PERKIN 2

Fluoro spin adducts and their modes of formation

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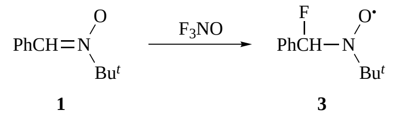
The reactions of two fluorinating reagents, XeF_2 and *N*-fluorodibenzenesulfonamide [$(PhSO_2)_2N$–F], with several spin traps have been investigated. In dichloromethane, the strong oxidant XeF_2 cleanly gives fluoro spin adducts with *N*-*tert*-butyl-α-phenylnitrone (PBN) or 5,5-dimethyl-1-pyrroline 1-oxide (DMPO) according to a mechanism mediated by the radical cation of the spin trap. In both cases, further fluorination takes place with replacement of the α hydrogen by fluorine.

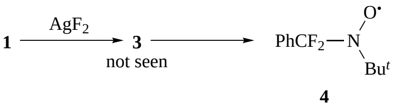
The much weaker oxidant $(PhSO_2)_2N$–F reacts with PBN or DMPO in dichloromethane giving both the fluoro adduct and an adduct formally derived from an *N*-centred radical, assigned the structure of $PhSO_2N(F)$–$PBN^{\cdot}$ or $(PhSO_2)_2N$–$DMPO^{\cdot}$, respectively. This type of reaction proceeds by a version of the Forrester–Hepburn mechanism, in which an acid HA, in this case HF, initially adds to the nitrone function to give a hydroxylamine derivative which is oxidized by $(PhSO_2)N$–F giving the fluoro spin adduct, a proton and the highly labile radical anion $(PhSO_2)_2N$–$F^{\cdot -}$. By decomposition of the latter to $PhSO_2(F)N^-$ and $PhSO_2^{\cdot}$, conditions are set up for propagation of the reaction by a new molecule of HA [now $PhSO_2(F)NH$] and thus formation of the $PhSO_2(F)N$ spin adduct.

Introduction

The formation of fluoro adducts of spin traps, like *N*-*tert*-butyl-α-phenylnitrone† (PBN, **1**) or 5,5-dimethyl-1-pyrroline 1-oxide (DMPO, **2**) has been achieved by treatment with fluorinating agents such as AgF_2 or F_3NO.[1,2] In the case of PBN, treatment with F_3NO in benzene gave the fluoro adduct **3** [reaction (1)], whereas AgF_2 gave the α,α-difluorobenzyl *tert*-butyl aminoxyl radical (**4**) by further rapid substitution of the α-hydrogen of **3** by fluorine [reaction (2)]. Similarly, DMPO gave the corresponding difluoro compound **5** by treatment with AgF_2 [reaction (3)]. These reactions were suggested to proceed *via* the formation of fluorine atoms.



(1)



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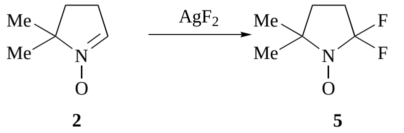


(3)

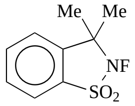
Later,[3] a mixture of **3** and **4** was generated by the oxidation of PBN to its radical cation by the strong oxidant, tris(4-bromophenyl)aminium ion ($\mathbf{6}^{\cdot+}$) in the presence of tetrabutylammonium fluoride, in agreement with the redox properties of the reagents involved.[4] $E°(\mathbf{6}^{\cdot+}/\mathbf{6})$ is 1.06 V (*vs.* SCE, all potentials given here will be referred to this electrode), meaning that $6^{\cdot+}$ can undergo a fast electron transfer reaction with PBN [$E°(PBN^{\cdot+}/PBN) = 1.46$ V][5] to give $PBN^{\cdot+}$, which then reacts with fluoride ion [$E°(F^{\cdot}/F^-) = 2.9$ V] to give **3**. $E°(\mathbf{3}^{\cdot+}/\mathbf{3})$ should be of the order of 0.7 V, as judged from a comparison with known redox potentials of aminoxyl radicals;[6] thus further oxidation in an electrochemical–chemical–electrochemical (ECE) type reaction with $\mathbf{6}^{\cdot+}$ and some base present should eventually give **4** (Scheme 1).

$(4\text{-}BrC_6H_4)_3N$

6

$(PhSO_2)_2NF$

8



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$$\mathbf{1} \xrightarrow{\mathbf{6}^{\cdot+}} \mathbf{1}^{\cdot+} \xrightarrow{Bu_4NF} \mathbf{3}$$

$$\mathbf{3} \xrightarrow[+F^-]{-e^-,\,-H^+,-e^-} \mathbf{4}$$

Scheme 1

A third mechanism already suggested by Forrester and Hepburn[7] in 1971 was utilized to produce **3** under weakly oxidizing conditions, namely by air oxidation of PBN in the presence of tetrabutylammonium fluoride in chloroform.[8] Fluoride ion adds to the nitrone function and the resulting hydroxylamine **7** is highly redox reactive, $E_{1/2}$ for oxidation at a mercury electrode being $-(0.2–0.3)$ V.[9] Thus oxygen with $E°(O_2/O_2^{\cdot-})$ at *ca.* −0.4 V can act as an oxidant to give **3** [reaction (4)] Under these conditions **4** was not formed, as expected.

$$\mathbf{1} + F^- + H^+ \longrightarrow \underset{\mathbf{7}}{PhCH(F)\text{–}N(OH)Bu^t} \xrightarrow{O_2} \mathbf{3} \quad (4)$$

In view of the high energy required to produce fluorine atoms from fluoride-ion containing species, a process which according to dogma cannot take place in homogenous medium by any known oxidizing agent, we deem it unlikely that any fluoro spin adduct can be formed by proper trapping of the fluorine atom. In what follows, two fluorinating agents of widely differing redox reactivity, XeF_2 and *N*-fluorodibenzenesulfonamide (**8**), are used to probe this problem. XeF_2 is a strong oxidant capable of forming radical cations of aromatic compounds with $E°(ArH^{\cdot+}/ArH) \le 2.0$ V,[10] whereas $E°(\mathbf{8}/\mathbf{8}^{\cdot-})$ should be much lower, in the range found for other *N*-fluoro reagents like the *N*-fluorosultam **9** with $E°(\mathbf{9}/\mathbf{9}^{\cdot-})$ of −0.14 V.[11] The peak potential E_{pc} for cathodic reduction of **8** in acetonitrile was found to be −0.54 V.[12]

Results and discussion

Formation of fluoro spin adducts by XeF_2 oxidation of spin traps in dichloromethane

Treatment of PBN with a deficit of XeF_2 (*ca.* 50% of the

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† The IUPAC name for PBN is *N*-(benzylidene)-*tert*-butylamine *N*-oxide.

Table 1 Fluoro adducts obtained from the reaction between spin traps and XeF_2 in dichloromethane or HFP

Spin trap	Solvent[a]	Ratio [spin trap]/[XeF_2]	a_N/mT	a_H/mT	a_F/mT	Assignment
1	DCM	2	1.26	0.117	4.58	F–PBN$^{\bullet}$ [b,c]
			1.27	—	2.11 (2 F)	**4**[d,e]
1	HFP	10	1.98	2.74	—	**14**$^{\bullet+}$ [f,g]
10	DCM	2	1.24	0.107	4.78	F–**10**$^{\bullet}$
10	HFP	10	1.38	0.133	4.03	F–**10**$^{\bullet}$
			1.99	2.76	—	*p*-NO_2–**14**$^{\bullet}$ [g,h]
12	DCM	20	1.27	0.127	4.48	F–**12**$^{\bullet}$ [b]
		10	1.27	—	2.08 (2 F)	*p*-MeO–**4**[i]
12	HFP	2	None			
11	DCM	20	1.22	0.288	5.60	F–**11**$^{\bullet}$
2	DCM	2	1.18 1.12	0.616	5.46	Also 0.139 (1 H), 0.200 mT (2 H): F–DMPO$^{\bullet}$ (see Fig. 2)
2	DCM	20		—	2.18 (2 F)	0.196 (2 H): **5**[j]
13	DCM	10	None			
13	HFP		None			**13**$^{\bullet+}$ [k]

[a] DCM = dichloromethane, HFP = 1,1,1,3,3,3-hexafluoropropan-2-ol. [b] *Ca*. 3 min after mixing. [c] Lit.[2] in benzene: 1.22, 0.118 and 4.56 mT. [d] *Ca*. 15 min after mixing. [e] Lit.[2] in benzene: 1.26, 2.14 (2 F) mT. [f] Lit.[5] in HFP: 2.00 and 2.80 mT. [g] The small couplings to the 4,4-methyl groups were not detectable due to the low intensity of the spectrum. [h] Lit.[5] in HFP: 1.95 and 2.73 mT. [i] *Ca*. 2 h after mixing. [j] Lit.[1] in benzene: 1.08, 2.16 (2 F) and 0.175 (2 H) mT. [k] Identical to spectrum published in ref. 5.

required amount, see Scheme 2) in dichloromethane produced an intense EPR spectrum of F–PBN$^{\bullet}$ (**3**) together with a weak signal of the difluoro derivative **4**. Hyperfine coupling constants (hfs) are given in Table 1. Upon standing, **3** was rapidly converted into **4**, the transformation being essentially complete after 15 min. Thus it appears that the formation of **3** is a relatively slow reaction leaving enough XeF_2 intact to allow for further oxidative fluorination of **3**. This behaviour would be expected for a radical cation mediated mechanism, as outlined in Scheme 2.

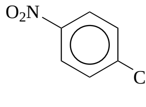
$$2\,\text{PBN} + XeF_2 \longrightarrow 2\,\text{PBN}^{\bullet+} + \text{Xe} + 2F^- \longrightarrow 2\,\text{F–PBN}^{\bullet}$$

$$\text{F–PBN}^{\bullet} \xrightarrow{-e^-} \text{F–PBN}^+ \xrightarrow{-H^+,\,-e^-,\,+F^-} \mathbf{4}$$

Scheme 2

The 4-nitro derivative of PBN, 4-NO_2PBN (**10**), upon treatment with a deficit of XeF_2 (*ca*. 50% of the required amount) in dichloromethane gave the fluoro spin adduct, the signal of which kept growing over 2 h and then slowly decayed. This spin trap is more difficult to oxidize than PBN, E_{pa}(**10**$^{\bullet+}$/**10**) = 1.7 V,[5] and apparently its fluoro spin adduct is stable against further oxidation by XeF_2. A still more oxidation resistant spin trap, pentafluoro-PBN (**11**) [E_{pa} (**11**$^{\bullet+}$/**11**) = 1.9 V], exhibited similar behaviour to 4-NO_2PBN.

In order to obtain the fluoro spin adduct from a more easily oxidized PBN derivative, 4-MeOPBN (**12**) [$E°$(**12**$^{\bullet+}$/**12**) = 1.16 V],[5] it was found necessary to decrease the likelihood of further fluorination by using a large excess of spin trap over XeF_2 (ratio > 20 : 1). The signal from the fluoro adduct increased over 30 min and then decayed; after 2 h practically only the difluoro derivative of 4-MeOPBN was present. The still more redox reactive nitrone, 4-Me_2NPBN (**13**) [$E°$(**13**$^{\bullet+}$/**13**) = 0.64 V],[5] upon treatment with XeF_2 in dichloromethane gave no paramagnetic species.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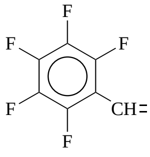
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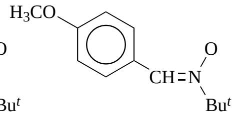
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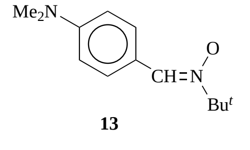
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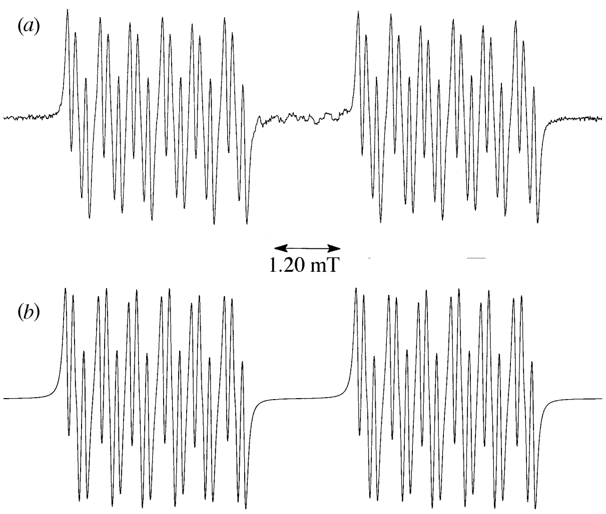


Fig. 1 (*a*) EPR spectrum of F–DMPO$^{\bullet}$ generated by the reaction between DMPO (0.10 mol dm^{-3}) and XeF_2 (5 mmol dm^{-3}) in dichloromethane. (*b*) The simulated spectrum used the hfs constants given for F–DMPO$^{\bullet}$ of Table 1.

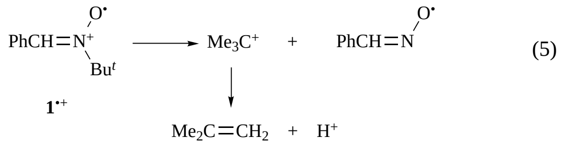
DMPO **2** upon treatment with XeF_2 (ratio [DMPO] : [XeF_2] = 20 : 1) in dichloromethane gave its fluoro spin adduct (EPR spectrum, see Fig. 1). This aminoxyl radical has not been characterized before. Under the conditions employed it decomposed with $k = 0.08$ min^{-1}. Use of a lower concentration ratio (2 : 1) gave only the known[1] difluoro derivative of DMPO [see reaction (3)].

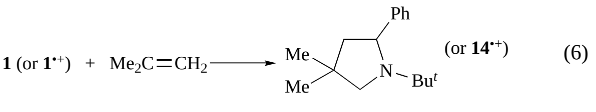
The results described above are best interpreted in terms of the radical cation mechanism of Scheme 2. A way of further testing this proposal is to conduct the reactions in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), a solvent in which nucleophilic reactivity is enormously attenuated due to strong hydrogen bonding to negatively charged species.[13] Thus the chloride ion is about 10^8 times less reactive toward **6**$^{\bullet+}$ in HFP than in acetonitrile and it is expected that the fluoride ion should be subject to a similar decrease in reactivity.

XeF_2 oxidation of spin traps in HFP

Reactions run as above, but in HFP instead of dichloromethane, proceeded according to the radical cation mechanism. We have previously[5] shown that the radical cations of PBN and its

4-substituted derivatives display different chemical behaviour when generated in HFP : PBN, PBNs which are more difficult to oxidize (4-NO_2, 4-F) and 4-MePBN are transformed into isoxazolidines by a de-*tert*-butylation–cycloaddition sequence [reactions (5) and (6)]. Under the oxidizing conditions the particular isoxazolidine formed (**14**) is transformed into its radical cation **14**$^{\bullet+}$ which has a characteristic EPR spectrum with $a_N = 2.0$ and $a_H = 2.8$ mT and small couplings of *ca.* 0.5 mT to the two ring methyl groups. It may also be that **14**$^{\bullet+}$ is formed directly from **1**$^{\bullet+}$ and isobutene.[14]





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On the other hand, the radical cations of PBNs with electron-donating groups in the ring [4-MeO, 3,4-(OCH_2O), 4-Me_2N] were stable enough to allow recording of their EPR spectra in HFP.[5]

Accordingly, upon oxidation of PBN with XeF_2 in HFP, a weak EPR signal of the isoxazolidine radical cation (**14**$^{\bullet+}$) was observed (Table 1); no signs of fluoro adducts **3** or **4** were detected. Thus the nucleophilicity of the fluoride ion is strongly decreased in HFP, allowing for the sequence of reactions (5) and (6) to compete with capture of PBN $^{\bullet+}$ by fluoride ion.

4NO_2PBN (**10**), corresponding to a more reactive cation, gave both the fluoro spin adduct and the isoxazolidine radical cation upon oxidation by XeF_2 in HFP, whereas 4-MeOPBN (**12**) gave no paramagnetic species. 4-Me_2NPBN (**13**) gave its persistent radical cation.

Formation of fluoro and *N*-centred spin adducts by treatment of spin traps with *N*-fluorodibenzenesulfonamide (8) in dichloromethane

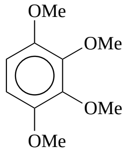
Compound **8** is a weak oxidant used for the fluorination of nucleophilic species like carbanions *via* a mechanism involving nucleophilic attack upon the fluorine atom.[15] We tested its one-electron oxidizing ability by allowing it to react with tris(4-anisyl)amine (**15**) [$E^\circ(\mathbf{15}^{\bullet+}/\mathbf{15}) = 0.52$ V] in HFP which produced the radical cation **15**$^{\bullet+}$ in a rapid reaction (within seconds). Tris(4-tolyl)amine (**16**) [$E^\circ(\mathbf{16}^{\bullet+}/\mathbf{16}) = 0.75$ V] reacted slower (within minutes) and 2,3-dimethyl-1,4-dimethoxybenzene (**17**) [$E^\circ(\mathbf{17}^{\bullet+}/\mathbf{17}) = 1.18$ V][16] gave a weak EPR spectrum of **17**$^{\bullet+}$ only after standing over night. To provide a calibration mark, it should be mentioned that *N*-bromosuccinimide ($E^\circ = 0.2$ V)[17] oxidized **17** instantaneously to **17**$^{\bullet+}$ in HFP,[18] thus indicating that $E^\circ(\mathbf{8}/\mathbf{8}^{\bullet-})$ must be considerably lower than 0.2 V. Therefore it is not possible for **8** to oxidize spin traps like PBN or DMPO *via* an electron transfer mechanism.

$(4\text{-}MeOC_6H_4)_3N$

15

$(4\text{-}MeC_6H_4)_3N$

16



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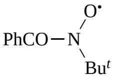

$PhCO{-}N(O^{\bullet})Bu^t$

18

Yet the spontaneous reaction between **8** and PBN in dichloromethane gave a weak EPR spectrum of the fluoro spin adduct **3**, the intensity of which increased and reached a shallow maximum after *ca.* 1.5 h (Fig. 2). Benzoyl-*N*-*tert*-butylnitrone (**18**, often denoted PBNOx) was formed as the final paramagnetic product, its concentration following a sigmoidal curve. This situation, a spontaneous thermal reaction between a spin trap and a weak electron acceptor to give a spin adduct is common but has previously been little understood. We recently investigated a similar reaction between PBN and trichloroacetonitrile in hexane[19] and concluded that the thermal reaction is initiated by addition of an acid HA to the nitrone function, followed by oxidation of the hydroxylamine by trichloroacetonitrile, giving dichlorocyanomethyl radical and HCl. The former adds to PBN and the latter can initiate a new cycle of hydroxylamine formation, oxidation, *etc.* [eqns. (7)–(9)].

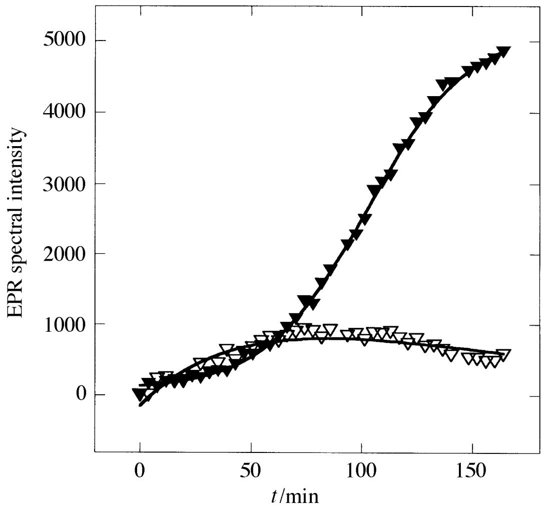

Fig. 2 Time dependence of F–PBN$^{\bullet}$ (**3**) (▽) and PBNOx (**18**) (▼), when formed from a solution of PBN (0.10 mol dm^{-3}) and **8** (0.09 mol dm^{-3}) in dichloromethane under thermal conditions. The curves represent the best fits to a sigmoidal curve and a double exponential curve, respectively (Tablecurve® curve fitting program).

$$\mathrm{PBN + HA \rightleftharpoons PBN(H)A} \qquad (7)$$

$$\mathrm{PBN(H)A + Cl_3CCN \longrightarrow A{-}PBN^{\bullet} + H^+ + Cl^- + Cl_2C{=}C{=}N^{\bullet}} \qquad (8)$$

$$\mathrm{Cl_2C{=}C{=}N^{\bullet} + PBN \longrightarrow Cl_2C{=}C{=}N{-}PBN^{\bullet}} \qquad (9)$$

With the promoting acid HA present in a low but finite concentration equimolar amounts of the spin adducts A–PBN$^{\bullet}$ and $Cl_2C{=}C{=}N{-}PBN^{\bullet}$ were formed. This mechanism is a version of the Forrester–Hepburn mechanism; a truly autocatalytic version of it was recently found in the reaction between *N*-chlorobenzotriazole and PBN, with benzotriazole as the autocatalyst.[20]

A similar situation can be envisaged for the reaction between PBN and **8** in dichloromethane. It is likely that the formation of a trace of HF will always accompany the dissolution of **8** in a solvent, leading to the initiation of a mechanism of the same type as above [eqns. (10) and (11)]. The radical anion **8**$^{\bullet-}$,

$$\mathrm{HF + PBN \longrightarrow PBN(H)F} \qquad (10)$$

$$\mathrm{PBN(H)F + (PhSO_2)_2NF \longrightarrow F{-}PBN^{\bullet} + H^+ + (PhSO_2)_2NF^{\bullet-}} \qquad (11)$$

presumably a highly unstable species, has two pathways open for cleavage [eqns. (12) and (13)] and it is not immediately

$$\mathrm{(PhSO_2)_2NF^{\bullet-} \longrightarrow (PhSO_2)_2N^{\bullet} + F^-} \qquad (12)$$

$$\mathrm{(PhSO_2)_2NF^{\bullet-} \longrightarrow PhSO_2^{\bullet} + (PhSO_2)(F)N^-} \qquad (13)$$

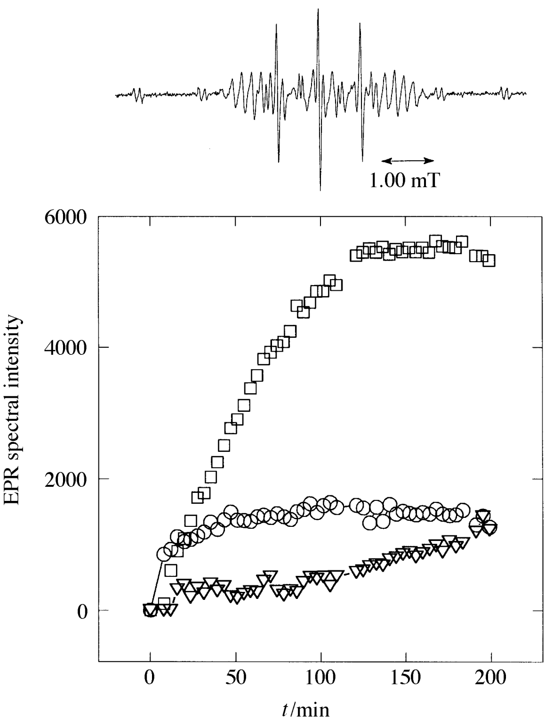

Fig. 3 Time dependence of F–PBN$^•$ **3** (▽), $PhSO_2(F)N$–PBN$^•$ **21** (○) and PBNOx **18** (□), when formed from a solution of PBN (0.1 mol dm^{-3}), **8** (0.09 mol dm^{-3}) and HF (7 mmol dm^{-3}) in dichloromethane under thermal conditions. The EPR spectrum was recorded after *ca.* 100 min.

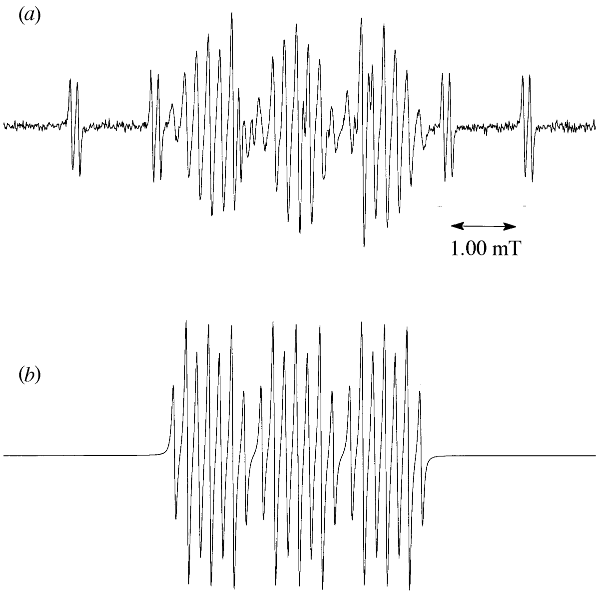

Fig. 4 EPR spectrum of $PhSO_2(F)N$–PBN$^•$ **21**, generated from a solution of PBN (0.1 mol dm^{-3}), **8** (0.09 mol dm^{-3}) and HF (7 mmol dm^{-3}) in dichloromethane under thermal conditions. The spectrum was recorded *ca.* 15 min after mixing of the reagents. The simulated spectrum used the hfs coupling constants from Table 2. The remaining lines belong to the EPR spectrum of F–PBN$^•$.

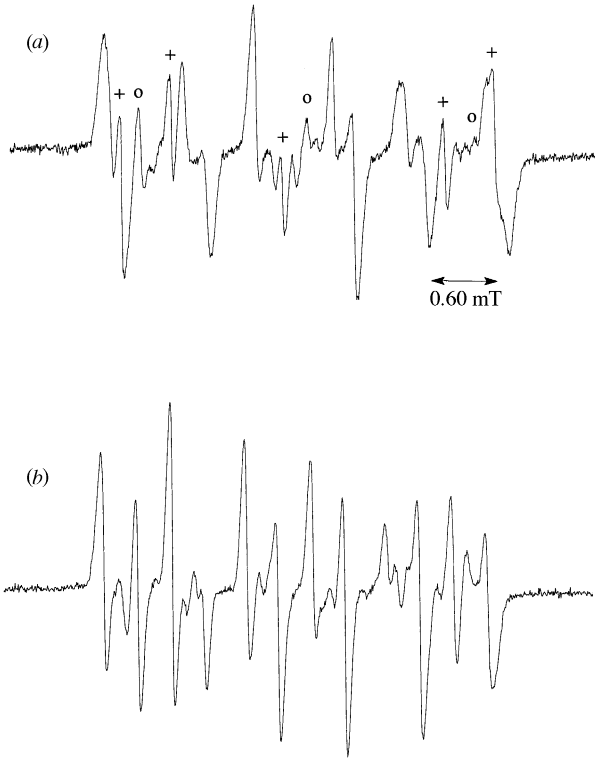

Fig. 5 EPR spectra obtained by irradiation (light of $\lambda > 400$ nm) of (*a*) a solution of $(PhSO_2)_2NH$ (20 mmol dm^{-3}), PBN (100 mmol dm^{-3}) and TAPT (*ca.* 1 mmol dm^{-3}) in dichloromethane. The $Bu^t_2NO^•$ lines are marked with 'o', those of $PhSO_2$–PBN$^•$ with '+'. Spectrum (*b*) was obtained similarly from 4-NO_2PBN.

obvious which will be the predominant one. However, the important feature is that a new molecule HA is formed in either step with the proton from eqn. (11), HF in eqn. (12) or $(PhSO_2)(F)NH$ in eqn. (13) and either of these acids can in principle propagate the reaction by adding to a new PBN molecule. Both the neutral radicals $(PhSO_2)_2N^•$ and $PhSO_2^•$ can add to PBN and give spin adducts $(PhSO_2)_2N$–PBN$^•$ (**19**) and $PhSO_2$–PBN$^•$ (**20**), of which the former might be persistent enough for detection and the latter known[3] to be rapidly transformed to PBNOx (**18**). Furthermore, propagation *via* $(PhSO_2)(F)NH$ will lead to the spin adduct $(PhSO_2)(F)N$–PBN$^•$ (**21**).

Thus the HA propagated reaction between PBN and **8** is predicted to give F–PBN$^•$ (**3**), one or two *N*-centred spin adducts (**19**, **21**) and PBNOx (**18**). In the spontaneous reaction (Fig. 2) only **3** and **18** appeared, indicating that only the autocatalytic process of eqns. (7)–(9) was operating and that the *N*-centred spin adduct **17** might be too reactive to survive under the conditions employed, thus ending up as PBNOx.

Addition of a low concentration of the autocatalyst HF (*ca.* 7 mmol dm^{-3}) led to the formation of F–PBN$^•$ **3**, at least one *N*-centred spin adduct, giving rise to an EPR spectrum consisting of a triplet of septets, and PBNOx **18**, developing with time as shown in Fig. 3. By aid of experiments with [α-^{2}H]PBN, which gave a spectrum consisting of a triplet of sextets by loss of one 0.19 mT coupling, it was eventually established that the *N*-centred adduct must be predominantly $(PhSO_2)(F)N$–PBN$^•$ (**21**). Its EPR spectrum was best described by four coupling constants, $a_N = 1.39$, $a_{N'} = 0.36$, $a_F = 0.19$ and $a_H = 0.20$ mT (Fig. 4). The same spectrum could also be generated by photolysis (UV) of solutions of PBN and **8** in dichloromethane and several other solvents. Simulation of the spectrum of **21**, using the coupling constants given above, does not give perfect agreement; one reason for this might be the formation of diastereoisomeric forms of **21** due to a non-planar arrangement of the $N(F)SO_2Ph$ group.

Attempts to record the EPR spectrum of $(PhSO_2)_2N$–PBN$^•$ (**19**) were made by oxidation of PBN and $(PhSO_2)_2NH$ in dichloromethane by irradiation by light of $\lambda > 400$ nm in the presence of 2,4,6-tris(4-anisyl)pyrylium tetrafluoroborate (TAPT), an often used photo-electron transfer reagent.[21] Its use for photo-initiated inverted spin trapping has been described earlier[8] and is presently being extended to a large number of nucleophilic species.[22] The EPR spectrum obtained is shown in Fig. 5(*a*). It was analysed as being composed of three spectra, namely (*i*) a weak signal with $a_N = 1.56$ mT ($Bu^t_2NO^•$), (*ii*) a 3 × 2 line spectrum with $a_N = 1.48$ and $a_H = 0.45$ mT (assigned

Table 2 Spin adducts from reactions between spin traps and $(PhSO_2)_2NF$ in dichloromethane

		F adduct			N adduct				
Spin trap	Reaction conditions	a_N/mT	a_H/mT	a_F/mT	a_N/mT	$a_{N'}$/mT	a_H/mT	a_F/mT	Remark
4-NO_2PBN (**10**)	Thermal	1.24	0.11	4.77	None				Weak signal
4-NO_2PBN (**10**)	UV	1.22	0.12	4.70	1.35	0.38	0.21	0.21	+NO_2PBNOx (0.78 mT)
4-NO_2PBN (**10**)	Thermal, [HF] ≈ 7 mM	1.22	0.11	4.71	1.33	0.39	0.20	0.20	+NO_2PBNOx (0.78 mT)
PBN (**1**)	Thermal	1.27	0.11	4.52	None				+PBNOx (0.80 mT)
PBN (**1**)	Thermal, [HF]] ≈ 7 mM	1.27	0.11	4.54	1.38	0.36	0.20	0.19	See Fig. 4
[α-^{2}H]PBN	Thermal, [HF] ≈ 7 m M	1.27	—	4.59	1.39	0.354	—	0.18	PBNOx (0.81 mT)
PBN (**1**)	Photolysis (UV)	1.27	0.11	4.54	1.36	0.36	0.19	0.18	
PBN (**1**)	Thermal; [AcOH] = 1.2 mM	1.25	0.11	4.52	None				+PBNOx (0.80), AcO–PBN$^•$ (1.33 mT, 0.13)
[α-^{2}H]PBN	Thermal; [AcOH] = 2.3 mM	1.26	—	4.53	None				+PBNOx (0.80), AcO–PBN$^•$ (1.33 mT)
DMPO (**2**)	Thermal	1.18	0.616	5.46	1.42	0.286	1.98	—	F–DMPO$^•$: also $a_{H'}$, $a_{H''}$ 0.200, 0.139

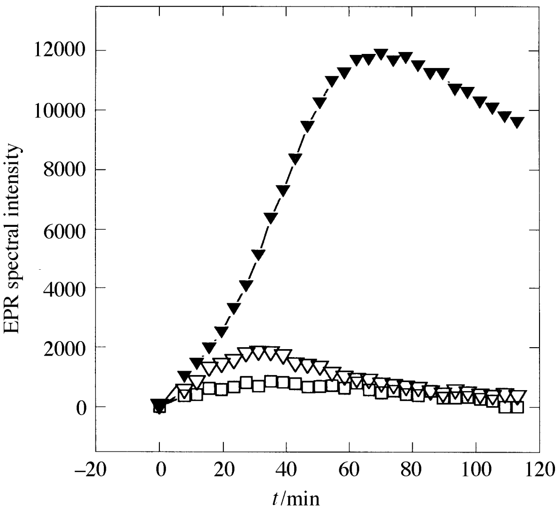

Fig. 6 Time dependence of F–PBN$^•$ (**3**) (▽), PBNOx (**18**) (▼) and AcO–PBN$^•$ (□) when formed from a solution of [α-^{2}H]PBN (0.10 mol dm^{-3}), **8** (0.09 mol dm^{-3}) and acetic acid (2.3 mol dm^{-3}) in dichloromethane under thermal conditions

to $PhSO_2$–PBN$^•$; an almost identical spectrum was obtained by TAPT–*hv* treatment of PBN on dichloromethane in the presence of 4-toluenesulfonic acid, $a_N = 1.52$ and $a_H = 0.476$ mT) and (*iii*) a 3 × 4 line spectrum with $a_N = 1.39$, $a_{N'} = 0.3$–0.4, $a_H = 0.72$ and $a_{H'} = 0.176$ mT. The large α-hydrogen coupling constant of 0.72 mT was verified by using [α-^{2}H]PBN as the substrate (loss of this coupling and appearance of a 1 : 1 : 1 triplet with $a_D = 0.12$ mT). The 3 × 4 line spectrum is preliminarily assigned to $PhSO_2NH$–PBN$^•$, in which one of the $PhSO_2$ groups has been split off. In the present context, note that the spectrum disappeared within 10 s after the light source had been shut off and thus the species corresponding to this spectrum cannot contribute to the spectrum of the *N*-centred spin adduct recorded during the thermal HF-promoted reaction of PBN and **8** in Fig. 3.

When 4-NO_2PBN, a stronger electrophile, was used in the same reaction a more distinct EPR spectrum of two overlapping spectra was obtained [Fig. 5(*b*)]. The more intense 3 × 4 lines spectrum has $a_N = 1.33$, $a_{N'} = 0.3$–0.4, $a_H = 0.64$ and $a_{H'} = 0.325$ mT, and thus should correspond to 4-NO_2PBN$^•$–N(H)SO_2Ph. The less intense spectrum could not be analysed with certainty but might have $a_N = 1.29$, $a_{N'} = 0.12$ and $a_H = 0.39$ mT and then possibly correspond to 4-NO_2PBN$^•$–N$(SO_2Ph)_2$.

Finally, 4-FPBN, a spin trap of reactivity in between those of PBN and 4-NO_2PBN on irradition with $(PhSO_2)_2NH$ and TAPT gave a spectrum which was similar to that of Fig. 5(*a*), being composed of three spectra of (*i*) $a_N = 1.56$ mT ($Bu^t_2NO^•$), (*ii*) 3 × 2 lines with $a_N = 1.50$ and $a_H = 0.44$ mT (assigned to $PhSO_2$–PBN$^•$; see above) and 3 × 4 lines with $a_N = 1.36$, $a_{N'} = 0.3$–0.4, $a_H = 0.70$ and $a_{H'} = 0.18$ mT.

The 4-tolylsulfonamido spin adduct, 4-$CH_3C_6H_4SO_2NH$–PBN$^•$, has been characterized in aqueous medium, $a_N = 1.56$, $a_{N'} = 0.175$ and $a_H = 0.338$ mT, from the acidification of a solution of chloramine-T (*N*-chlorotoluene-*p*-sulfonamide) and PBN in water.[23] This species was not stable, being converted into a new, unidentified radical with $a_N = 0.71$ and $a_{N'} = 0.42$ mT within a few minutes. The same unstable species, accompanied by other radicals, was detected during irradiation of analkaline solution of PBN and chloramine-T.

An experiment in which a low concentration (2.3 mmol dm^{-3}) of a weak acid, acetic acid, was added, supported the idea that acids of different kinds can be entered in eqn. (11) and promote the formation of spin adducts.[19] Fig. 6 shows the time dependence of the F–PBN$^•$ and PBNOx signals and that $[\text{F–PBN}^•]_{max}$ was now obtained after *ca.* 30 min. A low concentration of AcO–PBN$^•$ also developed, the time to reach $[\text{AcO–PBN}^•]_{max}$ being *ca.* 30 min.

The thermal reaction of DMPO **2** and **8** in HFP gave two superimposed spectra, one belonging to F–DMPO$^•$ (Fig. 1) and one to what had the appearance of a spectrum of an adduct of an *N*-centred radical (Table 2). The photolysis (light of $\lambda > 400$ nm) of DMPO with $(PhSO_2)_2NH$ in dichloromethane in the presence of TAPT gave an EPR spectrum of what presumably is $(PhSO_2)_2N$–DMPO$^•$ according to its coupling constants. This spectrum matched the second spectrum obtained from DMPO and **8**.

Coupling constants of the spin adducts obtained in the various reactions of spin traps with **8** in dichloromethane are given in Table 2.

Reactions of spin traps and 8 in HFP

As stressed above, HFP as a solvent strongly suppresses all kinds of nucleophilic reactivity.[13] It is therefore expected that the Forrester–Hepburn mechanism should not operate in HFP, since the addition of HA to a nitrone presumably should proceed in a nucleophilic addition–protonation sequence. This prediction was shown to be correct: spin traps **1**, **10** and **12** did not show any paramagnetic activity upon treatment with **8** in HFP under conditions otherwise similar to the ones used for reactions given in Table 2. This was true for both thermal and photo reactions (UV). However, 4-Me_2NPBN (**13**) underwent one-electron oxidation to give its persistent (many hours) radical cation as expected in view of its low oxidation potential of 0.64 V.

Conclusions

Two mechanisms of generating fluoro spin adducts from nitrones have been characterized. The first involves the use of a strong oxidant, XeF_2 and proceeds *via* initial formation of the nitrone radical cation, followed by its reaction with fluoride ion ('inverted spin trapping'). The second one uses an *N*-fluoro reagent, $(PhSO_2)_2NF$, which is a weak oxidant and exerts its action by oxidizing the hydroxylamine formed by addition of an acid HA to the nitrone (the Forrester–Hepburn mechanism). If HA is equal to HF, the fluoro spin adduct is formed. In a parallel reaction, spin adducts of *N*-centred radicals are formed, such as $PhSO_2$–N(F)–PBN$^{\bullet}$.

Experimental

Materials

PBN (**1**), DMPO (**2**) and 4-NO_2PBN (**10**) were purchased from Aldrich and used as received. 4-MeOPBN (**12**) and 4-Me_2-NPBN (**13**) were available from an earlier study[5] and F_5PBN (**11**) was prepared from pentafluorobenzaldehyde and 2-methyl-2-nitropropane according to ref. 24. Xenon(II) fluoride and *N*-fluorodibenzenesulfonamide (**8**) were from Aldrich and dibenzenesulfonamide from Fluka AG. $Bu_4NF\cdot 3H_2O$ was from Merck AG, and tris(4-methoxyphenyl)amine (**15**), tris(4-tolyl)-amine **16** and 2,3-dimethyl-1,4-dimethoxybenzene (**17**) were available from earlier studies.[16,17] All solvents used were of highest commercial quality available. TAPT was a gift from Professor E. Steckhan, University of Bonn. E_{pa} of F_5PBN (**11**) was measured in dichloromethane–Bu_4NPF_6 by differential pulse voltammetry (BAS-100 instrument, Pt button anode).

EPR spectral experiments

These were performed as described in earlier work. The HF containing solutions used for promotion of the reaction between PBN and **8** were made up by adding 10 μl (1 μl ≡ 1mm^3) of methanesulfonic acid to a solution of a 10–15% excess of $Bu_4NF\cdot 3H_2O$ in 20 cm^3 of dichloromethane and stirring for 15 min. Stock solutions of known concentrations of XeF_2 were made up in dichloromethane or HFP, but could only be kept for a limited period (3–4 h) while still keeping their activity.

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