Generation of acyloxyl spin adducts from *N-tert*-butyl-*α*-phenylnitrone† (PBN) and 4,5-dihydro-5,5-dimethylpyrrole 1-oxide (DMPO) *via* nonconventional mechanisms

Lennart Eberson and Ola Persson

Department of Chemistry, Lund University, PO Box 124, S-221 00 Lund, Sweden

The reaction between *N-tert*-butyl-α-phenylnitrone (PBN) and carboxylic acids has been studied. Two mechanisms are discernible: the generation of $PBN^{\bullet +}$ by oxidation of PBN with a photochemically produced excited state [from either 2,4,6-tris(4-methoxyphenyl)pyrylium ion 2^+ or tetrachlorobenzoquinone 4], followed by reaction with RCOOH, or the addition of RCOOH to PBN to give a hydroxylamine derivative, followed by thermal oxidation by a weak oxidant. The latter sequence is the Forrester–Hepburn mechanism. In this mechanism, neither 2^+ nor 4 is effective as an oxidant, whereas bromine could be used. Thus only oxidants with redox potentials $\geqslant$ 0.1 V (SCE) are reactive enough to oxidize the intermediate hydroxylamine. This behaviour is in agreement with the redox reactivity of hydroxylamines.

For the cyclic nitrone, 4,5-dihydro-5,5-dimethylpyrrole 1-oxide (DMPO), acyloxyl spin adducts have been prepared by the photochemical route.

The reaction between dibenzoyl peroxide and PBN to give $PhCOO–PBN^{\bullet}$ is not catalysed by added PhCOOH. It could be shown that the rate of formation of $PhCOO–PBN^{\bullet}$ is compatible with the rate of thermal decomposition of dibenzoyl peroxide. Thus dibenzoyl peroxide does not support the Forrester–Hepburn mechanism, in agreement with its redox potential of *ca.* −0.2 V.

Introduction

Acyloxyl radicals $RCOO^{\bullet}$ undergo decarboxylation with rate constants in the range of 10^4–10^{12} s^{-1}, depending upon the structure of R [eqn. (1)].[1] The large variation in rate constants

$$RCOO^{\bullet} \longrightarrow R^{\bullet} + CO_2 \qquad (1)$$

R = Substituted vinyl $10^6 - 10^7$ s^{-1}
R = Substituted Ph $(2–200) \times 10^4$ s^{-1}
R = Substituted ethynyl $(2–5) \times 10^5$ s^{-1}
R = Alkyl $(1–11) \times 10^9$ s^{-1}
R = Ph 2×10^6 s^{-1}
R = $Ar_2C(OH)$ $(1–8) \times 10^{11}$ s^{-1}

makes acyloxyl radicals and their spin adducts important diagnostic tools for spin trapping mechanisms. In such reactions, transient radicals $X^{\bullet}$ react with spin traps, for example *N-tert*-butyl-α-phenylnitrone (PBN, **1**) and can be characterized by EPR spectral examination of the persistent aminoxyl radicals formed [eqn. (2)]. Second-order rate constants for spin trapping

$$\underset{\mathbf{1}}{Ph–CH{=}N(O)Bu^t} + X^{\bullet} \longrightarrow Ph–CH(X)–N(O^{\bullet})Bu^t \qquad (2)$$

$X^{\bullet} = PhCOO^{\bullet}$ (PhH) 5×10^6 dm^3 mol^{-1} s^{-1}
$X^{\bullet} = Ph^{\bullet}$ (PhH) 2×10^5 dm^3 mol^{-1} s^{-1}
$X^{\bullet} = Me_3C^{\bullet}$ (PhH) 1×10^4 dm^3 mol^{-1} s^{-1}
$X^{\bullet} = Cl_3C^{\bullet}$ (CCl_4) 7×10^4 dm^3 mol^{-1} s^{-1}.

reactions by PBN at room temperature generally fall in the region between 1×10^4 and 10^7 dm^3 mol^{-1} s^{-1} for radicals of interest in the context of acyloxyl radical chemistry.[2]

An analysis of the kinetics of the putative trapping of acyloxyl radicals shows that it should be possible to trap with PBN the benzoyloxyl radical, generated by, for example, the thermal or photolytic decomposition of dibenzoyl peroxide, before it has had time to undergo decarboxylation. On the other hand, the decarboxylation rate of acetoxyl radical, 2×10^9 s^{-1}, is too high for trapping to be feasible,[3] the concentration of spin adduct being too low for EPR spectral detection if the rate of trapping of acetoxyl is taken to be the same as that of trapping the benzoyloxyl radical, 5×10^6 dm^3 mol^{-1} s^{-1}. This rate constant is presumably a maximal one; a lower estimate[4] gives 4×10^5 dm^3 mol^{-1} s^{-1} at 40 °C.

Yet acetoxyl radical spin adducts of PBN have been described. A number of oxidizing systems, such as $Pb(OAc)_4$ + a trace of HOAc, Me_3PbOAc–*hν*, $Hg(OAc)_2$–*hν*, AgOAc + Br_2, MeCOOOH–HOAc or $KMnO_4$–HOAc, in benzene gave AcO–$PBN^{\bullet}$, which was considered evidence for trapping of the acetoxyl radical.[5] Somewhat later,[6] it was shown that AcO–$PBN^{\bullet}$ was produced under mildly oxidizing conditions, oxidation by dioxygen of a solution of PBN in acetic acid containing some potassium acetate. This experiment excludes acetoxyl radical as an intermediate, since dioxygen [$E°(O_2/O_2^{\bullet -}) = -0.4$ V *vs.* saturated calomel electrode (SCE)] cannot possibly oxidize acetate ion [$E°(AcO^{\bullet}/AcO^{-}) = 2.2$ V *vs.* SCE] to acetoxyl radical.[7] Instead, a nucleophilic addition–oxidation mechanism was proposed, shown in its general form in eqns. (3)–(5), HA =

$$A^{-} + PBN \rightleftharpoons A–PBN^{-} \qquad (3)$$

$$A–PBN^{-} + H^{+} \rightleftharpoons A–PBN(H) \qquad (4)$$

$$A–PBN(H) + Ox \longrightarrow A\text{-}PBN^{\bullet} + H^{+} + Red \qquad (5)$$

HOAc and Ox = a general one-electron oxidant. The intermediate hydroxylamine is oxidized even by weak oxidants and thus it was concluded that 'results obtained from spin trapping experiments should be used with caution whenever anionic species are present in the reaction mixture'.[6]

Acetoxyl radical, as well as other aliphatic acyloxyl radicals, could also be formally 'trapped' when solutions of the appropriate tetrabutylammonium carboxylates and PBN [$E°(PBN^{\bullet +}/PBN) = 1.49$ V) were oxidized by strong oxidants, such as tris(4-bromophenyl)ammoniumyl or hexachloroosmate(v) [both with $E°$ above 1.1 V *vs.* SCE]; in such cases, the mechanism proposed involved the oxidation of PBN to its radical cation, followed by reaction with a carboxylate ion [eqns. (6)–(7)].[8]

---

† IUPAC name: *N*-(benzylidene)-*tert*-butylamine *N*-oxide.

$$\mathrm{PBN} \xrightarrow{-e^-} \mathrm{PBN}^{\bullet +} \qquad (6)$$

$$\mathrm{PBN}^{\bullet +} + \mathrm{RCOO}^- \longrightarrow \mathrm{RCOO{-}PBN}^{\bullet} \qquad (7)$$

We have recently shown [9] that acids HA can act as promotors or autocatalysts for the formation of spin adducts in the presence of oxidants of the general formula R–X, where the corresponding radical anion $\mathrm{R{-}X}^{\bullet -}$ undergoes fast cleavage. The initiating steps again involve formation of a hydroxylamine, as in eqns. (3) and (4), and $\mathrm{RX}^{\bullet -}$ cleaves to $\mathrm{R}^{\bullet}$ and X^- thereby generating HX [eqn. (8)] which can be entered into eqn. (3), *etc.* If HX = HA, the autocatalytic case is at hand.[10]

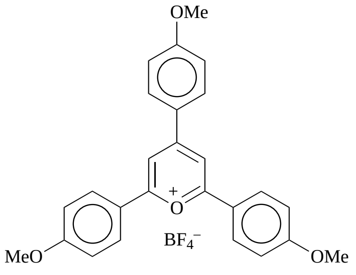
$$\mathrm{A{-}PBN(H)} + \mathrm{R{-}X} \longrightarrow \mathrm{A{-}PBN}^{\bullet} + \mathrm{H}^+ + \mathrm{R}^{\bullet} + \mathrm{X}^- \qquad (8)$$

In this context, carboxylic acids were used in the role of HA and various weak oxidants explored. We then became intrigued by the fact that 2,4,6-tris(4-methoxyphenyl)pyrylium ion [**2**$^+$; $E°(\mathbf{2}^+/\mathbf{2}^{\bullet}) = -0.6$ V *vs.* SCE; this compound is an efficient photoelectron transfer oxidant in its triplet state $^{\mathrm{T}}\mathbf{2}^{+*}$ with $E°(^{\mathrm{T}}\mathbf{2}^{+*}/\mathbf{2}^{\bullet}) = 1.8$ V *vs.* SCE][11,12] could seemingly be used to oxidize mixtures of PBN and various RCOOH to give RCOO–PBN$^{\bullet}$, thus providing easy access to these aminoxyl radicals. We now report the results of these studies.

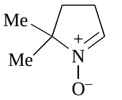
Results

Reaction of PBN, acetic acid and 2$^+$; effect of light

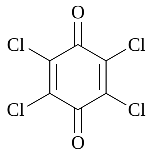
Our initial experiments involved preparation of the PBN–RCOOH solution in an EPR tube, deaeration by argon bubbling and final addition of the **2**$^+$ salt. These operations were carried out in laboratory light and the problem of a possibly photo-initiated reaction during the short interval (*ca.* 60 s) between the addition of **2**$^+$ and the introduction of the sample tube into the EPR cavity therefore must be addressed. The reaction with acetic acid was chosen for a closer study.



2^+ $\mathrm{BF_4}^-$



3



4

Mixing PBN (0.10 mol dm^{-3}) and $\mathrm{CH_3COOH}$ (0.35 mol dm^{-3}) in dichloromethane with rigorous exclusion of oxygen in a completely darkened environment gave an EPR-silent solution (Fig. 1, circles). After 20 min, **2**$^+$ (*ca.* 1 mmol dm^{-3}) was added to the solution and the paramagnetic activity monitored at intervals during 0.5–1 h. No paramagnetic activity was detected. The sample tube was then exposed to laboratory light for 20 s which led to the development of a strong signal of $\mathrm{CH_3COO{-}PBN}^{\bullet}$. Thus we conclude that the mixing of samples under conditions where the sample tube is exposed to laboratory light for a short period, allows for photogeneration of $\mathrm{CH_3COO{-}PBN}^{\bullet}$, and that **2**$^+$ is not active as a thermal oxidant in eqn. (5), A = $\mathrm{CH_3COO}$.

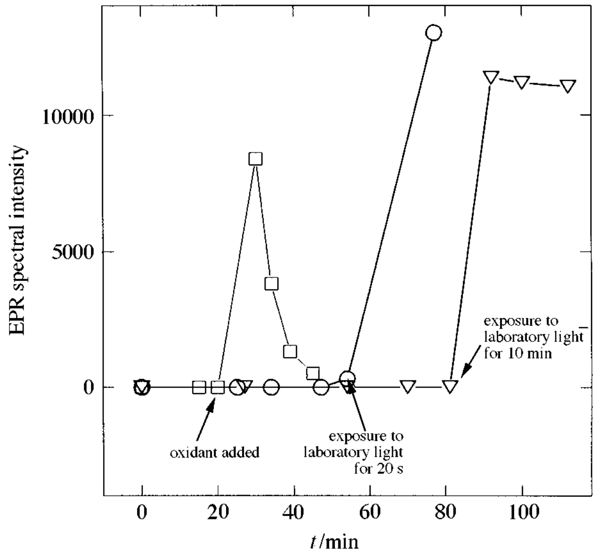


Fig. 1 Development of the $\mathrm{CH_3COO{-}PBN}^{\bullet}$ signal from solutions of PBN (0.10 mol dm^{-3}) and $\mathrm{CH_3COOH}$ (0.35 mol dm^{-3}) in dichloromethane, prepared in a completely darkened room. The oxidant was added after 20 min, and exposure to laboratory light was made at the points indicated. Circles, **2**$^+$ (1 mmol dm^{-3}); triangles, **4** (20 mmol dm^{-3}); squares, $\mathrm{Br_2}$ (50 mmol dm^{-3}).

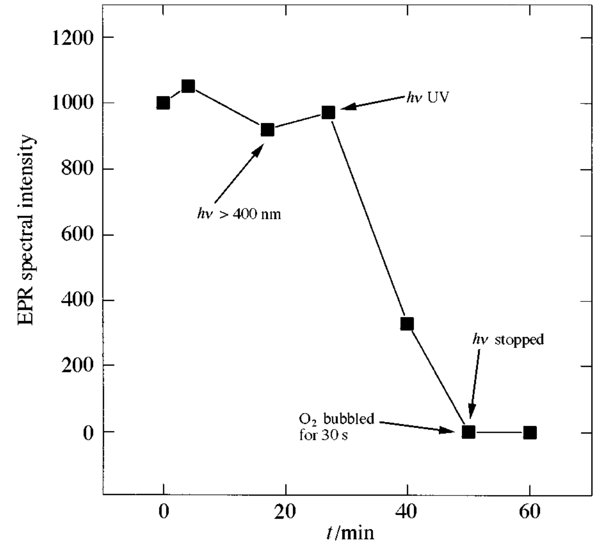


Fig. 2 Development of the $\mathrm{CH_3COO{-}PBN}^{\bullet}$ signal from a solution of PBN (0.10 mol dm^{-3}) and $\mathrm{CH_3COOH}$ (0.35 mol dm^{-3}) in dichloromethane, prepared under LLE conditions, upon irradiation and renewed treatment with dioxygen

A similar experiment was performed with the stronger oxidant, chloranil [tetrachlorobenzoquinone, **4**, $E°(\mathbf{4}/\mathbf{4}^{\bullet -}) = -0.02$ V *vs.* SCE], with similar results. No spin adduct was detected with complete exclusion of light, whereas exposure to laboratory light for 10 min developed a signal of AcO–PBN$^{\bullet}$, although not as rapidly as in the case of **2**$^+$ (see Fig. 1, triangles). A still stronger oxidant, bromine [$E°(\mathrm{Br_2}/\mathrm{Br_2}^{\bullet -})$ *ca.* 0.1 V] gave a strong signal for $\mathrm{CH_3COO{-}PBN}^{\bullet}$ even in complete darkness (Fig. 1, squares). This spectrum decayed rapidly with formation of *N*-benzoyl-*N*-*tert*-butylaminoxyl radical (PBNOx, not shown). Finally, the strong oxidant, 2,3-dichloro-5,6-dicyanobenzoquinone DDQ [$E°(\mathrm{DDQ}/\mathrm{DDQ}^{\bullet -}) = 0.54$ V], was employed in a similar experiment but now the only radical species detected within 2 min from mixing was $\mathrm{DDQ}^{\bullet -}$ in high concentration.

Reaction of PBN, acetic acid and oxygen

The results above raise the question why dioxygen [$E°(\mathrm{O_2}/\mathrm{O_2}^{\bullet -})$ *ca.* −0.4 V] can act as an oxidant toward PBN–HOAc but not **4**. Therefore we repeated the original Forrester–Hepburn experiment,[6] mixing PBN (0.08 mol dm^{-3}) and KOAc (0.090 mol dm^{-3}) in acetic acid in laboratory light with access of air for a short period before deaeration by argon. A weak signal of AcO–PBN$^{\bullet}$ was obtained (Fig. 2). This signal was unaffected by irradiation with light of $\lambda > 400$ nm but decreased to zero on irradiation with UV light.

Table 1 Hfs constants for spin adducts formed in the reaction between PBN and RCOOH (**5**–**18**) in the presence of $\mathbf{2}^+$ BF_4^- under LLE conditions or with irradiation by light of $\lambda > 400$ nm. For pK values, see ref. 33

No.	R in RCOOH	pK of RCOOH	Conditions[a]	a^N/mT	a^H/mT
5	H	3.75	DCM–LLE	1.33	0.144[b]
5	H		DCM–$h\nu$	1.33	0.143[b]
5	H		AN–LLE[c]	1.32	0.147[b]
5	H		AN–$h\nu$[d]	1.32	0.149[b]
5	H		HFP–LLE		No signal
5	H		HFP–$h\nu$ (UV)[c]	1.43	0.15[e]
5	H		Benzene–LLE[c]	1.31	0.14[b]
5	H		Benzene–$h\nu$	1.31	0.138[b]
6	D		DCM–LLE	1.35	0.147[f]
7	H_3C	4.76	DCM–LLE[g]	1.36	0.164
7	H_3C		HFP–LLE		No signal
7	H_3C		HFP–$h\nu$	1.47	0.205
7	H_3C		HFP–$h\nu$ (UV)	1.47	0.205
8	Me_2CH	4.84	DCM–LLE	1.35	0.161
8	Me_2CH		DCM–$h\nu$[d,h]	1.35	0.161
9	Me_3C	5.03	DCM–LLE[i]	1.34	0.149
9	Me_3C		DCM–$h\nu$[d,h]	1.34	0.149
9	Me_3C		HFP–LLE		No signal
9	Me_3C		HFP–$h\nu$ (also UV)[c]	1.45	0.182
10	CF_3	0.52	DCM–LLE[j]	1.29	0.148
10	CF_3		DCM–$h\nu$	1.29	0.148
11	Cl_3C	0.52	DCM–LLE	1.28	0.129
11	Cl_3C		DCM–$h\nu$	1.28	0.135
12	Ph	4.20	DCM–LLE[k]	1.35	0.160
12	Ph		DCM–$h\nu$	1.35	0.160
12	Ph		HFP–LLE		No signal
12	Ph		HFP–$h\nu$ (also UV)[c]	1.47	0.206
13	4-NO_2-Ph	3.44	DCM–$h\nu$[d]	1.34	0.166
14	4-MeO-Ph	4.47	DCM–$h\nu$[h]	1.41	0.282
14	4-MeO-Ph		HFP–LLE or $h\nu$	—	—
15	4-F-Ph	4.14	DCM–LLE	1.35	0.156
16	4-NH_2-Ph	4.89	DCM–$h\nu$[c]	1.49	0.24
17	4-MeO-naph	4.31	DCM–LLE[c,l]	1.35	0.156
17	4-MeO-naph		DCM–$h\nu$[d,h]		
18	$Ph_2C(OH)$	3.05	DCM–LLE[m]	1.33	0.131
18	$Ph_2C(OH)$		DCM–$h\nu$[c]	1.31	0.132

[a] LLE means exposure of the sample tube to laboratory light for *ca.* 60 s. DCM = dichloromethane, AN = acetonitrile, HFP = 1,1,1,3,3,3-hexafluoropropan-2-ol. [b] Coupling to two H (the second one to *H*-COO). [c] Weak signal. [d] The signal from $Bu^t_2NO^•$ also appeared ($a^N = 1.58$ mT). [e] Doublet (the coupling to *H*-COO was 0.20 mT). [f] No further resolution due to *D*-COO was seen. [g] Lit.[8b]: 1.36, 0.17 mT; in benzene[34] 1.27–1.31, 0.17–0.20 mT; 1.36, 0.18 mT; in acetic acid[34] 1.40, 0.20 mT. [h] Broad signal centred around $g = 2.003$ also seen. [i] Lit.,[8b]: 1.36, 0.15 mT. [j] Lit.[8a] 1.33, 0.14 mT. [k] Lit.[17]: 1.35, 0.15 mT; in benzene[34]: 1.26–1.29, 0.13–0.15 mT. [l] Lit.[35] : 1.29, 0.14 mT. [m] Second 3 × 2 lines signal: $a^N = 1.29$, $a^H = 0.104$ mT; the assignment of the two signals might be the reverse one.

The EPR-silent solution was then bubbled with dioxygen for 30 s, purged with argon and the EPR activity monitored. No signal whatsoever was detected after this treatment.

Redox reactivity of hydroxylamines

Literature reports on the electrochemistry of hydroxylamines give widely differing redox potentials for the oxidation of hydroxylamines under various conditions, as exemplified here by *N*-phenylhydroxylamine. In aqueous solution at pH 13, the redox active species must be the anion, $E_{1/2}(PhNHO^•/PhNHO^-)$ being −0.48 V *vs.* SCE at the Hg anode.[13a] Similarly, what was denoted '$E_{ox(A-)}$' = −0.75 V was determined by cyclic voltammetry at a Pt anode in dimethyl sulfoxide-Et_4NPF_6;[13b] this again is $E_{pa}(PhNHO^•/PhNHO^-)$. On the other hand, the peak potential measured by cyclic voltammetry of PhNHOH in acetonitrile–$NaClO_4$ at a glassy carbon electrode must refer to $E_{pa}(PhNHOH^{•+}/PhNHOH)$, a value of 0.45 V being reported.[14] Addition of a base, pyridine, gave an extra peak at a lower potential, 0.15 V, ascribed to oxidation of a 'partially ionized' hydroxylamine (pK_a of RNHOH estimated to be 12–13, see ref. 15).

In view of these discrepancies, we have determined $E_{pa}(PhNHOH^{•+}/PhNHOH)$ and $E_{pa}(PhNHO^•/PhNHO^-)$ in acetonitrile–Bu_4NBF_4 by cyclic voltammetry at a Pt anode, and obtained 0.61 and −0.75 V, respectively. The base used in the latter measurement was butyllithium (in deficit with respect to PhNHOH).

Reaction of PBN, RCOOH and 2^+ in laboratory light

Table 1 lists spin adducts obtained from the LLE (LLE = 'laboratory light exposed' being defined as 'exposed to laboratory light for ⩽60 s during mixing of the sample') reaction between PBN and RCOOH (**5**–**18**) in the presence of $\mathbf{2}^+$ (*ca.* 1 mmol dm^{-3}). Most reactions were performed in dichloromethane, but other solvents were tried for specific purposes, for example 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) in which nucleophilic reactivity is known to be strongly curtailed.[16] In general, EPR spectra with the expected hyperfine splitting (hfs) constants for acyloxyl adducts of PBN were recorded (*i.e.* showing typically low values of both a^N and a^H) which in the appropriate cases agreed with literature values.

It should be noted first that none of the LLE experiments in HFP gave any paramagnetic signal from spin adducts, in line with the strong attenuating effect exerted by HFP on the reactivity of nucleophiles. Thus the mechanisms involving nucleophilic attack [eqns. (3)–(4) and (7)] will be suppressed in this solvent, as found previously.[17] No such effect was noted with dichloromethane, benzene or acetonitrile.

Formic acid **5** gave a previously unknown spin adduct with a 1 : 2 : 1 triplet splitting due to two hydrogens with identical hfs constants, one from the α-H of PBN and the second from HCOO. The triplet structure persisted in both benzene and acetonitrile. With D-COOD (**6**) a doublet was seen since the coupling to *D*-COO could not be resolved.

Acetic acid (**7**) gave a strong signal, as already mentioned.

Table 2 Hfs constants for spin adducts formed in the reaction between PBN and ROH (**19**–**22**) in dichloromethane in the presence of $\mathbf{2}^+$ BF_4^- under LLE conditions or with irradiation by light of $\lambda > 400$ nm. For p*K* values, see ref. 33

No.	R in ROH	p*K* of ROH	Conditions	a^N/mT	a^H/mT
19	Ph_2CH	15.4 ($PhCH_2OH$)	LLE[a]	1.35	0.156
19	Ph_2CH		$h\nu$[b,c,d]	—	—
20	$Ph_2CCO_2CH_3$	—	LLE[a]	1.32	0.16
20	$Ph_2CCO_2CH_3$		$h\nu$[e]	1.32	0.16
21	Et	15.9	LLE[a,f]	1.401	0.225
21	Et		$h\nu$	1.399	0.227
22	Bu^t	19.2	LLE[a,g]	1.44	0.21
22	Bu^t		$h\nu$[b,c,d]	—	—

[a] Weak signal. [b] The signal from $Bu^t_2NO^{\bullet}$ also appeared ($a^N = 1.58$ mT). [c] Broad signal centred around $g = 2.003$ also seen. [d] The 3 × 2 lines signal disappeared while the signals referred to in [b,d] appeared. [e] The 3 × 2 signal increased in intensity for a short period and then decayed upon prolonged irradiation. [f] Lit.,[34] in ethanol: 1.44, 0.26 mT. [g] Lit.,[34] in benzene: 1.44, 0.19 mT.

Both stronger (trifluoro- and trichloro-acetic acid **10** and **11**) and weaker aliphatic acids (dimethyl- and trimethyl-acetic acid **8** and **9**) gave signals assigned to the corresponding acyloxyl adducts. The signal from **11** was shortlived and only lasted for *ca.* 5 min after mixing. Benzoic acid **12** and 4-fluorobenzoic acid **15** reacted smoothly, whereas 4-nitro- (**13**), 4-methoxy- (**14**) and 4-aminobenzoic acid (**16**) did not react. Benzilic acid (**18**), corresponding to the least stable acyloxyl radical known [eqn. (1)],[1f] reacted with formation of two spin adducts, of which one was assigned to the acyloxyl type and the second one to the alkoxyl type. Separately, it was shown that a few alcohols (**19**–**22**), including methyl benzilate **20**, undergo the same type of reaction (Table 2) under similar conditions.

Photochemical reaction of PBN, RCOOH and $\mathbf{2}^+$

Deliberate irradiation with light of $\lambda > 400$ nm to ensure that only $\mathbf{2}^+$ was excited (λ_{max} in acetonitrile 422 nm,[11] in HFP 408 nm) produced stronger signals of RCOO–PBN$^{\bullet}$ from reactions performed in dichloromethane, acetonitrile or benzene, typically by at least one order of magnitude. Sometimes, other signals were detectable, such as the persistent triplet from $Bu^t_2NO^{\bullet}$, a known product from the photolysis of PBN,[12] and a broad unresolved feature centred around $g = 2.003$ which presumably was due to $\mathbf{2}^{\bullet}$,[18] one of the products of the redox process initiated by the photochemical reaction [eqns. (9)–(10)]. It should be noted that RCOO–PBN$^{\bullet}$ was formed by photochemical activation also in HFP, presumably an effect of the higher rate of generation of PBN$^{\bullet+}$ under these conditions. It is likely that RCOO–PBN$^{\bullet}$ originates from the reaction between PBN$^{\bullet+}$ and RCOOH [eqn. (11)]. In another context,[17] we have found that PBN$^{\bullet+}$ does react with certain nucleophiles in HFP, especially neutral ones which are not so strongly solvated as are anions by HFP.

$$\mathbf{2}^+ \xrightarrow{h\nu\ >400\ \text{nm}} \mathbf{2}^{+}* \qquad (9)$$

$$\mathbf{2}^{+}* + \text{PBN} \longrightarrow \mathbf{2}^{\bullet} + \text{PBN}^{\bullet+} \qquad (10)$$

$$\text{PBN}^{\bullet+} + \text{RCOOH} \longrightarrow \text{RCOO–PBN}^{\bullet} + \text{H}^+ \qquad (11)$$

The increased rate of production of RCOO–PBN$^{\bullet}$ in the HFP–*hν* reaction made possible the resolution of the coupling to the two hydrogens in HCOO–PBN$^{\bullet}$, the coupling constant to the formyl hydrogen being increased from 0.14 to 0.20 mT due to the high polarity of HFP.[17]

The CH_3COO–PBN$^{\bullet}$ signal built up to a fairly high level during photolysis. When the light was turned off, the signal decayed with a half-life of *ca.* 1 min.

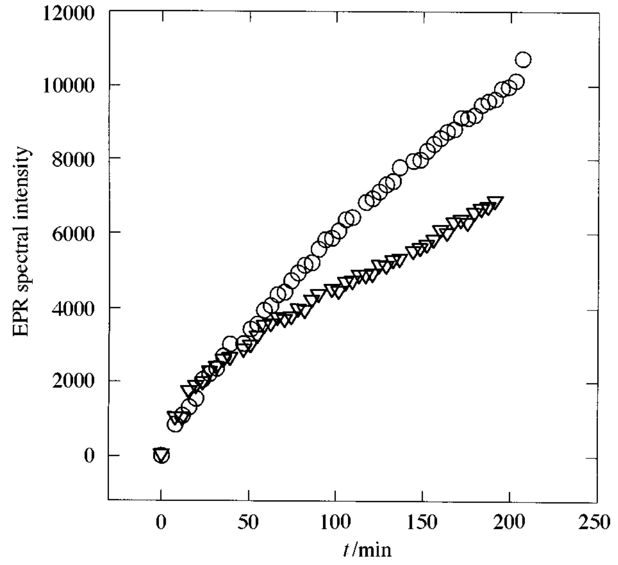


Fig. 3 Time development of the EPR signal of PhCOO–PBN$^{\bullet}$ in the reaction of dibenzoyl peroxide (0.135 mol dm^{-3}) and PBN (0.10 mol dm^{-3}) in dichloromethane at 22 °C. Triangles: no additive; circles: PhCOOH (0.064 mol dm^{-3}) added.

Formation of PhCOO–PBN$^{\bullet}$ by the spontaneous reaction between PBN and dibenzoyl peroxide

The reaction between dibenzoyl peroxide and PBN is known to give PhCOO–PBN$^{\bullet}$ in a thermal reaction, assumed to proceed by homolysis of the O–O bond of the peroxide and trapping of the benzoyloxyl radical by PBN.[4] However, since dibenzoyl peroxide is a weak electron transfer (ET) oxidant {it has a thermochemically estimated $E°[(PhCOO)_2/(PhCOO^{\bullet}\ PhCOO^-)]$ of 0.6 V in water and −0.2 V in a solvent like acetonitrile;[19] a kinetic study of the reaction between dibenzoyl peroxide and a series of hydroquinones in acetonitrile,[20] in combination with the Marcus theory, gave $E°[(PhCOO)_2/(PhCOO^{\bullet}\ PhCOO^-)] = -0.17$ V; an irreversible reduction potential of −0.1 V in benzene-methanol has been determined;[21] see also below} and is likely to contain and/or form small amounts of benzoic acid or peroxybenzoic acid upon dissolution, it cannot be excluded that the HA catalysed mechanism [eqns. (3)–(5), with HA = PhCOOH and/or $PhCO_3H$ and Ox = $(PhCOO)_2$] is the pathway for formation of PhCOO–PBN$^{\bullet}$.

Fig. 3 shows the result from runs in which [PhCOO–PBN$^{\bullet}$] was monitored in a solution of dibenzoyl peroxide (0.135 mol dm^{-3}) and PBN (0.10 mol dm^{-3}) without any additive (triangles) or with benzoic acid present (0.064 mol dm^{-3}; circles). The addition of benzoic acid in a sizeable concentration increased the initial rate of the reaction, but only by *ca.* 50%. When a similar reaction was carried out in HFP, no PhCOO–PBN$^{\bullet}$ was detected during the same period as the reactions shown in Fig. 3.

The PhCOO–PBN$^{\bullet}$ signal was calibrated against a solution of a stable aminoxyl radical, 2,2,6,6-tetramethylpiperidin-1-oxyl, TEMPO,[4] establishing that one unit (Int) on the spectral intensity axis of Fig. 1 corresponds to a radical concentration of 7×10^{-10} mol dm^{-3}. Thus the initial rates of PhCOO–PBN$^{\bullet}$ formation could be estimated at 4×10^{-10} mol dm^{-3} s^{-1} (‘uncatalysed’ run; triangles) and 6×10^{-10} mol dm^{-3} s^{-1} (‘catalysed’ run; circles).

In order to get a measure of the reactivity of a typical aminoxyl radical toward dibenzoyl peroxide, the EPR signal from a solution of TEMPO (0.27 mmol dm^{-3}), in dichloromethane in the presence of an excess of dibenzoyl peroxide (200 mmol dm^{-3}) was monitored. The rate constant of disappearance of the TEMPO signal was $9.1(2) \times 10^{-3}$ min^{-1}, corresponding to a second-order rate constant of 7.7×10^{-4} dm^3 mol^{-1} s^{-1}.

Table 3 Formation of radical cations from the thermal reaction between dibenzoyl peroxide (0.01–0.02 mol dm^{-3}) and ArH (0.04–0.05 mol dm^{-3}) in HFP at 22 °C

ArH	$E°(\mathrm{ArH}^{\bullet+}/\mathrm{ArH})$/V *vs.* SCE	Radical cation formed	Comment
4-Bu^{t}C$_6$H$_4$NMe$_2$	0.65	$\mathrm{ArH}^{\bullet+}$	Strong signal
Ph$_3$N	0.92	$\mathrm{Ar\text{-}Ar}^{\bullet+}$	Strong signal
2,3-Me$_2$-1,4-(MeO)$_2$-Benzene	1.18	$\mathrm{ArH}^{\bullet+}$	Strong signal
3,3′,4,4′-Me$_4$-1,1′-Binaphthalene	1.36	$\mathrm{ArH}^{\bullet+}$	Weak signal
Dibenzo-1,4-dioxine	1.37	$\mathrm{ArH}^{\bullet+}$	Strong signal
Pentamethylanisole	1.44	No signal	$\mathrm{ArH}^{\bullet+}$ detected upon UV irradiation

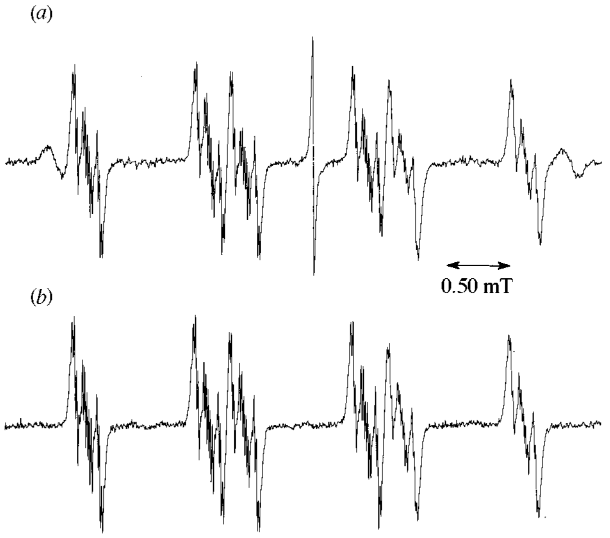


Fig. 4 EPR spectrum of PhCOO-DMPO$^{\bullet}$. (*a*) Generated by photolysis of DMPO (0.10 mol dm^{-3}), PhCOOH (0.05 mol dm^{-3}) and chloranil (0.03 mol dm^{-3}) in dichloromethane. The light was filtered (λ > 400 nm). The singlet in the middle is from $\mathrm{Cl_4Q}^{\bullet-}$. (*b*) Generated by the thermal reaction between DMPO (0.10 mol dm^{-3}) and dibenzoyl peroxide (0.05 mol dm^{-3}) in dichloromethane.

One-electron oxidizing properties of dibenzoyl peroxide

A classical problem in ET chemistry is the mechanism of the one-electron oxidation of easily oxidizable compounds, such as *N*,*N*-dimethylaniline, by dibenzoyl peroxide or other diacyl peroxides.[19,20,22] The strongly increased stability of radical cations in HFP,[17] in part caused by the vastly attenuated reactivity of nucleophiles due to strong hydrogen bonding, makes possible a semiquantitative estimate of the oxidizing power of dibenzoyl peroxide, as done previously for Tl$^{\mathrm{III}}$ oxidants,[23] bromine,[24] iodine chloride,[24] *N*-fluorodibenzenesulfonamide,[25] nitrogen dioxide[26] and chlorotricyanomethane.[27]

A series of aromatic compounds ArH was allowed to react with dibenzoyl peroxide [eqn. (12)] and the development of the primary radical cation $\mathrm{ArH}^{\bullet+}$ (or possibly a secondary radical cation) was monitored by EPR spectroscopy. The benzoate ion formed in eqn. (12) is virtually unreactive and thus normally

$$(\mathrm{PhCOO})_2 + \mathrm{ArH} \xrightarrow{\mathrm{HFP}} \mathrm{ArH}^{\bullet+} + \mathrm{PhCOO}^{\bullet} + \mathrm{PhCOO}^{-} \quad (12)$$

reactive $\mathrm{ArH}^{\bullet+}$ will persist. Table 3 shows the results of such experiments; the limit of $E°(\mathrm{ArH}^{\bullet+}/\mathrm{ArH})$ for which it was just possible to observe an EPR spectrum of $\mathrm{ArH}^{\bullet+}$ was *ca.* 1.4 V (SCE).

Photochemical reaction of DMPO, RCOOH and chloranil

The LLE reaction between DMPO (**3**, 4,5-dihydro-5,5-dimethylpyrrole 1-oxide) and PhCOOH in dichloromethane in the presence of **2**$^{+}$ did not give any spin adduct, nor did irradiation with light of λ > 400 nm. Irradiation of DMPO and PhCOOH in dichloromethane with chloranil (**4**) present gave an aminoxyl species with the expected EPR spectrum [a^{N} = 1.224, a^{H} = 0.963, a^{H} = 0.087 (2 H) mT, obtained from treatment of DMPO with dibenzoyl peroxide in benzene; found here: see Table 4]. In fact, further resolution of the spectrum was possible, the couplings to both the two 3-hydrogens (0.078, 0.111 mT and the six methyl hydrogens (0.018 mT) being obtained (Fig. 4). A similar experiment with C$_6$D$_5$COOH gave an identical spectrum.

Similarly, acetic acid and DMPO gave rise to an EPR spectrum of similarly high resolution (Table 4), the assignment being supported by the observation of an identical spectrum from CD$_3$COOD. Formic acid gave a signal with a spectrum with only the couplings to the 3-hydrogens resolved, in addition to that of the formyl hydrogen. The latter disappeared when DCOOD was employed. Trimethyl- and trifluoro-acetic acid also gave acyloxyl adducts by this procedure.

Formation of PhCOO-DMPO$^{\bullet}$ by the spontaneous reaction between DMPO and dibenzoyl peroxide

For spectral comparison, the thermal reaction between DMPO and dibenzoyl peroxide in dichloromethane was investigated. The same EPR spectrum as in Fig. 4 was obtained, confirming that the small couplings involve the 5,5-methyl groups.

Discussion

Formation of acyloxyl spin adducts under laboratory light exposure

Regardless of structure and decarboxylation rate of RCOO$^{\bullet}$, a carboxylic acid RCOOH reacts with PBN and **2**$^{+}$ in dichloromethane, benzene or acetonitrile under LLE conditions to give an acyloxyl adduct RCOO–PBN$^{\bullet}$ (Table 1). As shown in the experiments with PBN–acetic acid-**2**$^{+}$ which were carried out in complete darkness, the formation of RCOO–PBN$^{\bullet}$ is dependent on the photooxidation of PBN even during short exposure to the relatively weak laboratory light. The reaction is assumed to proceed *via* ET oxidation of PBN by excited **2**$^{+}$ [eqns. (9)–(10)] and reaction of $\mathrm{PBN}^{\bullet+}$ with RCOOH [eqn. (11)].[17] Irradiation by light of λ > 400 nm intensified the signals and thus also made possible the generation of RCOO–PBN$^{\bullet}$ in HFP. We note that a neutral nucleophile like RCOOH retains some reactivity in HFP, similarly to other cases studied previously.[17]

The failure of DMPO to give acyloxyl adducts upon LLE treatment with RCOOH and **2**$^{+}$ or chloranil can have several explanations. We suggest that the most likely one is that the activity of light under LLE conditions is not sufficient to create a detectable concentration of RCOO–DMPO$^{\bullet}$ due to the lower redox reactivity of DMPO compared to PBN (ΔE_{pa} = 0.2 V). Moreover, there are indications that RCOO–DMPO$^{\bullet}$ is more reactive toward further oxidation than RCOO–PBN$^{\bullet}$. Aminoxyl radicals have $E°(\mathrm{R_2N{-}O^{+}/R_2N{-}O^{\bullet}})$ in the region of 0.6–0.8 V (SCE)[28] and an important pathway for their disappearance should be ET oxidation. As shown[29] previously for the case of HA = benzotriazole, DMPO reacts much faster than PBN according to the Forrester–Hepburn mechanism [eqns. (3)–(5), with tetrabutylammonium 12-tungstocobalt(III)ate as the oxidant], but the *N*-benzotriazolyl adduct of DMPO disappears more rapidly.

It should be noted that there does not seem to be any correlation between the p*K* of the acid and its ability to form spin adducts according to eqns. (9)–(11). Tables 1,2 and 4 list acids in the p*K* range of 0–19, with no obvious difference between the extremes except that the spin adducts of strong acids are more short-lived, not surprising in view of the stronger leaving group tendencies of anions corresponding to strong acids.[30]

Table 4 Hfs constants for spin adducts formed in the reaction between DMPO and HA in dichloromethane by photolysis together with chloranil (light of $\lambda > 400$ nm)

HA	a^N/mT	a^H/mT	Other hfs constants/mT
CH_3COOH (**7**)	1.26	1.03	0.018 (3 H), 0.036 (3H), 0.109 (1H)
CD_3COOD	1.26	1.03	0.018 (3 H), 0.036 (3 H), 0.109 (1 H)
HCOOH (**5**)	1.26	1.01	0.074 (1 H), 0.097 (1 H), 0.190 (1 H)
DCOOD (**6**)	1.26	1.01	0.074 (1 H), 0.097 (1 H)[a]
Me_3CCOOH (**9**)[b]	1.27	0.94	0.080 (1 H), 0.105 (1 H)
CF_3COOH (**10**)	1.40	1.24	
PhCOOH (**12**)	1.26	0.97	0.078 (1 H), 0.114 (1 H), 0.018 (6 H)[c]
C_6D_5COOH	1.27	0.98	0.084 (1 H), 0.120 (1 H), 0.017 (6 H)
$(PhCOO)_2$[d]	1.26	0.97	0.111, 0.081, 0.018 (6 H)[c]

[a] Coupling to DCOO not resolved. [b] Weak signal. [c] Lit.,[34] (in PhH): 1.22; 0.96; 0.087 (2 H). [d] Thermal reaction.

Formation of acyloxyl spin adducts under irradiation

Photochemical activation of $\mathbf{2}^+$ leads to the triplet state $^{\mathrm{T}}\mathbf{2}^{+}*$ which is a one-electron oxidant with $E°(^{\mathrm{T}}\mathbf{2}^{+}*/\mathbf{2}^{\bullet}) = 1.8$ V *vs.* SCE, capable of rapidly removing an electron from PBN with $E°(\mathrm{PBN}^{\bullet +}/\mathrm{PBN}) = 1.49$ V with formation of $\mathrm{PBN}^{\bullet +}$. The latter reacts with nucleophiles to give spin adducts, as exemplified by eqn. (7). In this particular case, neutral carboxylic acids RCOOH act as nucleophiles [eqn. (11)].

The reaction between $^{\mathrm{T}}\mathbf{2}^{+}*$ and DMPO-RCOOH did not give any EPR-detectable concentration of $\mathrm{RCOO{-}DMPO}^{\bullet}$. This might be due to a less efficient production of $\mathrm{DMPO}^{\bullet +}$ due to the higher oxidation potential of DMPO, and/or a lower stability of $\mathrm{RCOO{-}DMPO}^{\bullet}$, as already discussed above. With a stronger and more efficient oxidant, the excited state of chloranil (**4***), the reaction works well.

Thermal reaction of CH_3COOH–PBN–oxidant under completely dark conditions

As shown above, the pyrylium ion $\mathbf{2}^+$ is remarkably efficient as a photoelectron oxidant and thus gave $\mathrm{RCOO{-}PBN}^{\bullet}$ also upon short exposure to laboratory light. In order to elucidate the scope of the Forrester–Hepburn mechanism [eqns. (3)–(5)], experiments were performed under completely darkened conditions. It then became clear that $\mathbf{2}^+$ is not a thermal oxidant in eqn. (5), $A = CH_3COO$, nor indeed is chloranil **4**. Only with bromine as the oxidant was $\mathrm{CH_3COO{-}PBN}^{\bullet}$ obtained by the thermal reaction, whereas the even stronger oxidant, DDQ, presumably gave $\mathrm{CH_3COO{-}PBN}^{\bullet}$ in a fast reaction but equally rapidly destroyed it, the net result being the appearance of a very strong signal of $\mathrm{DDQ}^{\bullet -}$.

These results can be understood in terms of the redox chemistry of hydroxylamines[13,14] and aminoxyl radicals,[28] as summarized in eqn. (13). Under the conditions normally employed

$$\mathrm{RCOO{-}PBN(H)} \xrightarrow{E_{\mathrm{pa}}\ ca.\ 0.6\ \mathrm{V}} \mathrm{RCOO{-}PBN}^{\bullet} \xrightarrow{E_{\mathrm{pa}} = 0.6\text{–}0.8\ \mathrm{V}} \mathrm{RCOO{-}PBN}^{+} \quad (13)$$

for generating spin adducts *via* the Forrester–Hepburn mechanism, hydroxylamines exist as such and are oxidized at E_{pa} *ca.* 0.6 V. This redox potential decreases under basic conditions, reaching a limit of *ca.* −0.7 V when the hydroxylamine proton has been fully removed. When the redox potential of the oxidant reaches 0.1 V (bromine) the thermal oxidation of the hydroxylamine becomes feasible; at the same time the further oxidation of the aminoxyl radical becomes fast. With DDQ (0.52 V) both reactions will be fast and no spin adduct will be detected.

The thermal reaction between PBN and dibenzoyl peroxide

The thermal reaction between PBN and dibenzoyl peroxide to give $\mathrm{PhCOO{-}PBN}^{\bullet}$, assuming 100% trapping efficiency and inertness of $\mathrm{PhCOO{-}PBN}^{\bullet}$ under the reaction conditions, has been investigated kinetically by an EPR spectral study in benzene at 38–48 °C and it was concluded that the spin adduct was formed by trapping of $\mathrm{PhCOO}^{\bullet}$ formed by homolytic decomposition of dibenzoyl peroxide [eqns. (14) and (15)].[4] At these

$$(\mathrm{PhCOO})_2 \longrightarrow 2\ \mathrm{PhCOO}^{\bullet} \quad (14)$$

$$\mathrm{PhCOO}^{\bullet} + \mathrm{PBN} \longrightarrow \mathrm{PhCOO{-}PBN}^{\bullet} \quad (15)$$

temperatures, the half-life of the reaction falls in the range of 5000–1000 h.

The Forrester–Hepburn mechanism of eqns. (3)–(5), applied to the reaction between PBN and dibenzoyl peroxide with adventitiously formed PhCOOH as the catalyst HA, takes the form of eqns. (16) and (17). It should be noted that the putative

$$\mathrm{PhCOOH} + \mathrm{PBN} \longrightarrow \mathrm{PhCOO{-}PBN(H)} \quad (16)$$

$$2\ \mathrm{PhCOO{-}PBN(H)} + (\mathrm{PhCOO})_2 \longrightarrow 2\ \mathrm{PhCOO{-}PBN}^{\bullet} + 2\ \mathrm{PhCOOH} \quad (17)$$

ET oxidation of the hydroxylamine intermediate by dibenzoyl peroxide gives a molecule of $\mathrm{RCOO}^{\bullet}$ which is assumed to be trapped with 100% efficiency in eqn. (15). Thus each peroxide molecule gives rise to two molecules of $\mathrm{PhCOO{-}PBN}^{\bullet}$, as in the homolytic mechanism of eqns. (14) and (15).

Various literature reports[19–21] place the redox potential of the dissociative electron transfer of dibenzoyl peroxide, $E°[(\mathrm{PhCOO})_2/(\mathrm{PhCOO}^{\bullet}\ \mathrm{PhCOO}^{-})]$, at *ca.* −0.2 V (SCE) in a dipolar aprotic solvent like acetonitrile or dichloromethane. Our study in HFP [eqn. (12), Table 3], a strongly polar solvent, showed that dibenzoyl peroxide can oxidize ArH with redox potentials up to 1.4 V to give persistent $\mathrm{ArH}^{\bullet +}$. By analogy with the redox properties of Br_2 under similar conditions,[24] one would then put $E°[(\mathrm{PhCOO})_2/(\mathrm{PhCOO}^{\bullet}\ \mathrm{PhCOO}^{-})]$ in HFP at *ca.* 0.4 V which is compatible with the value of −0.2 V above, considering the large difference in solvent polarity. As discussed above, the redox potential of −0.2 V is too low for the ET oxidation of PhCOO–PBN(H) according to eqn. (17), as judged from the results with $\mathbf{2}^+$ or **4** as oxidants. It is thus understandable why no catalysis by benzoic acid of the Forrester–Hepburn mechanism can be detected in the dibenzoyl peroxide–PBN system.

The reaction between PBN and $(\mathrm{PhCOO})_2$ in dichloromethane proceeded thermally at 22 °C, the initial rate of production of $\mathrm{PhCOO{-}PBN}^{\bullet}$ being 4×10^{-10} mol dm^{-3} s^{-1}. A rate constant of 3.5×10^{-9} s^{-1} for the homolytic decomposition of $(\mathrm{PhCOO})_2$ at 22 °C was obtained by extrapolation of data from the temperature range of 50–80 °C; strictly, these data were from the decomposition in benzene,[4] but the variation of rate of homolytic bond cleavage between different solvents is generally small.[31] At $[(\mathrm{PhCOO})_2] = 0.14$ mol dm^{-3}, this rate constant would correspond to an initial rate of production of $[\mathrm{PhCOO{-}PBN}^{\bullet}]$ of $2 \times 0.14 \times 3.5 \times 10^{-9} =$ *ca.* 1.0×10^{-9} mol dm^{-3} s^{-1}, assuming that the trapping efficiency of $\mathrm{PhCOO}^{\bullet}$ is 100% and $\mathrm{PhCOO{-}PBN}^{\bullet}$ does not undergo further reactions. With these assumptions and the experimental uncertainty of the calibration of $[\mathrm{PhCOO{-}PBN}^{\bullet}]$, the experimental initial rate can be explained as being due entirely to the homolytic decomposition of dibenzoyl peroxide [eqns. (14) and (15), as was found previously with benzene as solvent.

However, if a fast mechanism for the disappearance of $\mathrm{PhCOO{-}PBN}^{\bullet}$ might exist, the conclusion may change. In order to get a measure of the reactivity of an aminoxyl radical, the thermal reaction of TEMPO $[E°(\mathrm{R_2NO}^{+}/\mathrm{R_2NO}^{\bullet}) = 0.61$ V (SCE)] with dibenzoyl peroxide was used as a model. Most likely this reaction proceeds according to an ET mechanism [eqn. (18)]. It proceeded with a second-order rate constant of

$$R_2NO^{\bullet} + (PhCOO)_2 \longrightarrow R_2NO^+ + PhCOO^{\bullet} + PhCOO^- \quad (18)$$

7.7×10^{-4} dm^3 mol^{-1} s^{-1}, assuming that the benzoyloxyl radical formed in eqn. (18) is not trapped by TEMPO [eqn. (19)];

$$R_2NO^{\bullet} + PhCOO^{\bullet} \longrightarrow R_2N(O)OCOPh \quad (19)$$

with 100% trapping efficiency, the rate constant should be halved to 3.9×10^{-4} dm^3 mol^{-1} s^{-1}.

Application of the Marcus theory, using the redox potentials quoted above (0.61, −0.2 V), a reorganization energy of 40 kcal mol^{-1} (1 cal = 4.184 J) and a distance between the reacting centres of 6 Å in the transition state provides a calibration of this experimental rate constant. The calculation gives log $k_{ET} = -2.0$, to be compared with the experimental value of −3.1 or −3.4. Considering the uncertainty in the dibenzoyl peroxide redox potential, this difference is hardly significant (it corresponds to a potential change of *ca.* 0.06 V).

Aminoxyl radicals undergo oxidation with reversible potentials in a rather narrow range, 0.6–0.8 V (SCE). Among spin adducts of PBN, only Ph-PBN$^{\bullet}$ (0.7 V) appears to have been investigated.[28a] The introduction of the electron-withdrawing PhCOO group in PhCOO–PBN$^{\bullet}$ is expected to decrease the reactivity toward ET oxidation, and it is therefore safe to assume that PhCOO–PBN$^{\bullet}$ will react more slowly with dibenzoyl peroxide than TEMPO. Thus, assuming for a moment that the same rate constant applies to the reaction between PhCOO–PBN$^{\bullet}$ and dibenzoyl peroxide as for TEMPO, the initial rate of disappearance of the PhCOO–PBN$^{\bullet}$ signal at $[(PhCOO)_2] = 0.14$ mol dm^{-3} and $[PhCOO\text{–}PBN^{\bullet}] = 10^{-6}$ mol dm^{-3} (which is the estimated concentration of PhCOO–PBN$^{\bullet}$ after *ca.* 20 min in the uncatalysed reaction of Fig. 1) would be $(0.14 \times 10^{-6} \times 7.7 \times 10^{-4}) \approx 1 \times 10^{-10}$ mol dm^{-3} s^{-1}, which is *ca.* four times slower than the calculated initial rate of dibenzoyl peroxide decomposition. Thus, from considerations based upon the TEMPO–(PhCOO)$_2$ reaction, it seems that the rate of formation of PhCOO–PBN$^{\bullet}$ would be controlled by the rate of homolytic decomposition of dibenzoyl peroxide also in dichloromethane, as found previously for benzene.

Unfortunately, the rate of the reaction between PhCOO–PBN$^{\bullet}$ and (PhCOO)$_2$ cannot be measured directly, since each molecule of PhCOO–PBN$^{\bullet}$ oxidized gives rise to a new molecule of PhCOO$^{\bullet}$ [eqns. (20)–(22)]. Thus the net rate of

$$PhCOO\text{–}PBN^{\bullet} + (PhCOO)_2 \longrightarrow PhCOO\text{–}PBN^+ + PhCOO^{\bullet} + PhCOO^- \quad (20)$$

$$PhCOO^{\bullet} + PBN \longrightarrow PhCOO\text{–}PBN^{\bullet} \quad (21)$$

Net reaction:

$$PBN + (PhCOO)_2 \longrightarrow PhCOO\text{–}PBN^+ + PhCOO^- \quad (22)$$

disappearance of PhCOO–PBN$^{\bullet}$ will only reflect a trapping efficiency < 100% and not the desired reaction of eqn. (20). Thus again it seems that the thermal decomposition of dibenzoyl peroxide can account for the formation of PhCOO–PBN$^{\bullet}$. An ET mechanism involving PBN and dibenzoyl peroxide [eqn. (23), followed by eqn. (7), R = Ph] can be ruled out

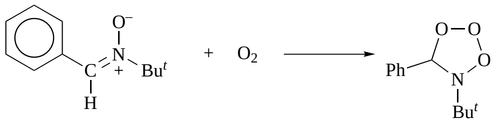
$$(PhCOO)_2 + PBN \longrightarrow PhCOO^- + PhCOO^{\bullet} + PBN^{\bullet +} \quad (23)$$

due to its high endergonicity (*ca.* 1.7 eV), corresponding to $k_{ET} < 10^{-18}$ dm^3 mol^{-1} s^{-1}. Yet a puzzling observation remains to be explained: why is the thermal decomposition of dibenzoyl peroxide not producing PhCOO–PBN$^{\bullet}$ in HFP? In itself, the photochemical generation of PhCOO–PBN$^{\bullet}$ in HFP is feasible, both under the conditions given in Table 1 and by photolysis of (PhCOO)$_2$.[17]

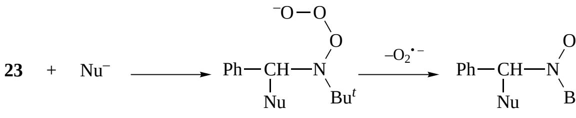
The role of dioxygen in the Forrester–Hepburn mechanism

Finally we need to address the problem of dioxygen acting as an oxidant in the Forrester–Hepburn mechanism, in spite of the fact that $E°(O_2/O_2^{\bullet -})$ is −0.4 V in water or even lower in organic solvents. Dioxygen has been implied as the oxidant in eqn. (5) not only in the formation of RCOO–PBN$^{\bullet}$ but also in the formation of F-PBN$^{\bullet}$[12] and *N*-heteroaryl-PBN$^{\bullet}$,[29] and it is therefore of interest to find an explanation for this effect which does not involve its redox reactivity. As shown in Fig. 2, the concentration of CH$_3$COO–PBN$^{\bullet}$ was rather low after oxidation by dioxygen. Once the signal had disappeared, it was not re-formed after a short treatment by dioxygen.

The latter behaviour is exactly what one would expect from its redox potential, and we therefore have considered an alternative explanation in terms of some credible dioxygen-dependent low-level impurity in PBN. One might for example envisage a very slow, possibly light-promoted reaction between solid PBN and dioxygen, taking place during storage and leading to the formation of a cycloadduct **23** [eqn. (24)].[32] Attack by a nucleophile at the ring carbon of **23** and loss of $O_2^{\bullet -}$ from the intermediate **24** [eqn. (25)] would produce a spin adduct. If this reaction is 100% effective, the level of **23** in PBN would need to be of the order of 0.001% to produce the observed concentration of spin adduct.



23 (24)



24 (25)

Experimental

Materials

PBN (**1**) and DMPO (**3**) were purchased from Aldrich and used as received. 4-MeOPBN, 2,3-dimethyl-1,4-dimethoxybenzene, 3,3',4,4'-tetramethyl-1,1'-binaphthalene, dibenzo-1,4-dioxine and pentamethylanisole were available from earlier studies.[17,23,24] All other chemicals and solvents used were of highest commercial quality available. The sensitizer $\mathbf{2}^+\,BF_4^-$ was a gift from Professor E. Steckhan, University of Bonn.

EPR spectral experiments

These were performed as described previously.[12,17,23] The 'completely darkened' environment had as the only source of light in the laboratory a dimmed computer screen at a distance of 2 m from the site of sample preparation. LLE conditions were equivalent to day-light from a northern window in November–February, 5 m from the site of sample separation, and one 30 W neon light at 70 cm distance.

Cyclic voltammetry

This was carried out in acetonitrile–Bu$_4$NPF$_6$ at a Pt anode, using the BAS-100 instrument. The sweep rate was 100 mV s^{-1}.

Acknowledgements

Financial support from the Swedish Natural Science Research Council and the Knut and Alice Wallenberg Foundation is gratefully acknowledged. We thank Professor E. Steckhan, University of Bonn, for a gift of **2**$^+$ BF_4^-.

References

1 (*a*) J. Chateauneuf, J. Lusztyk and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 2877, 2886; (*b*) J. Chateauneuf, J. Lusztyk, B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, 1988, **110**, 6727; (*c*) H. G-Korth, J. Chateauneuf, J. Lusztyk and K. U. Ingold, *J. Org. Chem.*, 1991, **56**, 2405; (*d*) D. E. Falvey and G. B. Schuster, *J. Am. Chem. Soc.*, 1986, **108**, 7419; (*e*) J. W. Hillborn and J. A. Pincock, *J. Am. Chem. Soc.*, 1991, **113**, 2683; (*f*) T. M. Bockman, S. M. Hubig and J. K. Kochi, *J. Am. Chem. Soc.*, 1996, **118**, 4502.

2 E. G. Janzen and D. L. Haire, in *Advances in Free Radical Chemistry, Vol. 1*, ed., D. D. Tanner, JAI Press, London, 1990, p. 253.

3 W. A. Pryor, C. K. Govindan and D. F. Church, *J. Am. Chem. Soc.*, 1982, **104**, 7563.

4 E. G. Janzen, C. A. Evans and Y. Nishi, *J. Am. Chem. Soc.*, 1972, **94**, 8236.

5 E. G. Janzen and B. J. Blackburn, *J. Am. Chem. Soc.*, 1969, **91**, 4481.

6 A. R. Forrester and S. P. Hepburn, *J. Chem. Soc.* (*C*), 1971, 701.

7 L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer-Verlag, Heidelberg, 1987.

8 (*a*) L. Eberson and M. Nilsson, *Acta Chem. Scand*, 1993, **47**, 1129; (*b*) L. Eberson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 1907.

9 L. Eberson, J. J. McCullough and O. Persson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, 133.

10 As demonstrated for HA = benzotriazole and RX = *N*-chlorobenzotriazole, see: P. Carloni, L. Eberson, L. Greci and P. Stipa, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 1297.

11 M. Martiny, E. Steckhan and T. Esch, *Chem. Ber.*, 1993, **126**, 1671.

12 Earlier attempts to use TAP as sensitizer for the photooxidation of spin traps in the presence of strong anionic nucleophiles were only partially successful (L. Eberson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1994, 171) due to the competing reaction between TAPT and the nucleophiles (for a review, see: K. Ohkata and K.-Y. Akiba, *Adv. Heterocycl. Chem.*, 1996, **65**, 283).

13 (*a*) P. E. Iversen and H. Lund, *Anal. Chem.*, 1969, **41**, 1322; (*b*) F. G. Bordwell and W.-Z. Liu, *J. Am. Chem. Soc.*, 1996, **118**, 8777; the experimental description of these measurements can be found in: F. G. Bordwell and M. J. Bausch, *J. Am. Chem. Soc.*, 1986, **108**, 8777.

14 S. Ozaki and M. Masui, *Chem. Pharm. Bull.* (*Tokyo*), 1978, **26**, 1364; H. Sayo, S. Ozaki and M. Masui, *Chem. Pharm. Bull.* (*Tokyo*), 1973, **21**, 1988.

15 P. A. S. Smith, *The Chemistry of Open-Chain Organic Nitrogen Compounds*, Benjamin, New York, 1966, vol. 2, p. 3.

16 L. Eberson, M. P. Hartshorn, O. Persson and F. Radner, *Chem. Commun.*, 1996, 2105.

17 L. Eberson, M. P. Hartshorn and O. Persson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 141.

18 The EPR spectrum of **2**$^\bullet$ has been denoted 'broad structureless': H. Kawata and S. Niizuma, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 2279.

19 L. Eberson, *Chem. Scr.*, 1982, **20**, 39.

20 W. Adam and A. Schönberger, *Chem. Ber.*, 1992, **125**, 2149.

21 E. J. Kuta and F. W. Quackenbush, *Anal. Chem.*, 1960, **32**, 1069; V. L. Antonovskii, Z. S. Frolova, T. T. Shleina and M. M. Buglanova, *Zh. Obshch. Khim.*, 1969, **39**, 368.

22 A short summary is given in ref. 7, pp. 138–141. See also: G. B. Schuster, *Acc. Chem. Res.*, 1979, **12**, 366; S. Srinivas and K. G. Taylor, *J. Org. Chem.*, 1990, **55**, 1779; X.-K. Jiang, C.-X. Zhao and Y.-F. Gong, *J. Phys. Org. Chem.*, 1991, **4**, 1; L. Grossi, *Res. Chem. Intermed.*, 1993, **19**, 697.

23 L. Eberson, M. P. Hartshorn and O. Persson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 1735.

24 L. Eberson, M. P. Hartshorn, F. Radner and O. Persson, *Chem. Commun.*, 1996, 215.

25 L. Eberson and O. Persson, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, in press.

26 L. Eberson, M. P. Hartshorn, O. Persson and F. Radner, *Res. Chem. Intermediat.*, 1996, **22**, 799.

27 L. Eberson and J. J. McCullough, manuscript in preparation.

28 (*a*) A. J. Bard, J. C. Gilbert and R. D. Goodin *J. Am. Chem. Soc.*, 1974, **96**, 620; (*b*) W. Sümmerman and U. Deffner, *Tetrahedron*, 1975, **31**, 593; (*c*) J. M. Bobbitt and C. L. Flores, *Heterocycles*, 1988, **27**, 509.

29 A. Alberti, P. Carloni, L. Eberson, L. Greci and P. Stipa, *J. Chem. Soc.*, *Perkin Trans. 2*, 1997, in press.

30 M. J. Davies, B. C. Gilbert, J. K. Stell and A. C. Whitwood, *J. Chem. Soc.*, *Perkin Trans. 2*, 1992, 333.

31 As found for the thermal decomposition of azoisobutyronitrile: C. Walling, *Free Radicals in Solution*, Wiley, New York 1957.

32 Nitrones are substrates in 1,3-dipolar cycloadditions: P. N. Confalone and E. M. Huie, *Org. React.* (*NY*), 1988, **36**, 1.

33 G. Kortüm, W. Vogel and K. Andrussow, *Dissociation Constants of Organic Acids in Aqueous Solution*, Butterworths, London, 1961; E. P. Sarjeant and B. Dempsey, *Ionisation Constants of Organic Acids in Aqueous Solution*, Pergamon Press, Oxford, 1979.

34 G. R. Buettner, *Free Radical Biol. Med.*, 1987, **3**, 259.

35 L. Eberson, M. P. Hartshorn, F. Radner and J. O. Svensson, *Acta Chem. Scand.*, 1996, **50**, 885.

Paper 7/01479A
Received 3*rd March* 1997
Accepted 18*th March* 1997