

The Pronounced Differences in Reactivity of Perfluoro-t-butoxyl and t-Butoxyl Radicals

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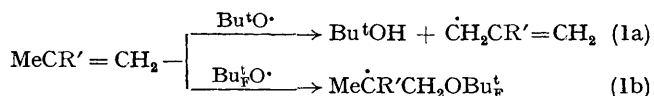
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Summary Perfluoro-t-butoxyl radicals differ from t-butoxyl radicals in that they add to double bonds rather than abstract allylic hydrogens, and abstract hydrogen from the alkyl groups of trialkyl phosphites or trialkylboranes in preference to exclusive attack at the metal centre.

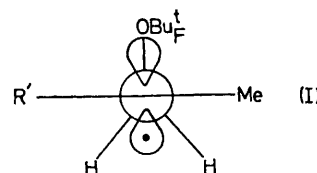
ALTHOUGH sources of perfluoroalkoxyl radicals are now available, little is known of their properties compared with those of alkoxyl radicals. We have now compared the reactions of perfluoro-t-butoxyl radicals with those of t-butoxyl radicals, towards alkenes, trialkyl phosphites, and trialkylboranes, and find that the two types of radical differ markedly in their behaviour.

Perfluoro-t-butoxyl radicals ($\text{Bu}_2\text{FO}^\bullet$) were generated by u.v. irradiation of solutions containing perfluorodi-t-butyl peroxide¹ and the substrate, *in situ* in the cavity of an e.s.r. spectrometer.² The steady state concentration of the carbon-centred radicals which is observed parallels their relative rates of production.² The Table lists the radicals detected and their hyperfine splittings.

t-Butoxyl radicals react with propene or 2-methylpropene by abstracting an allylic hydrogen atom (equation 1a)⁴ and even with ethylene no adduct radical can be detected.⁵



Perfluoro-t-butoxyl radicals undergo preferential addition to all three alkenes (equation 1b), and no allylic radicals



were detectable. The β -hydrogen coupling constants of the adduct radicals indicate that the preferred conforma-

TABLE

Substrate	Radical detected	Temp/°C	Hyperfine splittings/G
CH ₂ =CH ₂	Bu _F ^t OCH ₂ ĊH ₂	-60 ^a	<i>a</i> (αH) 21.3 (2H); <i>a</i> (βH) 25.6 (2H); <i>a</i> (F) 0.75 (9F)
CH ₂ =CHMe	Bu _F ^t OCH ₂ ĊHMe	-36	<i>a</i> (αH) 21.5 (1H); <i>a</i> (βH) 15.5 (2H); <i>a</i> (βH) 24.8 (3H); <i>a</i> (F) 0.8 (9F)
CH ₂ =CMe ₂	Bu _F ^t OCH ₂ ĊMe ₂	-60	<i>a</i> (βH) 13.5 (2H); <i>a</i> (βH) 23.5 (6H); <i>a</i> (F) 0.8 (9F)
MeCH ₂ OH	MeĊHOH ^b	-25	<i>a</i> (αH) 15.2 (1H); <i>a</i> (βH) 21.8 (3H); <i>a</i> (OH) 0.6 (1H)
(MeCH ₂ O) ₃ P	(EtO) ₂ POĊHMe ^c	-30	<i>a</i> (αH) 16.5 (1H); <i>a</i> (βH) 22.3 (3H); <i>a</i> (P) 8.3 (1P)
(MeO) ₃ P	(MeO) ₂ POĊH ₂	-25	<i>a</i> (αH) 18.6 (2H); <i>a</i> (P) 7.1 (1P)
Pr ⁿ ₃ B	MeCH ₂ ĊH ₂ ^d	-60	<i>a</i> (αH) 21.3 (2H); <i>a</i> (βH) 28.3 (2H); <i>a</i> (γH) 0.3 (3H)

^a At this temperature the lines corresponding to radicals with $M_I(\beta H) = 0$ were broader than those with $M_I(\beta H) = \pm 1$, indicating out-of-phase modulation of the β -hydrogen h.f.s., probably as a result of restriction of rotation about the C_β-O bond.

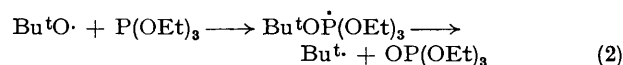
^b No ĊH₂CH₂OH was detectable.

^c At -90° two weak phosphoranyl radicals were also detected. The one with larger phosphorus hyperfine splitting [*a*(P)1020G, *a*(F) 10G (6F)] is assigned the structure (EtO)₃P[•]OBU_F, the other [*a*(P)824G, *a*(F)27G (3F)] is probably (EtO)₃P[•]CF₃. Trimethyl phosphite showed similar behaviour. The radical (EtO)₃P[•]OBU_F was also detected in the reaction of ethoxyl radicals with (EtO)₂-POBU_F.³

^d Radicals produced by hydrogen abstraction from the propyl groups attached to boron were also detected.

tions of Bu_F^tOCH₂ĊHMe and BuO_F^tCH₂ĊMe₂ are as shown in (I; R' = H or Me).

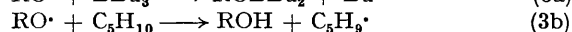
t-Butoxyl radicals react with trialkyl phosphites at close to the diffusion-controlled limit to bring about overall oxidation to phosphate *via* an intermediate phosphoranyl radical (*e.g.* equation 2).⁶



In contrast, perfluoro-t-butoxyl radicals preferentially abstract hydrogen from the alkoxy groups (see Table).

t-Butoxyl radicals react rapidly and selectively at the boron centre in trialkylboranes to displace an alkyl radical (*e.g.* equation 3a). There is no evidence for competitive abstraction of hydrogen from the alkyl side chain, and when

the reaction is conducted in the presence of cyclopentane (equation 3b), the ratio k_{3a}/k_{3b} (R = Bu^t) is 10³ at -20°.² Perfluoro-t-butoxyl radicals are much less selective, k_{3a}/k_{3b} (R = Bu_F^t) being *ca.* 4 at -20°.



The fact that the perfluoro-t-butoxyl radical is much more electrophilic than the t-butoxyl radical must in part account for its different behaviour, but clearly absolute rate constants for the reaction of the Bu_F^tO[•] radical are needed.

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¹ D. E. Gould, C. T. Ratcliffe, L. R. Anderson, and W. B. Fox, *Chem. Comm.*, 1970, 216.

² See for example, A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc. (B)*, 1971, 1823.

³ A. G. Davies, R. W. Dennis, R. C. Dobbie, and B. P. Roberts, unpublished results.

⁴ J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1968, **90**, 7157.

⁵ P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, 1971, **93**, 846.

⁶ A. G. Davies, D. Griller, and B. P. Roberts, *Angew. Chem. Internat. Edn.*, 1971, **10**, 738; *J.C.S. Perkin II*, 1972, 993.