullet PF_5$-, with a square-planar structure, with one axial ligand (**2**).[3]



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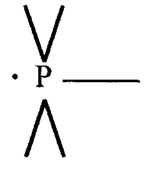

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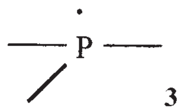
Recently, a problem arose regarding the possible structures of the $\bullet P(OCH_3)_3$-radical anion.[4] One of the radicals detected by EPR spectroscopy had parameters characteristic of a phosphoranyl radical. The other had a small, largely anistropic ^{31}P hyperfine coupling characteristic of a π-radical, so it was identified as $\bullet P(OCH_3)_2$.[4] However, a very similar π-radical was also detected.

Using $P(OCH_3)_3$ in methanol (CD_3OD) glasses at 77 K only electron-adducts were expected. However, the primary phosphoranyl radicals were not detected, and only a single π-type radical appeared in the spectra. A more extensive study, coupled with another report of irridated pure trimethyl phosphite[5] led to the suggestion that one of the species identified as $\bullet P(OCH_3)_2$ radicals was really $\bullet P(OCH_3)_3$ having a planar T-structure, with the unpaired electron in a π orbital normal to the plane (see **3**).[6]



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Discussion

With this background, a re-examination of results for radical species formed from PF_3 seemed to be worthwhile. Some data are given in Table 1. Although there is considerable variation in the EPR parameters, identification as $\bullet PF_2$ radicals is reasonable in all cases. In particular, species studied by Wei *et al.*,[7] formed thermally from P_2F_4 and matrix isolated in argon, or by photolysis of HPF_2 in solid argon must surely be correctly identified.

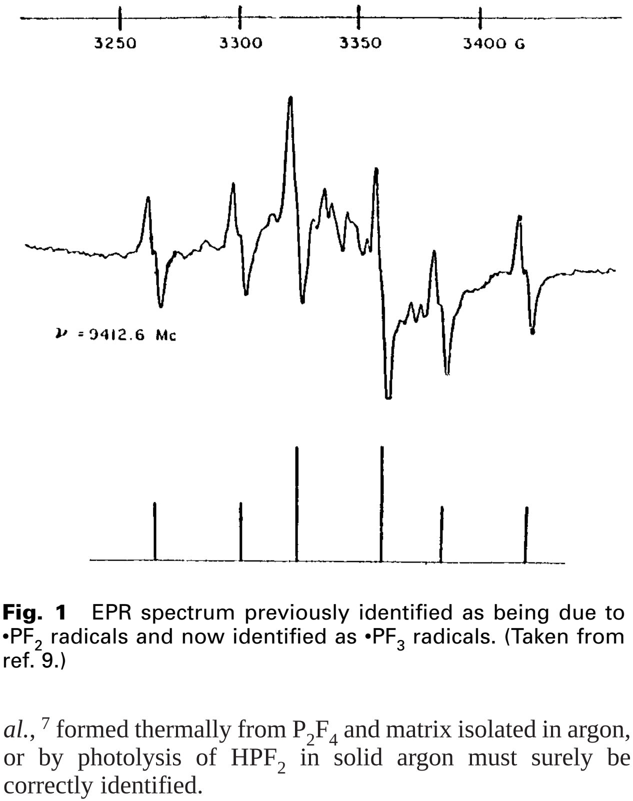

Fig. 1 EPR spectrum previously identified as being due to $\bullet PF_2$ radicals and now identified as $\bullet PF_3$ radicals. (Taken from ref. 9.)

In work by Gordy and his co-workers[8] concern was expressed over the differences in the ^{31}P and ^{19}F hyperfine parameters, although they were satisfied that the π-centre of interest must be $\bullet PF_2$. (I stress that several other, quite distinct, centres were formed in some of these studies. However, these are not my concern herein.) The first EPR study of the π-radical species was that of Wan *et al.*,[9] who irradiated ND_4+PF_6- and obtained an isotropic, very narrow set of six lines which were assigned to $\bullet PF_2$ (Table 1 and Fig. 1).

There is a small extra splitting of ~4 G on these features which has not been discussed previously, as far as I know.

Table 1 EPR hyperfine parameters for various $\bullet PL_2$ and $\bullet PL_3$-radicals

Radical	Nucleus	Isotropic hyperfine coupling (G)[a]	Refs
$\bullet P(OCH_3)_2$	^{31}P	96	5
$\bullet P(OCH_3)_3^-$	^{31}P	8	6[b]
•PF2	^{31}P	36	7
	^{19}F	60.5	
$\bullet PF_3^-$	^{31}P	47	9, b
	^{19}F	65	

[a] 1 G = 10^{-4}T
[b] This work.

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[*] To receive any correspondence. E-mail: sk_gndu@yahoo.com
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

I suggest that, as with $\bullet PF_5^-$,[3] these extra doublet splittings stem from an extra weakly coupled ^{19}F nucleus. Hence the species is probably $\bullet PF_3^-$ with the planar T-structure proposed for the second form of $\bullet P(OMe)_3^-$, which is isostructural with $\bullet PF_3$-.

So far as I know, $\bullet PF_3$- radical-anions have not been previously identified.

Received 23 April 2000; accepted 22 May 200
Paper 00/277

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