Inverted spin trapping. Part V.† 1,1,1,3,3,3-Hexafluoropropan-2-ol as a solvent for the discrimination between proper and inverted spin trapping

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1,1,1,3,3,3-Hexafluoropropan-2-ol (HFP) has been tested as a solvent for spin trapping experiments. It sustained proper spin trapping of alkyl and aryl radicals generated in secondary cleavage reactions with no obvious complications, and also other neutral, stable radicals could be generated and kept stable for long periods in this solvent.

The extreme persistency of radical cations in HFP was shown to be at least partly due to a strong attenuation of nucleophile reactivity. Hard nucleophiles reacted $> 10^7$ times slower with tris(4-bromophenyl)aminium ion in HFP than in acetonitrile, and also soft nucleophiles experienced large rate decreases, for example by a factor of $> 10^3$ for trinitromethanide ion. This means that the inverted spin trapping mechanism, possible under conditions in which a spin trap and a nucleophile is treated by an oxidizing agent, becomes severely impeded in HFP. This was demonstrated in a number of cases, for example, benzotriazolate ion, trinitromethanide ion and 3,5-lutidine. Even rather small proportions of HFP in dichloromethane (10–30%) had a completely inhibiting effect on the inverted spin trapping mechanism, and only triethyl phosphite and related esters underwent this reaction type in neat HFP, yielding trialkoxyphosphonio spin adducts from PBN. In addition, triphenylphosphine reacted in this way.

Anions of imides become protonated in HFP, an additional factor inhibiting inverted spin trapping from potential imidyl radical sources. Thus conditions could be established for the unambiguous trapping of imidyl radicals. No radical from a ring-opened imidyl could be detected.

Spin trapping is an often used method to trap and identify highly reactive radicals from various types of reactions.[1] A spin trap, ST, is a compound prone to add a radical R˙ with formation of a spin adduct R–ST˙, which is persistent enough to be detected and identified by electron paramagnetic resonance (EPR) spectroscopy [eqn. (1)]. However, spin adducts can be

$$\mathrm{R^{\bullet} + ST \longrightarrow R{-}ST^{\bullet}} \qquad (1)$$

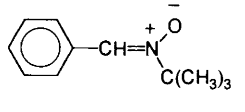
formed by other routes which do not involve R˙, causing problems as to how results of spin trapping studies should be interpreted. An early[2] source of false spin adducts was identified in situations in which a nucleophilic species ($\mathrm{Nu^-}$) was treated with a one-electron oxidant in the presence of a spin trap, with the aim of trapping Nu˙. Here it was sometimes noted that $\mathrm{Nu^-}$ would add to ST in a nucleophilic process, followed by oxidation of the adduct formed [eqns. (2) and (3)]. This type

$$\mathrm{Nu^- + ST \rightleftharpoons Nu{-}ST^-} \qquad (2)$$

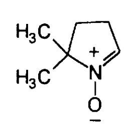
$$\mathrm{Nu{-}ST^- + Ox \longrightarrow Nu{-}ST^{\bullet} + Red} \qquad (3)$$

of reaction was found with spin traps of the nitrone type, such as *N-tert*-butyl-α-phenylnitrone **1** (recommended IUPAC name, *N*-benzylidene-*tert*-butylamine *N*-oxide) or 2,2-dimethyl-3,4-dihydro-2*H*-pyrrole *N*-oxide **2** and with $\mathrm{Nu^-}$ equal to a carbanion.

In the same $\mathrm{Nu^-}$–ST system another route to Nu–ST˙ can be realized if ST can be oxidized to its radical cation ($\mathrm{ST^{\bullet +}}$) which then reacts with $\mathrm{Nu^-}$, as shown in eqns. (4) and (5). This mechanism has been invoked a number of times[3] in order to explain certain spin trapping phenomena, and was recently further developed by studies of model systems and application



1 PBN



2 DMPO

$$\mathrm{ST + Ox \longrightarrow ST^{\bullet +} + Red} \qquad (4)$$

$$\mathrm{ST^{\bullet +} + Nu^- \longrightarrow Nu{-}ST^{\bullet}} \qquad (5)$$

of electron transfer theory.[4] Because of the inverted electron distribution of the starting materials as compared with normal spin trapping, the process was denoted 'inverted spin trapping'. The radical cation of **1** was recently identified and studied by a combination of fast UV spectroscopy and EPR spectroscopy at 77 K in glassy alkyl chloride media.[5] Upon slow warming to 240 K, $\mathbf{1}^{\bullet +}$ reacted with chloride ion and gave the chlorine spin adduct.

We have recently discovered that radical cations are exceptionally persistent in 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP),[6] a non-nucleophilic alcohol with high ionizing power.[7] Half-lives of radical cations were of the order of 100 times longer in HFP than in trifluoroacetic acid, usually considered to be a good solvent for stabilizing radical cations. It was even possible to detect certain radical cations such as that of 1,4-dimethoxybenzene by EPR spectroscopy at room temperature in the presence of trinitromethanide ion,[8] a nucleophile of similar strength as fluoride ion.[9] Thus it appeared possible that inverted spin trapping might be suppressed in HFP and allow for a clear distinction between it and *bona fide* spin trapping. In what follows, we report studies in HFP of various experimental situations leading to the detection of spin adducts, and how

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† Part IV, see ref. 4(*d*).

Table 1 Known radical trapping reactions, performed in HFP at 22 °C

Trap	Radical	Source	EPR hfs constants in HFP/mT	EPR hfs constants in benzene[1d]/mT
PBN	$PhCOO^{\bullet}$	$(PhCOO)_2$–UV light	a^N 1.47, a^H 0.200[a]	PhCOO adduct: 1.32, 0.14
	$Ph^{\bullet}$		a^N 1.62, a^H 0.39[a]	Ph adduct: 1.44, 0.221
PBN	$CH_3^{\bullet}$	$(Bu^tO)_2$–UV light	a^N 1.67, a^H 0.330	1.42, 0.340
PBN	$CH_3^{\bullet}$	Me_4Sn–UV light	a^N 1.63, a^H 0.329[b]	1.42, 0.340
PBN	$C_2H_5^{\bullet}$	Et_4Sn–UV light	a^N 1.65, a^H 0.331	1.40, 0.320
PBN	$C_3H_7^{\bullet}$	Pr_4Sn–UV light	a^N 1.66, a^H 0.326[c]	1.46, 0.34
PBN	$i\text{-}C_3H_7^{\bullet}$	$Pr^i{}_4Sn$–UV light	a^N 1.64, a^H 0.257[b]	1.47, 0.258
MNP	$PhCH_2^{\bullet}$	$(Bu^tO)_2$–toluene (5%)–UV light	a^N 1.56, a^H 0.857 (2 H)[d]	1.50, 0.750 (2 H)
MNP	$CH_3^{\bullet}$	$(Bu^tO)_2$–UV light	a^N 1.73[d]	a^N 1.50
MNP	$Ph^{\bullet}$	$(PhCOO)_2$–UV light	a^N 1.57, a^H 0.260 (3 H), 0.123 (2 H)	1.25, 0.180 (3 H), 0.087 (2 H)
TBNB	$CH_3^{\bullet}$	$(Bu^tO)_2$–UV light or MeI–Bu_3SnH	a^N 1.41, $a^{m\text{-}H}$ 0.102 (2 H), a^H 1.51 (3 H)	1.17, 0.103 (2 H), 1.233 (3 H)
TBNB	$Ph^{\bullet}$	$(PhCOO)_2$–UV light	$a^N = 3.56$, a^H 0.106 (9 H), a^H 0.366 (1 H)[e]	$TBNB^{\bullet +}$: 3.60, 0.09 (9 H), 0.35 (1 H)
DMPO	$Ph^{\bullet}$	$(PhCOO)_2$–UV light	(*1*) *Unstable:* a^N 1.60, a^H 2.49.	Ph adduct: 1.38, 1.92
	$PhCOO^{\bullet}$		(*2*) *Stable:* a^N 1.09, a^H 1.41, a^H 0.072, 0.096 (1 H each)	PhCOO adduct: 1.22, 0.963, 0.087 (2 H)
DMPO	$C_2H_5^{\bullet}$	Et_4Sn–UV light	a^N 1.63, a^H 2.35	a^N 1.46, a^H 2.05

[a] At low [PBN] (25 mmol dm^{-3}) only the PhCOO adduct was detected; at high [PBN] (250 mmol dm^{-3}) both spin adducts were seen. [b] Weak signal. [c] Taken from the butyl adduct. [d] Intense triplet from $(Bu^t)_2NO^{\bullet}$, no Me signal seen as known from literature. [e] Only the spectrum of the TBNB radical cation could be analysed. The Ph–$TBNB^{\bullet}$ adduct was seen, but in low proportion and partly obscured by the $TBNB^{\bullet +}$ spectrum.

HFP can be used to identify cases of proper spin trapping.

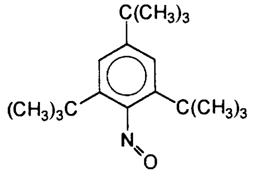
Results

Unambiguous cases of spin trapping in HFP

It was first necessary to study some unambiguous cases of spin trapping in HFP in order to see if radicals can be trapped in this solvent and if so, which characteristics the hfs constants of the spin adducts possess. The following spin traps were tested: *N*-*tert*-butyl-α-phenylnitrone **1** (abbreviated PBN), 2,2-dimethyl-3,4-dihydro-2*H* pyrrole *N*-oxide **2** (DMPO), 2-methyl-2-nitrosopropane **3** (MNP) and 2,4,6-tri(*tert*-butyl)nitrosobenzene **4** (TBNB), and the reactions were chosen to produce the radical to be trapped, $R^{\bullet}$, as a *secondary product of cleavage* of an initially formed, highly labile species, such as an excited state. By this criterion, the occurrence of reactions (2) and/or (5) is scrupulously avoided.

$(CH_3)_3C{-}N{=}O$

3 MNP



4 TBNB

Table 1 shows that spin trapping was possible with spin traps **1**–**4** in HFP with carbon centred radicals generated by photoinduced cleavage of suitable precursors. In two cases (PBN or DMPO photolysis with dibenzoyl peroxide) an oxygen centred radical, $PhCOO^{\bullet}$, was trapped and may represent an unambiguous case of spin trapping of an acyloxyl radical (see Discussion). For TBNB, the corresponding radical cation is a relatively stable one,[10] and therefore was formed as the major radical species, presumably resulting from the photooxidation of TBNB [eqns. (6) and (7)]. This means that $TBNB^{\bullet +}$ can coexist with benzoate ion in HFP. The analysis of the second, much weaker signal (not included in Table 1), was obscured by the middle group of the $TBNB^{\bullet +}$ spectrum, but from the width and appearance of the outer parts of the spectrum it probably originated from the phenyl–$TBNB^{\bullet}$ adduct.

$$TBNB \xrightarrow{h\nu} TBNB^{*} \qquad (6)$$

$$TBNB^{*} + (PhCOO)_2 \longrightarrow TBNB^{\bullet +} + PhCOO^{\bullet} + PhCOO^{-} \qquad (7)$$

The hfs constants of spin adducts in HFP were larger than in benzene, especially the nitrogen coupling constant, as expected in going from a nonpolar to a polar solvent. The coupling constants to the hydrogen on the α carbon were much less affected.

Also a few stable neutral radicals other than spin adducts were investigated in HFP (see Experimental section). They all behaved normally with respect to expected stability and hfs constants.

Attempted oxidation of mixtures of PBN and various nucleophiles by tris(4-bromophenyl)aminium ($TBPA^{\bullet +}$) in HFP and mixtures thereof

As shown previously, the oxidation of mixtures of PBN and various nucleophiles by tris(4-bromophenyl)aminium hexachloroantimonate,[4a] tetraphenylphosphonium hexachloroosmate(v)[4b] or photolysis in the presence of a suitable electron acceptor[4c] gave EPR signals of spin adducts when carried out in dichloromethane or acetonitrile with nucleophiles such as water, hydrogen diacetate ion, chloride ion, 3,5-lutidine (3,5-dimethylpyridine), triethyl phosphite, trinitromethanide or benzotriazolate ion.

In HFP, no spin adducts were detected over a period of 20 h from oxidation reactions with $TBPA^{\bullet +}$ involving the nucleophiles mentioned above, except triethyl phosphite and related phosphorus compounds (see below), the only EPR signal seen being that of $TBPA^{\bullet +}$. The latter decayed very slowly over this period. Separate UV spectroscopically monitored experiments at 20.0 °C gave the rate constants for the reaction between $TBPA^{\bullet +}$ and various nucleophiles of interest shown in Table 2. The negatively charged nucleophiles, chloride, bromide, hydrogen diacetate and benzotriazolate ion reacted very slowly, in the appropriate cases 10^7–10^8 times slower than in acetonitrile. Trinitromethanide ion also reacted slowly, but the rate compared with acetonitrile was only 3×10^3 times slower. Iodide ion reacted much faster in what presumably must be an electron transfer reaction. The neutral nucleophiles pyridine and 3,5-lutidine reacted slowly, whereas triethyl phosphite underwent a relatively fast reaction with $TBPA^{\bullet +}$.

Table 2 Rate constants for the reaction between TBPA$^{\cdot+}$ and various nucleophiles (as tetrabutylammonium salts in the relevant cases) in HFP at 20 °C. Rate data for reactions in acetonitrile were taken from refs. 23 and 32. Values of n_{CH_3I} were obtained from refs. 9 and 33

Nucleophile	log(k/dm^3 mol^{-1} s^{-1}) in HFP	Acetonitrile	Difference	n_{CH_3I}
Chloride ion	−4.4	2.7[a]	7.1	4.37
Bromide ion	−3.5	4.5[b]	8.0	5.79
Hydrogen diacetate ion	−4.1	4.8[a]	8.9	4.3[c]
Trinitromethanide ion	−3.1	0.4[b]	3.5	2.9
Pyridine	−3.4	—	—	5.23
3,5-Lutidine	−2.7	—	—	5.23[d]
Iodide ion	> 3	> 6[b]	—	7.42
Benzotriazolate ion	−2.8	—	—	—
Triethyl phosphite	−0.2	—	—	≈5.2[e]

[a] Oxidative substitution took place. [b] Electron transfer took place. [c] For acetate ion. [d] For pyridine. [e] For trimethyl phosphite.

In order to obtain detectable spin adduct concentrations, experiments were performed instead in mixtures of dichloromethane and HFP. Oxidation of PBN (0.13 mol dm^{-3}) and 3,5-lutidine (0.13 mol dm^{-3}) with TBPA$^{\cdot+}$ in dichloromethane–HFP (9:1 v/v) at 22 °C gave the spin adduct signal (a^{N1} = 0.235, a^{N2} = 1.33 and a^{H} = 0.297 mT; lit.,[4a] in dichloromethane: a^{N1} = 0.220, a^{N2} = 1.34 and a^{H} = 0.303 mT) superimposed on the broad singlet of TBPA$^{\cdot+}$. The latter disappeared within 20 min and the spin adduct signal was left. The same experiment, but performed in 70% dichloromethane–30% HFP (v/v), gave a weaker signal of the spin adduct superimposed on the more intense, very broad signal from TBPA$^{\cdot+}$ (Fig. 1). Both species were monitored with time; the spin adduct signal (a^{N1} = 0.270, a^{N2} = 1.34 and a^{H} = 0.270 mT) remained constant, but the signal from TBPA$^{\cdot+}$ decayed with $\tau_{1/2}$ = 17(1) min. In 60% dichloromethane–40% HFP (v/v) very little spin adduct was detectable and the signal of TBPA$^{\cdot+}$ decayed slower, $\tau_{1/2}$ being 46(4) min.

Tetrabutylammonium benzotriazolate did not give any spin adduct in dichloromethane–HFP (4:1, v/v). Only when the percentage of HFP was below ≈8.5% did a well developed spin adduct signal appear, a^{N} = 1.38, $a^{N'}$ = 0.342 and a^{H} = 0.178 mT, lit., for benzotriazol-1-yl–PBN$^{\cdot}$: a^{N} = 1.38, $a^{N'}$ = 0.352 and a^{H} = 0.160 mT in dichloromethane,[4b] a^{N} = 1.36, $a^{N'}$ = 0.42 and a^{H} = 0.17 mT in benzene.[11] At 10% [HFP], the signal was very weak and distorted; at 5% [HFP] a strong signal was seen, a^{N} = 1.38, $a^{N'}$ = 0.346 and a^{H} = 0.170 mT.

Among the nucleophiles studied, only triethyl phosphite with PBN and TBPA$^{\cdot+}$ gave a strong signal (denoted 'new') of a spin adduct in HFP, a^{N} = 1.52, a^{H} = 0.688 and a^{P} = 1.75 mT. With PBN, deuteriated in the α position ([^{2}H]PBN), the hydrogen signal appeared as a 1:1:1 triplet with a^{2H} = 0.102 mT (expected: 0.688/6.51 = 0.106 mT). This set of hfs constants differs appreciably from that determined earlier for the spin adduct (the 'old' signal) obtained by the same reaction in dichloromethane,[4a] a^{N} = 1.47, a^{H} = 0.348 and a^{P} = 2.33 mT, and a more detailed study was therefore performed in mixtures of HFP and dichloromethane. Table 3 shows that the two signals must be derived from different species; even by adding as little as 1% HFP to dichloromethane, both signals were obtained, but the new signal disappeared within 5–10 minutes after mixing. With an increasing proportion of HFP, the new signal became more stable, and the old one was not at all seen with ⩾30% HFP present. At 10% HFP the rate constants of disappearance and appearance, respectively, of the two signals were determined to be 0.067(3) and 0.061(4) min^{-1}. Thus it appears that the species corresponding to the new signal is a precursor of the species corresponding to the old signal.

Similar spectra were obtained from other phosphites, trimethyl phosphite giving a spin adduct with a^{N} = 1.52, a^{H} = 0.759 (with [^{2}H]PBN, a^{2H}s was 0.114 mT) and a^{P} = 1.64 mT. In dichloromethane, a signal with a^{N} = 1.46, a^{H} = 0.360 and a^{P} = 2.31 mT was obtained. Triphenyl phosphite, reacted with PBN in HFP in the same way as above, gave a strong signal with a^{N} = 1.52, a^{H} = 0.852 (with [^{2}H]PBN, a^{2H} was 0.129 mT) and a^{P} = 1.38 mT. In dichloromethane, a weaker signal was obtained, a^{N} = 1.45, a^{H} = 0.368 and a^{P} = 2.39 mT.

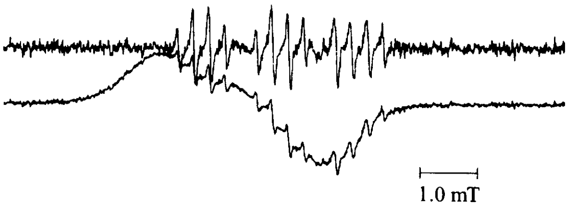


Fig. 1 EPR signal from the oxidation of a solution of PBN (0.13 mol dm^{-3}) and 3,5-lutidine (0.13 mol dm^{-3}) in HFP–dichloromethane (30:70 v/v) by TBPASbCl$_6$ (0.01 mol dm^{-3}) at 22 °C. The lower trace is the actual spectrum, whereas the upper one is the result of a forward–back Fourier transform operation to remove the low-frequency component.

Triphenylphosphine upon TBPA$^{\cdot+}$ oxidation in HFP in the presence of PBN gave rise to an EPR signal with a^{N} = 1.50, a^{H} = 0.557 (with [^{2}H]PBN, a^{2H} was 0.084 mT) and a^{P} = 1.25. In dichloromethane, no spin adduct signal was obtained from the same reaction.

Trinitromethanide ion

It is well known[9,12] that tetranitromethane upon photolysis (light of λ > 430 nm) with PBN in many solvents gives a spin adduct of a^{N} ≈ 1.45 and a^{H} ≈ 0.4 mT (see Table 4). It was suggested[12] that this signal should be assigned to (NO$_2$)$_3$C–PBN$^{\cdot}$, formed by trapping of the trinitromethyl radical. Later studies[4a,9] have indicated another possible mechanism of formation, reaction between trinitromethanide ion and PBN$^{\cdot+}$, as indicated in eqns. (6) and (7). The brilliant orange–red colour

$$C(NO_2)_4 \cdots PBN \longrightarrow PBN^{\cdot+}\ (NO_2)_3C^-\ NO_2 \quad (6)$$

$$PBN^{\cdot+} + (NO_2)_3C^- \longrightarrow (NO_2)_3C\text{–}PBN^{\cdot} \quad (7)$$

of the solutions attests to the formation of a charge transfer complex between PBN and tetranitromethane, and the electron transfer step of light excitation is well established.[13] Since the redox properties of trinitromethanide ion place it as a borderline case between species undergoing bond formation to radical cations and those undergoing electron transfer, the distinction between these mechanisms is not trivial.

Further evidence for the nature of this spin adduct was obtained by the resolution of a third coupling of 0.030 mT to the three nitrogens of the trinitromethyl group (in [^{2}H]chloroform) (see Fig. 2).[14] The use of [^{2}H]PBN also demonstrated the existence of this coupling in dichloromethane; the spectrum consisted of a triplet (a^{N} = 1.45 mT) of broad, partly resolved lines. The middle line could be resolved into 11 visible lines of

Table 3 EPR signals from the treatment of PBN and triethyl phosphite with $TBPA^{\bullet +}$ in mixtures of HFP and dichloromethane

% HFP in dichloromethane	a^H/mT	a^N/mT	a^P/mT	$\tau_{1/2}$/min	Signal intensity after 20 h
New signal					
0	—	—	—	—	—
1	0.731	1.48	1.60	1.3	—
5	0.712	1.48	1.64	4.3	—
10	0.700	1.49	1.67	10	—
30	0.699	1.49	1.70	246	Weak
100	0.688	1.52	1.75	Stable	Medium
Old signal					
0	0.348	1.466	2.33		Strong
1	0.391	1.47	2.22		Strong
5	0.418	1.49	2.16		Strong
10	0.430	1.50	2.14		Strong
30	—	—	—		—
100	—	—	—		—

Table 4 EPR data for the spin adduct obtained from the photolysis of tetranitromethane and PBN in various solvents (light of λ > 430 nm). Temperature 22 °C, unless otherwise noted

Solvent	a^N/mT	a^H/mT	$a^{N'}$ (3 N)/mT
Hexane	1.43	0.36	
Benzene[a]	1.44	0.42	
Dichloromethane	1.44	0.44	0.026
Dichloromethane at −60 °C	1.45	0.41	
Dichloromethane[b]	1.45	0.065	0.026
[^{2}H]Chloroform	1.46	0.42	0.030
Acetonitrile	1.47	0.50	
Diglyme[a]	1.44	0.45	

[a] From ref. 14. [b] Experiment with [^{2}H]PBN.

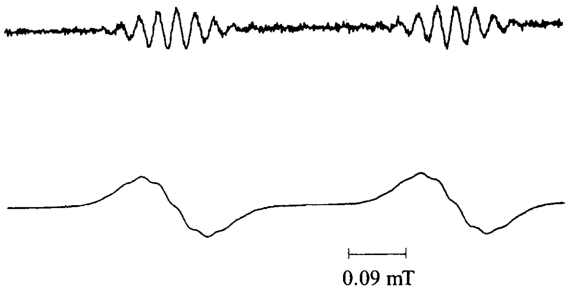


Fig. 2 EPR signal from the photolysis by light of λ > 430 nm of a deuteriochloroform solution of PBN (0.1 mol dm^{-3}) and tetranitromethane (0.5 mol dm^{-3}) at 22 °C. The middle pair of lines of the 3 × 2 line spectrum is shown, the lower trace being the actual spectrum and the upper one the result of a forward–back Fourier transform operation to remove the low-frequency component.

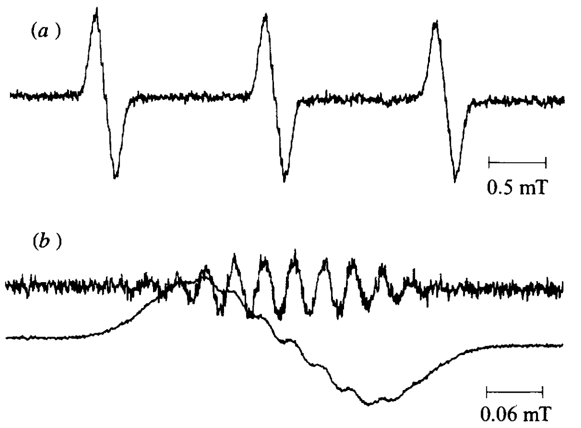


Fig. 3 (a) EPR signal from the photolysis by light of λ > 430 nm of a deuteriochloroform solution of [^{2}H]PBN (0.1 mol dm^{-3}) and tetranitromethane (0.5 mol dm^{-3}) at 22 °C. (b) The middle line of the triplet is shown, the lower trace being the actual spectrum and the upper one the result of a forward–back Fourier transform operation to remove the low-frequency component.

spacing 0.026 mT (Fig. 3); theoretically, with the expected coupling constant to one deuterium atom = 4.4/6.5 = 0.065 mT and a line-width of 0.030 mT, one should see 13 lines with spacing ≈0.03 mT. However, the outer pair of lines is too weak to be visible under the experimental conditions of Fig. 3.

With the additional evidence described above, the identity of the signal ascribed to $(NO_2)_3C$–$PBN^\bullet$ can hardly be in doubt. The mode of formation in the photochemical experiment, a case of inverted spin trapping [eqns. (6) and (7)], is also the most probable one in the range of solvents listed in Table 4. However, experiments carried out in HFP deviated significantly from those performed in other solvents and warranted a more detailed study of the possible mechanism for formation of $(NO_2)_3C$–$PBN^\bullet$.

Photolysis of PBN and tetranitromethane in HFP with light of λ > 430 nm gave a weak signal of a spin adduct with a^N = 1.55 and a^H = 0.489 mT; the third coupling to the trinitromethyl group nitrogens could not be determined due to the low intensity of the signal. The fact that these hfs constants are somewhat larger than those found in less polar solvents (Table 4) leaves no doubt that this signal corresponds to $(NO_2)_3C$–$PBN^\bullet$. It should be noted that the initial HFP solution of PBN and tetranitromethane is almost colourless, and that only a very weak band extends into the visible region (Fig. 4).

Oxidation of PBN (0.1 mol dm^{-3}) and tetrabutylammonium trinitromethanide (0.1 mol dm^{-3}) in HFP by $TBPA^{\bullet +}$ did not give an EPR spectrum which could be attributed to $(NO_2)_3C$–$PBN^\bullet$ over a period of 20 h; only the $TBPA^{\bullet +}$ signal was seen. Experiments with solutions in mixtures of HFP and dichloromethane showed that a weak spin adduct signal (a^N = 1.48 and a^H = 0.461 mT) started to appear at HFP concentrations of ⩽10%. At 5% [HFP], the signal was strong, a^N = 1.46, $a^{N'}$ = 0.028 (3 N) a^H = 0.446 mT.

In order to study the effect of spin trap radical cation reactivity on the reaction of eqn. (7), a range of 4-substituted PBNs with $E_{pa}(ST^{\bullet +}/ST)$ varying between 1.3 and 1.9 V (Ag/AgCl reference) were photolysed with tetranitromethane in HFP and DCM. The results are shown in Table 5. Only spin traps with $E°(ST^{\bullet +}/ST)$ ⩾ that of PBN gave rise to spin adducts from this reaction. No signals of any kind were seen in the two other cases.

Imidyl spin trapping in HFP

It was shown earlier[4d] that the trapping of imidyl radicals in a solvent like dichloromethane is a good example of the interpretational difficulties caused by spin trapping mechanisms other than the proper one. In many cases, the appearance of a

Table 5 Electrochemical data for spin traps and EPR data for spin adducts obtained by photolysis (light of λ > 430 nm) of solutions of 4-X-substituted PBNs and tetranitromethane

		CH_2Cl_2			HFP	
X	E_{pa}/V *vs.* Ag/AgCl	a^N/mT	a^H/mT	$a^{N'}$ (3 N)/mT	a^N/mT	a^H/mT
NO_2	1.91 [ref. 4(*b*)]	1.45	0.37	Not resolved	1.52	0.39
F	1.56	1.46	0.41	0.027	1.56	0.47
H	1.53 [ref. 4(*b*)]	1.44	0.44	0.026	1.55	0.49
CH_3	1.48	1.46	0.44	Not resolved	No signal seen	
OCH_3	1.29[a]	1.46	0.44	0.029	No signal seen	

[a] Reversible potential at a sweep rate of 2 V s^{-1}.

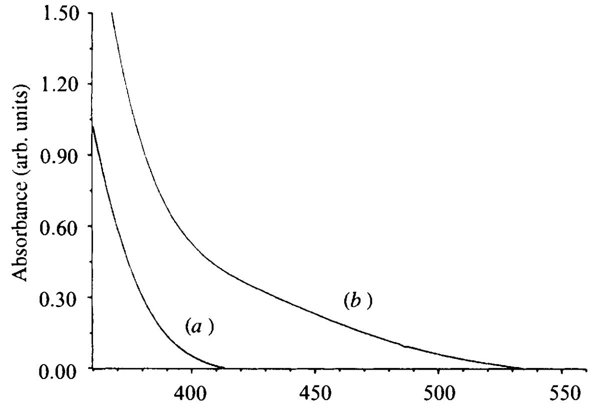


Fig. 4 UV-VIS spectrum of a solution of PBN (0.044 mol dm^{-3}) and tetranitromethane (0.45 mol dm^{-3}) in (*a*) HFP and (*b*) dichloromethane. Cell length, 2 mm.

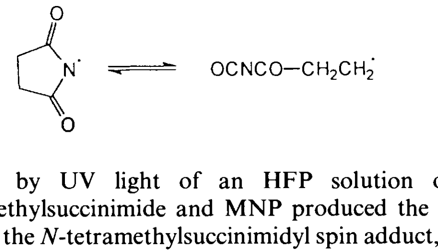
spin adduct signal could not be assigned unambiguously to a single mechanism from the available ones: spin trapping proper, inverted spin trapping and/or nucleophilic addition–oxidation. With HFP as the solvent, two factors militate strongly against the inverted and nucleophilic addition mechanisms [eqns. (4), (5) and (2), (3), respectively] in the trapping of imidyls, namely (*i*) the extremely low reactivity of charged nucleophiles in HFP (Table 2) and (*ii*) the fact that imide anions should be protonated to a large extent in HFP (p*K* of HFP 9.3, of imides > 10).[15] We therefore adopt as a working hypothesis that these mechanisms cannot operate in HFP on the time-scale of a normal spin trapping experiment (< 2 h). This was confirmed by the fact that as little as 2% HFP in dichloromethane was enough to almost completely suppress the formation of the *N*-tetramethylsuccinimidyl spin adduct of PBN from the oxidation of tetrabutylammonium tetramethylsuccinimidate and PBN by $TBPA^{•+}$. At this [HFP], the ratio of [HFP]/[Nu] was 3.5; at half this ratio, 1.7, a weak signal of the tetramethylsuccinimidyl spin adduct was detectable.

2-Methyl-2-nitrosopropane **3** (MNP) gave strong signals of imidyl spin adducts in dichloromethane when irradiated by light of λ > 530 nm in the presence of *N*-chloro- and *N*-bromo-imides (Im–X).[4d] In this wavelength region, only MNP can be excited, and it was therefore concluded that MNP* reduced Im–X which either cleaved to Im^- and $X^•$ (X = Br) and led to inverted spin trapping, or cleaved to $Im^•$ and X^- (X = Cl) giving the spin adduct either by proper trapping or *via* a succession of X–$MNP^•$ and nucleophilic substitution of X by Im^-.[16]

In HFP, MNP exhibited some characteristics which differed strongly from its behaviour in other solvents. In the solid state, MNP exists as a dimer which dissociates into the active spin trap, Bu^tNO, within minutes upon dissolution in solvents like benzene or dichloromethane and gives strongly blue-coloured solutions.[16] In HFP, the dissociation process was slow and led to a faintly bluish solution within hours (typically, a 0.1 mol dm^{-3} solution of the MNP dimer exhibited an absorbance of $\approx$0.25 at 650 nm after 3–4 h, no further change being observed over the next 20 h). Thus photochemical excitation of MNP in HFP with light of λ > 530 nm should be less efficient than in normal solvents, even with the precaution taken here, to use solutions of MNP dimer in HFP which had been aged in the dark for > 2 h. An advantage with the decreased photoactivity of MNP in HFP is that the normal strong triplet signal of $(Bu^t)_2NO^•$ seldom appeared in the experiments performed in HFP and, if it did, the intensity was fairly low. Separately, it was established by irradiation of MNP alone in HFP by light of λ > 530 nm or UV light that the $(Bu^t)_2NO^•$ triplet had a^N = 1.74 mT (1.58 mT in dichloromethane). The signal was medium strong and disappeared after 5–10 min of irradiation.

Irradiation for 30 min of MNP and Im–X (*N*-chloro- and bromo-succinimide, *N*-chloro- and bromo-glutarimide and *N*-bromotetramethylsuccinimide) in HFP with light of λ > 530 nm gave no signals of spin adducts, or of $(Bu^t)_2NO^•$. This shows that none of the three mechanisms listed above can operate in HFP or that any spin adduct formed is destroyed under the conditions employed, for example by being oxidized by the Im–X inevitably present in the solution.

With UV light, the classical homolytic photoinitiated cleavage mechanism of Im–Br should become feasible. This mechanism is assumed to operate in many photoinitiated *N*-bromoimide reactions,[17] and HFP should be a good medium to trap $Im^•$ and possibly also the product of its ring-opening, exemplified for succinimidyl radical in eqn. (8). The latter type of radical has only been detected in one case, and then in a reductive process from an open-chain halide.[18]



(8)

Irradiation by UV light of an HFP solution of *N*-bromotetramethylsuccinimide and MNP produced the 3 × 3 line signals of the *N*-tetramethylsuccinimidyl spin adduct, a^N = 1.71 and $a^{N'}$ = 0.182 mT (lit.,[4d] 1.64 and 0.181 mT in dichloromethane). The coupling to the *tert*-butyl group was not discernible. With *N*-bromoglutarimide, the same reaction gave a signal of the *N*-glutarimidyl spin adduct, a^N = 1.68, $a^{N'}$ = 0.192 and a^H = 0.027 (9 H) mT (lit.,[18] 1.59, 0.191 and 0.027 mT in CD_3CN).

On the other hand, when *N*-bromosuccinimide was subjected to the same treatment, no spin adduct signal was detectable. The differing behaviour of the two other *N*-bromoimides might be due to the higher ring-opening rate of succinimidyl radical [eqn. (8), k_8 = 8 × 10^4 s^{-1} in water and possibly as high as 10^8 s^{-1} in dichloromethane].[19] In this case, why is the ring-opened radical not trapped to give $OCNCOCH_2CH_2$–$MNP^•$? The EPR signal of such a species would have easily recognizable hfs constants, at least when judged from those of the closely related radical [$EtOCOCH_2CH_2$–$MNP^•$, a^N = 1.54, $a^{H\gamma}$ = 1.23 (2 H) and $a^{H\delta}$ = 0.063 (2 H) mT in 2,2,5,5-tetramethyltetrahydrofuran][18] and other radicals with a methylene group bonded to

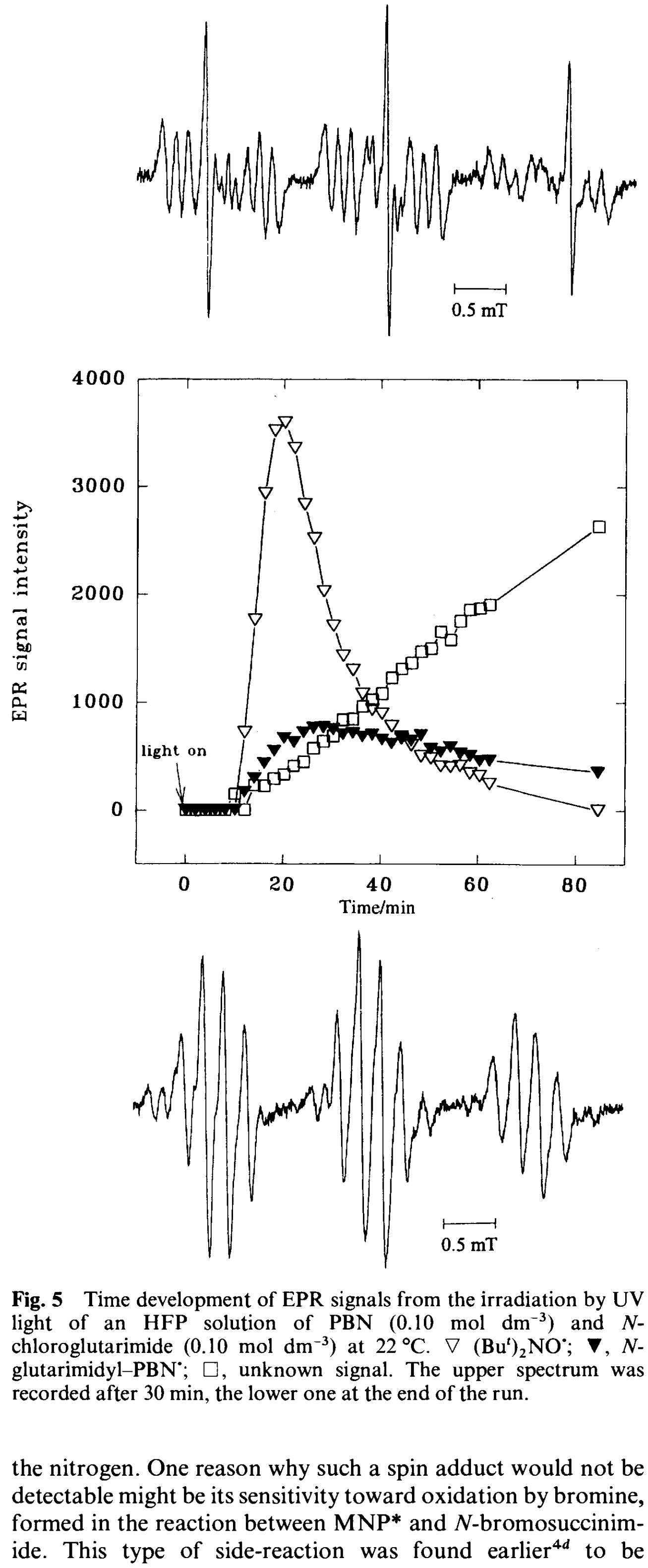


Fig. 5 Time development of EPR signals from the irradiation by UV light of an HFP solution of PBN (0.10 mol dm^{-3}) and *N*-chloroglutarimide (0.10 mol dm^{-3}) at 22 °C. ▽ $(\mathrm{Bu}^t)_2\mathrm{NO}^\bullet$; ▼, *N*-glutarimidyl–PBN$^\bullet$; □, unknown signal. The upper spectrum was recorded after 30 min, the lower one at the end of the run.

the nitrogen. One reason why such a spin adduct would not be detectable might be its sensitivity toward oxidation by bromine, formed in the reaction between MNP* and *N*-bromosuccinimide. This type of side-reaction was found earlier[4d] to be responsible for the lack of succinimidyl spin adduct from the irradiation of *N*-bromosuccinimide and PBN in dichloromethane and could be prevented by adding an alkene to catch the bromine atoms formed. However, this procedure introduced a new problem, namely that the intermediate bromoalkyl radical gave an additional spin adduct.

Irradiation of MNP, *N*-bromosuccinimide and cyclohexene by UV light in HFP gave a not entirely well defined EPR spectrum of a spin adduct $a^{\mathrm{N}} = 1.51$ and $a^{\mathrm{H}} = 0.17$ mT which we assign to 2-bromocyclohexyl–MNP$^\bullet$ ($a^{\mathrm{N}} = 1.40$ and $a^{\mathrm{H}} = 0.203$ mT in dichloromethane).[4d] There was no sign of any spin adduct with the characteristics expected for $\mathrm{OCNCOCH_2CH_2}$–MNP$^\bullet$.

Neither *N*-chlorosuccinimide nor *N*-chloroglutarimide in concentrations around 0.1 mol dm^{-3} gave any distinct spin adduct signals with MNP upon irradiation together by UV light in HFP. However, intense bubbling from the irradiated region was detrimental to spectral recording, and might be the cause of the rather defective signals. This necessitated measurements at lower [ImCl]. Also, under such conditions, any oxidizing effect by ImCl upon possibly formed spin adducts should be less pronounced.

Irradiation of MNP and *N*-chloroglutarimide (10 mmol dm^{-3}) by UV light in HFP in the first 3 min produced the 3 × 3 line signal of the *N*-glutarimidyl spin adduct ($a^{\mathrm{N}} = 1.68$, $a^{\mathrm{N}'} = 0.200$, a^{H} not possible to determine due to the low intensity of the spectrum). After another 5 min of irradiation, this signal had been replaced by a second 3 × 4 line signal, best described by the hfs constants $a^{\mathrm{N}} = 2.05$ and $a^{\mathrm{H}} = 0.481$ (3 H) mT.

The irradiation of PBN and either of *N*-bromosuccinimide, *N*-bromotetramethylsuccinimide or *N*-bromoglutarimide by UV light in HFP produced a 3 × 2 line signal, $a^{\mathrm{N}} = 1.45$ and $a^{\mathrm{H}} = 0.20$ mT. No signal due to the succinimidyl adduct ($a^{\mathrm{N}} = 1.44$, $a^{\mathrm{N}'} = 0.135$ and $a^{\mathrm{H}} = 0.54$ mT in dichloromethane, see also below) could be detected. In the presence of cyclohexene, the same experiments gave no signal whatsoever.

The irradiation of PBN and *N*-chlorosuccinimide by UV light in HFP produced a 3 × 3 × 2 line signal, $a^{\mathrm{N}} = 1.54$, $a^{\mathrm{N}'} = 0.133$ and $a^{\mathrm{H}} = 0.62$ mT, assigned to the succinimidyl adduct (hfs constants in dichloromethane, see above). In the beginning of the experiment, there was a fleeting appearence of the 3 × 2 signal also seen in the *N*-bromosuccinimide run, $a^{\mathrm{N}} = 1.45$ and $a^{\mathrm{H}} = 0.20$ mT, but it was later superseded by the signal from succinimidyl–PBN$^\bullet$.

Similarly, the irradiation of PBN and *N*-chloroglutarimide by UV light in HFP produced a 3 × 3 × 2 line signal, $a^{\mathrm{N}} = 1.56$, $a^{\mathrm{N}'} = 0.125$ and $a^{\mathrm{H}} = 0.82$ mT, lit.,[4d] in chloroform for *N*-glutarimidyl–PBN$^\bullet$, $a^{\mathrm{N}} = 1.44$, $a^{\mathrm{N}'} = 0.135$ and $a^{\mathrm{H}} = 0.735$ mT, with the time development shown in Fig. 5 (▼). In addition, the triplet from $(\mathrm{Bu}^t)_2\mathrm{NO}^\bullet$ (a^{N} 1.74 mT; separately generated by irradiation of MNP in HFP and found to be 1.74 mT) was seen (▽). After 20 min of irradiation a third signal appeared (Fig. 5, □) and grew steadily until it had almost completely replaced the two other signals after about 1.5 h. This signal is best described by the hfs constants $a^{\mathrm{N}} = 1.49$, $a^{\mathrm{N}'} = 0.200$ and $a^{\mathrm{H}} = 0.210$ (1 H) mT.

The experiment was repeated in the same way, but with [^{2}H]PBN instead. The first signal seen was a triplet of quintets, $a^{\mathrm{N}} = 1.55$, $a^{\mathrm{N}'} = 0.127$ and $a^{\mathrm{D}} = 0.127$ mT (expected 0.82/6.5 = 0.126 mT) which is ascribed to *N*-glutarimidyl–([^{2}H]PBN)$^\bullet$. An intermediate signal appeared after ≈20 min, but could not be analysed due to overlapping signals. The final signal (after 1 h of irradiation) was identical with that in the PBN experiment, $a^{\mathrm{N}} = 1.49$, $a^{\mathrm{N}'} = 0.200$ and $a^{\mathrm{H}} = 0.210$ (1 H) mT.

Discussion

HFP as a solvent for proper spin trapping

HFP has been shown to exert an extraordinarily large stabilizing effect upon radical cations, as seen in persistencies $> 10^2$ times larger than in trifluoroacetic acid under otherwise similar conditions. It is classified as a non-nucleophilic, strongly ionizing solvent by the usual solvolysis criteria, and appears to be the only solvent which is more polar than water on the Reichardt $E_{\mathrm{T}}(30)$ scale.[20] Exactly how this affects the stability of radical cations (or carbenium ions, for that matter) is not clear, but one significant component clearly must lie in the deactivation of nucleophiles which are present accidentally or deliberately are added. This effect is demonstrated by the rate data of Table 2; hard, charged nucleophiles are most strongly affected, presumably due to strong hydrogen bonding to HFP. Also 3,5-lutidine, a hard but uncharged nucleophile, exhibits strong deactivation in HFP, whereas the soft, charged species, iodide and trinitromethanide ion, are not so strongly affected. Among the nucleophiles studied, triethyl phosphite and related phosphorous compounds are the only ones which sustain high nucleophilic reactivity in HFP. It should also be kept in mind that HFP is a weak acid, pK = 9.3 (ref. 15), which makes the study of certain charged nucleophiles, such as cyanide ion and imide anions, impossible.

Notwithstanding the strong influence of HFP upon nucleophilic species, HFP does not seem to influence reactions of neutral radicals, as shown by the results of spin trapping in Table 1. Here alkyl or aryl radicals have been generated by follow-up reactions of photochemically produced radical ions and trapped by four of the commonly used spin traps (**1**–**4**). The trapping of PhCOO$^{\bullet}$ by PBN or DMPO in the photolysis with dibenzoyl peroxide is most likely of the proper type, in view of the expected strong attenuation of the reactivity of benzoate ion [eqn. (7)] toward ST$^{\bullet+}$. Also other stable neutral radicals, such as trityl, 2,4,6-tri-*tert*-butyl- and 2,4,6-triphenyl-phenoxyl, 2,2-diphenylindolinone-*N*-oxyl (3-oxo-2,2-diphenyl-2,3-dihydro-1*H*-indol-1-yloxy) and 1,1-diphenyl-2-picrylhydrazyl (DPPH) could be generated and kept stable in HFP without problems (see Experimental section).

Inverted spin trapping in HFP

Only one nucleophile, triethyl phosphite, gave a spin adduct in neat HFP upon oxidation by TBPA$^{\bullet+}$ in the presence of PBN. The same reaction failed to give spin adducts with water, hydrogen diacetate ion, chloride ion, 3,5-lutidine, trinitromethanide or benzotriazolate ion. In some cases studied in more detail, dilution with dichloromethane eventually established a critical concentration at and below which the spin adduct started to appear: 3,5-lutidine (40% HFP), benzotriazolate ion (8.5% HFP) and trinitromethanide ion (10% HFP). For the special case of tetramethylsuccinimide anion, the level of HFP allowing for observation of the spin adduct is below 2%, since only then will some percentage of the anion have escaped protonation.

Triethyl phosphite gave a new spin adduct in HFP, a^{N} = 1.52, a^{H} = 0.688 and a^{P} = 1.75 mT, which was stable for extended periods (Table 5). Earlier studies in dichloromethane[4a] showed the formation of a spin adduct with a^{N} = 1.47, a^{H} = 0.348 and a^{P} = 2.33 mT, then preliminarily assigned the structure of $(EtO)_3P^{+}$–PBN$^{\bullet}$. In the anodic oxidation of ArH and triethyl phosphite, this type of species is the first intermediate to be formed from an aromatic radical cation and triethyl phosphite,[21] followed by formation of the final product, a diethyl arylphosphonate, by the formal loss of ethyl cation, an electron and a proton [eqns. (9) and (10)], and it was

$$ArH^{\bullet+} + P(OEt)_3 \longrightarrow Ar(H)^{\bullet}P^{+}(OEt)_3 \qquad (9)$$

$$Ar(H)^{\bullet}P^{+}(OEt)_3 \xrightarrow[-e^{-},\,-H^{+}]{-Et^{+}} ArP(O)(OEt)_2 \qquad (10)$$

therefore natural to assume that the spin adduct would have this structure. However, from the data in Table 5 it is now obvious that the new spin adduct must be $(EtO)_3P^{+}$–PBN$^{\bullet}$ in view of the strong radical cation stabilizing properties of HFP, and that the previously recorded one should be of phosphonate type, $(EtO)_2P(O)$–PBN$^{\bullet}$. With decreasing polarity of the solvent, the latter becomes the more stable species. The photolysis of diethyl phosphonate, $(EtO)_2P(O)H$, with PBN in benzene was assumed earlier[22] to give $(EtO)_2P(O)$–PBN$^{\bullet}$, and the similarity of the hfs constants obtained, a^{N} = 1.475, a^{H} = 0.318 and a^{P} = 2.475 mT, with the ones obtained in dichloromethane (see above) supports this assignment. The same work also reported the generation of $(PhO)_2P(O)$–PBN$^{\bullet}$, a^{N} = 1.43, a^{H} = 0.325 and a^{P} = 2.525 mT, by photolysis of diphenyl phosphonate and PBN in benzene, presumably the same as that generated from triphenyl phosphite, PBN and TBPA$^{\bullet+}$ in dichloromethane, a^{N} = 1.45, a^{H} = 0.368 and a^{P} = 2.39 mT. The spin adduct formed in HFP, a^{N} = 1.52, a^{H} = 0.852 and a^{P} = 1.38 mT, then should be assigned to $(PhO)_3P^{+}$–PBN$^{\bullet}$. Finally, the spin adduct from triphenylphosphine, PBN and TBPA$^{\bullet+}$ in HFP in consequence should be assigned to Ph_3P^{+}–PBN$^{\bullet}$, supported by the similarity of the hfs coupling constants and the fact that conversion to a phosphonate adduct is not feasible.

The R_3P^{+}–PBN$^{\bullet}$ adduct in the reactions described above is formally the product of trapping a radical cation, $R_3P^{\bullet+}$, by PBN. To our knowledge, adducts of radical cations and spin traps have not been described before, and HFP therefore offers the possibility to study such species.

Trinitromethyl trapping in HFP

The results of Figs. 2 and 3 leave no doubt that the spin adduct obtained in various ways from PBN and trinitromethyl derivatives has the structure of $(NO_2)_3C$–PBN$^{\bullet}$. Its EPR signal (Table 4) has the characteristically large coupling to hydrogen for a *C*-attached radical, and the small coupling constant to the three nitrogens of the trinitromethyl group has been detected and measured in several solvents. The trinitromethyl spin adducts obtained with the 4-substituted PBNs also have similar EPR characteristics (Table 5).

Although the oxidation of PBN and trinitromethanide ion by TBPA$^{\bullet+}$ in HFP gave no spin adduct, the photolysis of tetranitromethane and PBN did produce a weak signal of what must be $(NO_2)_3C$–PBN$^{\bullet}$, as judged from the hfs constants and the mode of formation. The difference in behaviour might be explained in the following way. Trinitromethanide ion is relatively easy to oxidize, with an E_{pa} of $\approx$1.9 V (NHE), similar to that of bromide ion, known to undergo electron transfer to TBPA$^{\bullet+}$. Therefore, trinitromethanide ion should be a borderline case between nucleophilic and electron transfer reactivity.[23] The photochemical generation of the components to the right of eqn. (6) simultaneously produces trinitromethanide ion and PBN$^{\bullet+}$, the latter with E(PBN$^{\bullet+}$/PBN) $\approx$ 1.7 V and obviously capable of oxidizing trinitromethanide ion in a fast process. While it is likely that the trinitromethyl radical is a thermodynamically unstable species,[24] rapidly falling apart to a mixture of NO_2, NO and CO *via* dinitrocarbene,[25] there still might be a chance of it being trapped by PBN to give the weak signal actually observed. In agreement with this behaviour, spin traps of higher redox potential, give stronger signals in the photochemical reaction. In the thermal reaction between TBPA$^{\bullet+}$ and PBN–trinitromethanide ion, reactions will be much slower due to the lower ET reactivity of TBPA$^{\bullet+}$ [E°(TBPA$^{\bullet+}$/TBPA) = 1.3 V] and hence the trapping reaction much less efficient.

Imidyl spin trapping in HFP

The properties of HFP would seem to make it an ideal solvent for finding out how imidyl spin adducts are formed.[4d,18] Inverted spin trapping is ruled out both from the fact that imide anions are protonated in HFP and thus rendered inactive as nucleophiles, and from the general attenuation of nucleophilic reactivity in HFP experienced by hard, charged nucleophiles (Table 2). Thus it is a safe assumption to state that neither inverted spin trapping nor nucleophilic addition–oxidation should be possible with succinimide anions in HFP; only proper spin trapping should occur.

Imidyls have been shown to form photochemically by either homolytic cleavage of excited *N*-bromoimides[26] [eqn. (11)] or

$$\text{Im–Br} \xrightarrow{h\nu} \text{Im–Br}^{*} \longrightarrow \text{Im}^{\bullet} + \text{Br}^{\bullet} \qquad (11)$$

by photochemically induced formation and cleavage of the radical anions of *N*-chloroimides[4d,19b] [eqn. (12)] together with

Table 6 Predictions about the formation and observation of spin adducts in dichloromethane and HFP, based on eqns. (11)–(13)

Reaction type	Spin trapping mechanism	Spin trap	Light	Solvent	Predicted imidyl adduct	Observed imidyl adduct
Eqn. (11) + eqn. (13)	Proper	MNP	UV	DCM	Yes	Yes
	Inverted				Yes	
Eqn. (12)	Proper	MNP	$\lambda > 530$ nm	DCM	Yes	Yes
	Inverted				Yes	
Eqn. (13)	Inverted	MNP	$\lambda > 530$ nm	DCM	Yes	Yes
Eqn. (11)	Proper	MNP	UV	HFP	Yes	Yes
Eqn. (12)	Proper	MNP	$\lambda > 530$ nm	HFP	Yes	No
Eqn. (12)	Proper	MNP	UV	HFP	Yes	Yes
Eqn. (13)	Inverted	MNP	$\lambda > 530$ nm	HFP	No	No
Eqn. (11)	Proper	PBN	UV	DCM	Yes	Yes
Eqn. (12)	Proper	PBN	UV or $\lambda > 295$ nm	DCM	Yes	Yes
	Inverted				Yes	
Eqn. (13)	Inverted	PBN	UV	DCM	Yes	Yes
Eqn. (11) + eqn. (13)	Proper	PBN	UV	HFP	Yes	No[a]
Eqn. (12)	Proper	PBN	UV	HFP	Yes	Yes

[a] Only 3 × 2 line signal seen.

$$\mathrm{Im{-}Cl} + \mathrm{ST} \xrightarrow{h\nu} \mathrm{Im}^{\bullet} + \mathrm{Cl}^{-} + \mathrm{ST}^{\bullet +} \qquad (12)$$

the radical cation of the spin trap. In the latter reaction, reaction of chloride ion and the radical cation of the spin trap is prohibited in HFP. The reaction type of eqn. (12), applied to *N*-bromoimides, leads to the opposite cleavage mode[27] and thus formation of imide anion and bromine atom [eqn. (13)]. In

$$\mathrm{Im{-}Br} + \mathrm{ST} \xrightarrow{h\nu} \mathrm{Im}^{-} + \mathrm{Br}^{\bullet} + \mathrm{ST}^{\bullet +} \qquad (13)$$

HFP, only the two former reactions should give spin adducts, and then by proper spin trapping of $\mathrm{Im}^{\bullet}$, whereas the reaction of eqn. (13) should not give any spin adduct since also the $\mathrm{ST}^{\bullet +}$–imide anion reaction is 'forbidden' in HFP.

Table 6 shows the predictions about spin adduct sightings and the underlying mechanisms which are possible based upon eqns. (11)–(13) in dichloromethane and HFP, assuming that inverted spin trapping is not possible in HFP. The HFP results are less ambiguous than the ones obtained in dichloromethane, and indicate that proper spin trapping of imidyls can take place both with MNP and PBN.

One problem which remains to be addressed, is the possibility of trapping the ring-opened form of an imidyl radical,[4d,18] as exemplified for succinimidyl in eqn. (8). No spin adduct signal of the expected appearance [$a^{\mathrm{N}} \approx 1.6$, $a^{\mathrm{H}\gamma} \approx 1.2$, $a^{\mathrm{H}\delta} \approx 0.06$ (2 H) mT][18] was seen from photolysis of MNP and an *N*-bromoimide in HFP under the conditions of eqn. (11). Similar treatment of PBN and either of three *N*-bromoimides in HFP gave no imidyl adduct but a 3 × 2 line signal ($a^{\mathrm{N}} = 1.45$, $a^{\mathrm{H}} = 0.20$ mT) which in principle might qualify as the spin adduct of the ring-opened form. However, as seen from Table 1, alkyl radicals with a $\mathrm{CH_2}$ attached to the aminoxyl nitrogen have $a^{\mathrm{H}} > 0.3$ mT and it is not likely that the inductive effect of a remote OCNCO group would bring this value down to 0.20 mT. From the a^{H} values of different types of alkyl radical adducts,[1d] it is also to be expected that *N*-bromotetramethylsuccinimide should give an a^{H} different from the two others if the ring-opened form had been trapped (*tert*-alkyl *vs.* primary alkyl radical).

The experiment involving irradiation of PBN and *N*-chloroglutarimide in HFP (Fig. 5) might in principle have offered a second candidate for a spin adduct of a ring-opened radical. However, no such signal could be identified, possibly in part due to experimental problems with overlapping signals. Only the *N*-glutarimidyl adduct was identified with certainty, and the final, 3 × 4 line signal cannot correspond to the species sought since the same signal was obtained with PBN and [^{2}H]PBN. We therefore regard the proper trapping of the ring-opened form, obtained *via* initial imidyl generation, as an unsolved problem.

The radical cation of PBN, detectable in HFP?

The favourable properties of HFP for the generation of radical cations immediately suggests the possibility of generating a solution of $\mathrm{PBN}^{\bullet +}$ itself. However, despite many attempts to realize this goal with the usual thermal and photochemical oxidants, no credible EPR spectral candidate for $\mathrm{PBN}^{\bullet +}$ could be characterized. It was recently[5] shown that the rate constant of disappearance of $\mathrm{PBN}^{\bullet +}$ in aqueous solution is $2 \times 10^{6}\ \mathrm{s}^{-1}$, meaning that a very strong attenuation of its reactivity in HFP is necessary for EPR observation. In view of the drastic reactivity changes reported in Table 2, this would not seem to be completely unrealistic, and we plan to continue our efforts to obtain the solution EPR spectrum of $\mathrm{PBN}^{\bullet +}$.

Conclusions

HFP sustains proper spin trapping of various alkyl and aryl radicals, generated by cleavage of unstable radical species. It attenuates the reactivity of many nucleophiles in an unprecedented way and is therefore a suitable solvent for studying reactions in which the intermediacy of the radical cation of a spin trap is suspected. Thus it could be demonstrated that trinitromethyl radical can be trapped by PBN and certain of its 4-substituted derivatives, and also that imidyl radicals can be properly trapped in suitable experiments. In neat HFP, only strong nucleophiles like triethyl phosphite and triphenylphosphine underwent inverted spin trapping, yielding phosphonium spin adducts.

Experimental

Materials

All chemicals were of highest commercial quality available or otherwise prepared and purified as described in earlier reports.[4] 2,4,6-Triphenylphenoxyl radical was a gift from Professor K. Dimroth, University of Marburg, and 2,2-diphenylindolinone-*N*-oxyl a gift from Professor L. Greci, University of Ancona, Italy. The 4-X-PBNs and [^{2}H]PBN were prepared from 2-methyl-2-nitropropane and the appropriately substituted benzaldehydes according to published procedures.[28] To the best of our knowledge, [^{2}H]PBN has not been prepared before.

Methods

EPR spectra were recorded by the Upgrade Version ESP 3220-200SH of a Bruker ER-200D spectrometer. Photolyses were performed in the photolysis cavity (ER 4104 OR), using light from the 50 W high-pressure Hg lamp from Bruker (ER 202). The EPR experiments were performed as described earlier (100 kHz modulation frequency, microwave effect 0.4–1.6 mW, modulation amplitude 0.01–0.04 mT).

UV spectral kinetic measurements were performed on a Hewlett-Packard 8452A spectrophotometer, equipped with the appropriate software. Cells of path length 2 mm were used, and the disappearance of tris(4-bromophenyl)aminium ion was monitored at its maximum at 720 nm, the temperature of the cell block being kept at 20.0 °C.

Cyclic voltammetry was performed by the BAS-100 instrument in dichloromethane–tetrabutylammonium hexafluorophosphate (0.15 mol dm^{-3}). The values given in Table 5 were recorded at a sweep rate of 0.2 V s^{-1}, unless otherwise noted.

Generation and EPR properties of stable free radicals

Trityl radical was prepared from a solution of trityl chloride in HFP by reduction with tetrabutylammonium iodide. Trityl chloride was almost completely dissociated into trityl cation and chloride ion in HFP and the solution was stable for long periods.[29] The 2,4,6-tri(*tert*-butyl)phenoxyl radical was prepared by oxidation of a solution of sodium 2,4,6-tri(*tert*-butyl)phenolate in HFP by TBPA$^{\bullet +}$. The EPR spectra of these radicals, as well as those of the 2,4,6-triphenylphenoxyl radical, 2,2-diphenylindolinone-*N*-oxyl and DPPH, agreed well with published spectra,[30,31] taking into account the generally somewhat larger hfs constants in HFP. The solutions were stable for extended periods.

Acknowledgements

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