Stereochemical Non-rigidity of Fluorophosphoranyl Radicals

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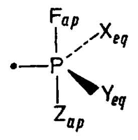
Summary The e.s.r. spectra of some fluorophosphoranyl radicals in solution show that these species are stereochemically non-rigid, undergoing exchange of apical and equatorial fluorine ligands.

THE isotropic e.s.r. spectrum of the tetrafluorophosphoranyl radical,[1] generated by electron irradiation of PF_3 in SF_6, exhibits hyperfine splittings from phosphorus and from two pairs of equivalent fluorine nuclei at 135 K, consistent with the trigonal bipyramidal structure (**1**; $X=Y=Z=F$).[2]

γ-Irradiation of solid NH_4PF_6 gave rise to an e.s.r. spectrum assigned to $\cdot PF_4$ which exhibited hyperfine splitting from four apparently equivalent fluorine nuclei at 295 K.[3,4a] It was concluded[4] that $\cdot PF_4$ was stereochemically non-rigid and that exchange of apical and equatorial fluorine ligands was rapid on the e.s.r. time scale at 295 K. However, it has recently been shown[5] that the radical produced by γ-irradiation was probably $\cdot\overline{P}F_5$ rather than $\cdot PF_4$, and the question of possible ligand exchange in fluorophosphoranyl radicals remains unanswered.



(1)

We have studied the e.s.r. spectra of a series of fluorophosphoranyl radicals in solution (see Table) and detected

TABLE. E.s.r. parameters for fluorophosphoranyl radicals in solution

Radical[a]	Temp./K	Hyperfine splittings/G				Fluorine exchange	
		a(P)	$a(\mathrm{F}_{ap})$	$a(\mathrm{F}_{eq})$	Others	k_{exch}/s^{-1}[c]	Temp./K
$\mathrm{EtO\dot{P}F_3}$[b]	212	1267	285 (2F)	63·0 (1F)	—	1 × 10^7[d]	265
$\mathrm{Bu^tO\dot{P}F_3}$[b]	148	1257	288 (2F)	58·2 (1F)	—	5 × 10^6[e]	203
$\mathrm{CF_3O\dot{P}F_3}$	200	1244	278 (1F)	45·0 (2F)	7·0 (3F)	1 × 10^7	228
$\mathrm{(EtO)_2\dot{P}F_2}$	240	1201	280 (2F)	—	—	—	—
$\mathrm{(EtO)_3\dot{P}F}$	151	1033	306 (1F)	—	—	—	—

[a] Produced by addition of photochemically generated alkoxyl radicals to the appropriate fluorophosphine in cyclopropane. All g-factors were 2·002 ± 0·001. [b] Similar line-shape effects were apparent over a similar temperature range in the more viscous iso-octane solvent. [c] Determined using the modified Bloch equations; the values are only approximate since second-order effects are not accounted for. [d] Some evidence for exchange of apical fluorine with equatorial ethoxy ligands was also found. [e] Weak signals: rapid β-scission above 203 K.

temperature dependent line-shape effects indicating rapid exchange of apical and equatorial fluorine ligands.† The magnitudes of the hyperfine splittings[2] from the fluorine ligands allow unambiguous assignment of X, Y, and Z in (**1**). Thus, whilst ethoxy and t-butoxy groups are both less apicophilic[6] than fluorine, trifluoromethoxy is more apicophilic, in accord with its high group electronegativity.

The Figure illustrates the low field portion of the spectrum of $\mathrm{EtO\dot{P}F_3}$ (**1**; X=Z=F, Y=EtO) and clearly shows the effects of exchange of apical and equatorial fluorine ligands, which may[6] or may not be coupled with inversion of configuration at phosphorus. The signs of $a(\mathrm{F}_{ap})$ and $a(\mathrm{F}_{eq})$ must be the same, presumably positive.[2]

From the temperature variation of k_{exch}, obtained by computer simulation of the spectra, we derive an approximate activation energy of 30 kJ mol^{-1} for fluorine ligand exchange in $\mathrm{EtO\dot{P}F_3}$. The different widths of the wing lines in the high temperature spectrum (see Figure) are probably due to exchange with a less stable isomer in which the ethoxy group is apical (**1**; X=Y=F, Z=EtO).

We are grateful to Dr. T. Thirunamachandran for help in calculating the hyperfine coupling constants from the observed resonance fields.

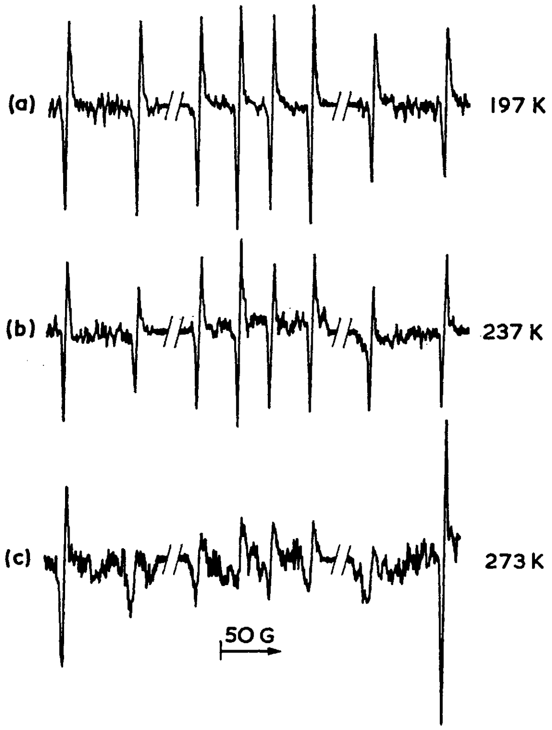


FIGURE. E.s.r. spectra of $\mathrm{EtO\dot{P}F_3}$ in cyclopropane at 9·09 GHz showing the low field $[m_I(^{31}\mathrm{P}) = +\frac{1}{2}]$ lines at (a) 197 K; (b) 237 K; and (c) 293 K.

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† After most of this work had been completed, a report appeared describing the low-temperature e.s.r. spectra of some of the radicals listed in the Table, although the possibility of fluxional behaviour was not discussed (A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Phys. Chem.*, 1975, **79**, 651).

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