'Inverted Spin Trapping'. Reactions between the Radical Cation of α-Phenyl-N-tert-butylnitrone* and Ionic and Neutral Nucleophiles

Lennart Eberson
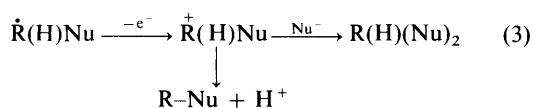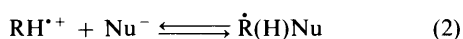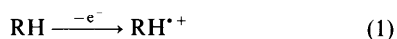*MAX Chemistry, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden*

Tris(4-bromophenyl)aminium ion, TBPA$^{\cdot+}$, is both an efficient electron transfer oxidant and an electrophile. Its reactivity toward nucleophiles reflects this dichotomy, in that bond formation occurs with nucleophiles that are not readily oxidized, such as carboxylate, cyanide and chloride ion, whereas less oxidation-resistant nucleophiles, such as bromide, iodide and trinitromethanide ion react with electron transfer.

This property has been utilized to study spin-trapping reactions with α-phenyl-N-tert-butylnitrone (PBN) under oxidative conditions. The reaction between TBPA$^{\cdot+}$ and a solution of PBN and nucleophile gave the corresponding spin adducts from both categories of nucleophiles, provided the nucleophilic/solvolytic reactivity of the spin adduct was not too high. Spin adducts from the oxidation-resistant nucleophiles [F$^-$, CN$^-$, CNO$^-$, pyridine(s), succinimidate(s), triethyl phosphite, RCO$_2{}^-$] must then be formed in the reaction between the nucleophile and the radical cation of PBN, generated in an initial electron-transfer step ('inverted spin trapping'). Only in the case of the more easily oxidizable nucleophiles [SCN$^-$, (NO$_2$)$_3$C$^-$, N$_3{}^-$] does proper spin trapping occur, i.e., the radical is formed by the TBPA$^{\cdot+}$/nucleophile reaction and is then trapped by PBN.

Spin traps have found widespread use in free-radical chemistry.[1] Limitations to their use frequently depend on the chemical properties of the spin traps, such as susceptibility to attack by nucleophiles[1b,2] or to oxidation,[1b,3] or the reactivity of the spin adducts formed, such as nucleophilic displacement of the initially trapped radical.[4,5]
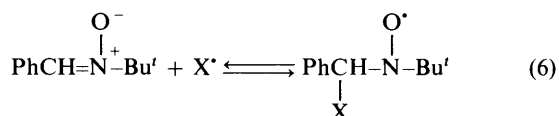
The first set of problems defined above is a particularly intriguing one, since it relates to a subclass of oxidative reactions in which a neutral organic compound, here symbolized by RH, is allowed to react with a nucleophile (Nu$^-$) under conditions which allow for withdrawal of electrons (anodic, metal ion, photochemical oxidation).[6] Such reactions most often take place *via* initial one-electron oxidation of RH to its radical cation [eqn. (1)], to which Nu$^-$ is added in a reversible step, to yield a radical intermediate [eqn. (2)] which is further oxidized to a carbocation.[7] The latter leads to products *via* proton abstraction (oxidative substitution) and/or nucleophile addition (oxidative addition), as shown in eqn. (3).

$$RH \xrightarrow{-e^-} RH^{\cdot+} \qquad (1)$$

$$RH^{\cdot+} + Nu^- \rightleftharpoons \dot{R}(H)Nu \qquad (2)$$

$$\dot{R}(H)Nu \xrightarrow{-e^-} \overset{+}{R}(H)Nu \xrightarrow{Nu^-} R(H)(Nu)_2 \qquad (3)$$
$$\downarrow$$
$$R-Nu + H^+$$

A less common mechanism [eqns. (4), (5)], valid for highly electron-deficient molecules, consists of initial addition of Nu$^-$ to a double bond of RH with formation of a carbanion (a Meisenheimer complex if RH is an aromatic compound) which is oxidized to the same radical intermediate as in eqn. (2).[6a]

$$RH + Nu^- \rightleftharpoons R(H)Nu^- \qquad (4)$$

$$R(H)Nu^- \xrightarrow{-e^-} \dot{R}(H)Nu \qquad (5)$$

If RH is a spin trap, like α-phenyl-N-tert-butylnitrone (PBN), it is immediately apparent that the spin adduct is equivalent to the radical intermediate R(H)Nu$^\cdot$ and thus represents a way of arresting oxidative reactions at this stage [eqn. (6)]. Viewed

$$\underset{PhCH=N-Bu^t}{\overset{O^-}{\underset{|}{\overset{|}{+}}}} + X^\cdot \rightleftharpoons \underset{\underset{X}{\overset{|}{PhCH-N-Bu^t}}}{\overset{O^\cdot}{\overset{|}{}}} \qquad (6)$$

from this perspective, the spin trapping reaction may be an additional source of information on the mechanisms of oxidative reactions, especially the chemical behaviour of the spin adduct, equal to PBN–Nu$^\cdot$ for PBN.

The mechanism of eqns. (4), (5) is already well established in spin-trap chemistry, as exemplified by the reaction between PBN and alkyllithium compounds, followed by air oxidation to obtain the alkyl spin adduct.[2] The radical cation mechanism [eqns. (1), (2)], although sometimes alluded to,[3] has however not been fully explored with the whole variety of nucleophiles available and against the more general background defined above.

This problem arose when attempts were made to trap radicals, R$^\cdot$, by PBN from the oxidation of carboxylates, RCO$_2{}^-$, by the strong oxidant, OsCl$_6{}^-$. Evidence from product studies showed clearly that R$^\cdot$ were intermediates, but the only species trapped were acyloxy adducts.[8] Since acyloxy radicals are very prone to decarboxylation ($k = 10^7–10^9$ s^{-1}),[9] it was deemed unlikely that they would be trapped as such by neutral PBN; instead oxidation of PBN to PBN$^{\cdot+}$, followed by reaction with the carboxylate, would be the most likely route to PBN–OCOR$^\cdot$.

The idea could be tested unambiguously by changing the oxidant to tris(4-bromophenyl)aminium ion (TBPA$^{\cdot+}$), a reagent often employed as an electron transfer reagent in organic reactions.[10] However, this radical cation also shows other reaction modes typical of radical cations, such as coupling and substitution (in the 2-position) by nucleophiles. Specifically, it has been shown earlier[11-13] that acetate, cyanide and chloride substitute exclusively at the 2-position of TBPA$^{\cdot+}$, whereas bromide, iodide and trinitromethanide ion react by one-electron transfer. For the case at hand, this means that acetoxy

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* IUPAC-recommended name: N-tert-butylbenzylideneamine N-oxide.

Table 1 Spin adducts from the reaction between TBPA·+SbCl6− and PBN-nucleophile in dichloromethane (unless otherwise stated). AN = acetonitrile

Nucleophile	Found a^N/mT	a^H/mT	a^{Nu}/mT	Literature a^N/mT	a^H/mT	a^{Nu}/mT	Spin adduct from
F⁻	1.27	0.105	4.57	1.22	0.118	4.56	F[a]
F⁻	1.28	—	2.12	1.17	—	1.93	F₂[b]
CN⁻	1.51	0.195	—				NC–
CN⁻ in AN	1.51	0.195	—	1.50	0.198	—	NC–[c]
CNO⁻	1.38	0.181	0.322	1.51	0.315	0.184	OCN–[d]
Cl⁻	0.81	—	—				O=
Pyridine	1.33	0.225	0.287				Py⁺
3,5-Lutidine	1.34	0.220	0.303				Lu⁺
2,6-Lutidine	1.33	0.220	0.291				Lu⁺
PhSO₂⁻	0.81	—	—				O=
NO₃⁻	0.81	—	—				O=
Succinimidate	1.44	0.54	0.135				N-Succinimido
Me₄-succinimidate	1.43	0.52	0.133				Me₄-N-succinimido
Me₄-succinimidate in AN	1.43	0.51	0.141				Me₄-N-succinimido
Triethyl phosphite	1.47	0.345	2.33				⁺P(OEt)₃
CF₃CO₂⁻	0.81	—	—				O=
PhCO₂⁻	1.35	0.161	—	1.32	0.144	—	PhCO₂[e]
(AcO)₂H⁻	1.35	0.134	—				CH₃CO₂
AcO⁻	1.37	0.166	—	1.34	0.14	—	CH₃CO₂[f]
(Bu^tO₂)₂H⁻	1.36	0.15	—				Bu^tCO₂
Br⁻	No signal						
SCN⁻	1.52	0.21	—				NCS–
(NO₂)₃C⁻	1.46	0.44	—				(NO₂)₃C
(NO₂)₃C⁻ in AN	1.47	0.50	—	1.46	0.46	—	(NO₂)₃C[g]
N₃⁻	1.42	0.177	0.177	1.41	0.189	0.189	N₃[d]

[a] In benzene [ref. 1(a)]. [b] In benzene (ref. 15). [c] Ref. 3(e). [d] In AN [ref. 3(e)]. [e] Ref. 16. [f] Ref. 17. [g] Ref. 18.

radical cannot be formed by TBPA·+ oxidation and thus that any PBN–OAc· detected could be formed only via the radical cation pathway. The addition of a TBPA·+ solution to a solution of tetrabutylammonium hydrogendiacetate and PBN indeed gave the acetoxy adduct and thus confirmed the above assumption.

This paper presents an extension of this reaction to a large number of nucleophiles, both of the oxidation-resistant type, such as F⁻, RCO₂⁻ and pyridine, and more easily oxidizable ones, such as N₃⁻, SCN⁻ and (NO₂)₃C⁻. Taken together, these results suggest that the radical cation mechanism of eqns. (1)–(3) might be far more prevalent than assumed previously. The mechanism may be adequately denoted 'inverted spin trapping' and as such is of some interest since it can be exploited for generating spin adducts from formally very strongly oxidizing radicals. New examples include inverse spin adducts from PBN and succinimidyl, pyridinyl or triethoxyphosphoranyl.

Results and Discussion

Electron Transfer Properties of PBN and TBPA·+.—The electrochemical properties of PBN have been described before,[3] and a limited CV study confirmed that it undergoes irreversible oxidation at 1.5 V vs. the Ag/AgCl electrode in acetonitrile–tetrabutylammonium hexafluorophosphate. Attempts to generate stable solutions of its radical cation in TFA[14] failed, as expected from the fairly high redox potential and concomitant high reactivity of the radical cation.

The redox potential of TBPA·+, 1.30 V vs. NHE, is sufficient for relatively fast oxidation of PBN, as was established by a kinetic study. The reaction between TBPA·+SbCl6− (0.22 mmol dm⁻³) and PBN (concentration range 3–20 mmol dm⁻³) in dichloromethane proceeded with an overall second-order rate constant of 6.2 ± 0.5 dm³ mol⁻¹ s⁻¹ at 20.0 °C. Since the rate constants for the substitution reaction between TBPA·+ and nucleophiles like hydrogendiacetate, cyanide and chloride lie in the region 10³–10⁵ dm³ mol⁻¹ s⁻¹ (in acetonitrile),[11,13] it is

obvious that the competition between PBN and the nucleophile is often strongly in favour of the latter. Therefore PBN was normally used in excess to compensate for the rate difference.

Table 1 lists a number of TBPA·+/PBN/Nu⁻ reactions performed and the hyperfine splitting constants of the spin adducts and their assignments. The order of the reactions is approximately according to decreasing $E°(Nu·/Nu⁻)$ values according to Table 2, although lack of accurate data sometimes obscures the exact order. Table 2 also lists two other properties of interest, namely the nucleophilicity constants of Nu⁻ and the pK of their conjugate acids.

Fluoride Ion.—Fluoride ion is extremely difficult to oxidize and is a strong nucleophile in aprotic solvents. If successful, spin trapping of fluorine from a system such as TBPA·+–PBN–Bu₄NF belongs to the rare variety of absolute confirmations of a hypothesis. Oxidation of F⁻ to F· by any reagent in a homogeneous medium is considered extremely difficult, and TBPA·+ would be an impossible oxidant by any standard.
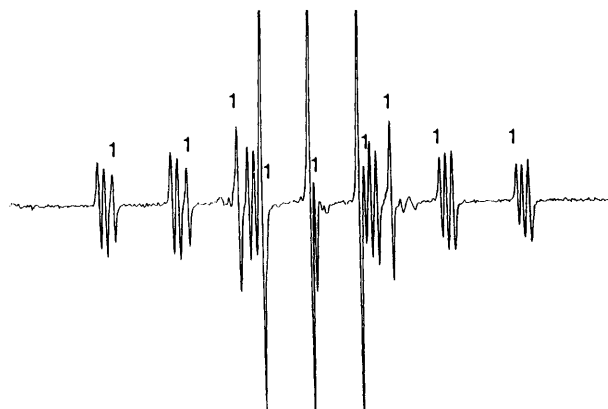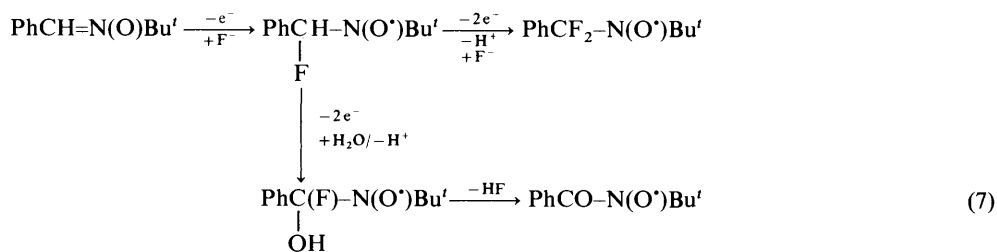
Yet addition of a TBPA·+ solution to a dichloromethane solution of PBN and Bu₄NF, 3 H₂O produced two spin adducts containing fluorine (Fig. 1), namely the fairly unstable F adduct (half-life ≈ 7 min under the experimental conditions used, temperature 23 ± 1 °C) and the much more long-lived F₂ species, both known from previous work [1a,15] where PBN was treated with trifluoroamine oxide, presumably a fairly strong ET oxidant. In addition, the characteristic triplet (a^N = 0.81 mT) from PhCON(O·)Bu^t was seen, a common side-product in PBN spin-trapping experiments [1b] and usually believed to be formed by further oxidation of the hydroxyl spin adduct [eqn. (7)].

Thus the first spin adduct is sensitive to further oxidation, as expected from the rather low oxidation potentials of aminoxyls [$E(R₂NO⁺/R₂NO·)$] between 0.8 and 1.1 V],[25] and with a suitable base/nucleophile such as fluoride ion present, an ECEC type mechanism can lead to substitution of the hydrogen by fluorine. Also, the intermediate carbocation can react with

Table 2 Standard potentials for oxidation of Nu^-, nucleophilicity constants of Nu^- and pK of Nu–H[a]

Nu⁻	$E^\circ(Nu^\bullet/Nu^-)$ in water/V vs. NHE	$n(CH_3I)$ in MeOH	pK of NuH in water	Spin adduct
F^-	3.3	≈2.7	3.2	Yes, but unstable
CN^-	2.5	6.7	9.2	Yes
CNO^-	(2.5)[b]			Yes, but unstable
Cl^-	2.4	4.37	−7	No
Pyridine	2.4	5.23	5.2	Yes
NO_3^-	2.3	(1.5)	−1.4	No
Succinimidate	2–2.5[c]		9.6	Yes
Me_4-succinimidate	2–2.5[d]		>9.6	Yes
Triethyl phosphite	2.3	5.2	2.6	Yes
CF_3CO_2			0.5	No
$PhCO_2$		4.5	4.2	Yes, but unstable
CH_3CO_2	2.1	4.3	4.8	Yes, but unstable
$(CH_3)_3CCO_2^-$			5.0	Yes
Br^-	1.9	5.79	−9	No
$(NO_2)_3C^-$	1.9[e]		0.2[f]	Yes
SCN^-	1.7	6.7	0.9	Yes
N_3^-	1.3	5.8	4.7	Yes

[a] Data from compilations in refs. 19–21, unless otherwise noted. [b] Ref. 3(e) (see the text). [c] Ref. 22. [d] Estimated to be somewhat lower than that of succinimidate. [e] Ref. 23. [f] Ref. 24.

$$PhCH=N(O)Bu^t \xrightarrow[+F^-]{-e^-} PhC\underset{\underset{F}{|}}{H}-N(O^\bullet)Bu^t \xrightarrow[\substack{-H^+\\+F^-}]{-2e^-} PhCF_2-N(O^\bullet)Bu^t$$

$$\downarrow \substack{-2e^-\\+H_2O/-H^+}$$

$$PhC\underset{\underset{OH}{|}}{(F)}-N(O^\bullet)Bu^t \xrightarrow{-HF} PhCO-N(O^\bullet)Bu^t \tag{7}$$

Fig. 1 EPR spectrum obtained 4 min after mixing a dichloromethane solution of $Bu_4NF\cdot3H_2O$ and PBN with a solution of $TBPA^{\bullet+}\text{-}SbCl_6^-$ in dichloromethane. The intense triplet ($a^N = 0.81$ mT) originates from $PhCON(O^\bullet)Bu^t$, the lines labelled 1 from the F_2 adduct and the remaining six doublets with $a^H = 0.105$ from the F adduct. The last-mentioned signal disappeared after 1 h. Sweep width 10.0 mT.

water, to give a hydroxyl/fluorine adduct which is unstable and loses hydrogen fluoride to give the benzoyl aminoxyl.

These results show definitively that spin adducts can be obtained by a reaction other than radical/spin trap interaction. It is still possible that the first fluorine can be introduced by one or both of the sequences of eqns. (1), (2) or (4), (5), but the second one must proceed via an electron-transfer-initiated ECEC mechanism; the hydrogen in the F spin adduct is not acidic enough for proton abstraction/carbanion oxidation to be feasible. By inference, it is suggested that also the first fluorine is introduced via the radical cation [eqns. (1), (2)], by analogy to oxidative fluorination by other methods (anodic oxidation,[26] metal-ion oxidation).[27]

Cyanide Ion.—Contrary to common belief based on evidence from its electrochemical behaviour, cyanide ion emerges as being very difficult to oxidize from calculations based on thermochemical cycles.[19] It is a strong nucleophile in aprotic solvents.

The system $TBPA^{\bullet+}$–PBN–tetrabutylammonium cyanide produced a strong, stable EPR signal of the cyano spin adduct, known from previous work where it was produced by anodic oxidation of cyanide salt in the presence of PBN.[3e] It is known[12] that cyanide reacts with substitution with $TBPA^{\bullet+}$ and that formation of cyano radical is unlikely in view of the endergonicity of the ET reaction. In general, it has been well established that oxidative cyanation, induced photochemically as well as anodically, proceeds by initial formation of a radical cation,[28] and there is no compelling reason that PBN should behave differently.

Attempts to produce the isocyano spin adduct by using silver(I) cyanide as a source of CN^- failed.

Cyanate.—The redox potential of the $CNO^\bullet/CNO^-$ system was not included in Pearson's work, but it is known that cyanide and cyanate ion have almost identical anodic peak potentials in acetonitrile (1.65 and 1.60 V vs. SCE, respectively),[3e] and thus cyanate would be expected to possess the same type of reactivity as cyanide. It supports anodic substitution reactions via radical cations.[29]

In the Bu_4NOCN–PBN–$TBPA^{\bullet+}$ system a weak signal of the cyanate spin adduct was obtained, the H and 2N splittings being almost identical with published values. These were obtained from the anodic oxidation of a PBN–tetrabutylammonium cyanate solution at a controlled potential of 0.90 V (SCE), where, presumably, PBN was the electroactive species.[3e]

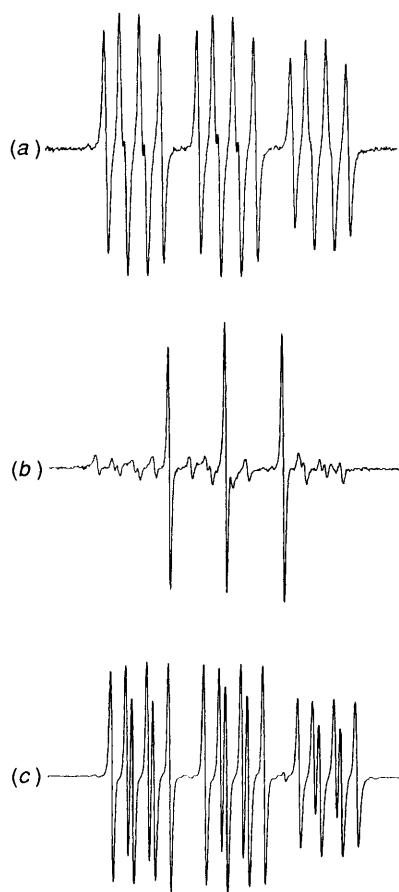*Chloride Ion.*—This ion is among the most difficult to oxidize

Fig. 2 EPR spectrum obtained 4 min after mixing a dichloromethane solution of (a) pyridine, (b) 2,6-lutidine or (c) 3,5-lutidine and PBN with a solution of TBPA^{*+}SbCl$_6^-$ in dichloromethane. The sweep width is 5.0 mT. The intense triplet in (b) belongs to PhCON(O*)Bu^t.

and is a weaker nucleophile than fluoride ion in aprotic solvents. It reacts with TBPA^{*+} with substitution,[12] as is also generally assumed for anodically generated radical cations.

In the PBN–TBPA^{*+} system, it behaved differently from the fluoride and cyanide cases, in that no chlorine spin adduct was seen (at least after the 3–4 min period necessary for degassing, tuning, etc.) but instead a very strong signal from PhCO–N(O*)Bu^t.

It was recently demonstrated for aqueous media that spin adducts of atoms or groups which are capable of acting as good leaving groups (Cl, SO$_4^-$, Cl$_2^{*-}$), can undergo nucleophilic substitution by water so that, sometimes, the hydroxyl adduct is the sole spin adduct detected.[2] This reaction might occur in the present system too, both because of the crystal water associated with tetrabutylammonium chloride and by adventitious water in the solvent used, formally present in concentrations high enough to be compatible with EPR spectrally detectable radical concentrations. If this is the case, the hydroxyl adduct must be further oxidized by TBPA^{*+} to PhCON(O*)Bu^t. Both are feasible processes, although the low reactant concentrations in combination with the weakness of water as a nucleophile (if the reaction is of the S$_N$2 type) and the reasonable stability of PBN–Cl* when generated in acetonitrile by other methods make this mechanism less attractive.

An alternative and more likely possibility would be initial formation of the chlorine adduct, followed by its fast oxidation to a chlorine/hydroxyl adduct with concomitant elimination of HCl, as suggested for the fluoro system above [eqn. (7)].

Pyridine and Other Pyridine Nucleophiles.—Pyridine is very

oxidation-resistant and a reasonably strong nucleophile. Anodic pyridination via radical cation mechanisms is well established[30] and it was therefore of interest to see whether a pyridinium spin adduct could be made from PBN^{*+} and pyridine according to eqns. (1) and (2), Nu$^-$ = pyridine.

Using the same method as before, a strong signal of a spin adduct with one H and two N couplings, was obtained [Fig. 2(a)]. 2,6-Lutidine gave a very similar spin adduct, although this signal was much weaker than that from pyridine [Fig. 2(b)]. Use of 3,5-lutidine [Fig. 2(c)] produced a much stronger signal. This difference must be due to the steric requirements of 2,6-lutidine, earlier[31] found to be 40–60 times less reactive toward radical cations than the 3,5-isomer.

Nitrate.—The nitrate ion has resistance toward oxidation similar to that of chloride ion and is a weak nucleophile. It reacted with PBN/TBPA^{*+} with formation of a very strong signal of PhCON(O*)Bu^t, with no indication of any other spin adduct. Again further oxidation of a nitrooxyl spin adduct, followed by reaction with water, might explain this result.

Benzenesulfinate.—This ion is difficult to oxidize and is a weak nucleophile. The reaction with PBN–TBPA^{*+} gave a very strong signal of PhCON(O*)Bu^t, with no indication of any other spin adduct. The analogy with nitrate ion is obvious.

Succinimidate and Tetramethylsuccinimidate.—As judged by a pulse-radiolytic study, succinimidate should be difficult to oxidize, its redox potential for conversion into succinimidyl radical being estimated to be around 2.5 V in water.[22] Tetramethylsuccinimidate should be oxidizable at a somewhat lower potential. Both anions are reasonably strong nucleophiles. No oxidative substitutions are known for this type of nucleophile, but their properties should be well suited for, e.g., anodic succinimidylation of aromatics.

Mixing a solution of TBPA^{*+} with a solution of tetrabutylammonium succinimidate–PBN or tetramethylsuccinimidate–PBN gave a strong signal with two N couplings and one hydrogen coupling (Fig. 3, Table 1), assigned to the N-succinimido or tetramethylsuccinimido spin adduct, respectively. The signal was stable for many hours.

Triethyl Phosphite.—This nucleophile is difficult to oxidize according to Pearson's calculations (Table 2). Oxidative phosphonylation via reaction between a radical cation, generated by chemical or anodic oxidation, and a trialkyl phosphite, is an established mechanism for electron-rich aromatics, such as 1,4-dimethoxybenzene.[32]

The reaction between triethyl phosphite and PBN–TBPA^{*+} produced a strong, stable signal (Fig. 4, Table 1) from what is probably the triethoxyphosphonium spin adduct, with a characteristic a^P value of 2.33 mT [cf. a^P = 2.17 and 1.60 mT for PBN adducts of –PO$_3^{2-}$ and –(H)PO$_2^-$, respectively, in aqueous medium].[1c]

Carboxylate Ions.—Carboxylate ions, as such or as their homoconjugated species, corresponding to carboxylic acids in the pK interval around 5, are difficult to oxidize. Acetate ion reacts with TPBA^{*+} to give substitution products exclusively,[33] electron transfer taking place to an extent of $< 10^{-3}$%. A wealth of electrochemical and other information on oxidative acetoxylation is in agreement with the radical cation mechanism of eqns. (1) and (2).[6b,d,7]

As already demonstrated,[8] the PBN–hydrogendiacetate ion–TBPA^{*+} system gave a strong signal of the acetoxy spin adduct. The signal decayed with a rate constant of $\approx 0.027 \pm 0.003$ min^{-1} and at the same time a weak signal of a new spin adduct developed (Fig. 5). The same behaviour was previously
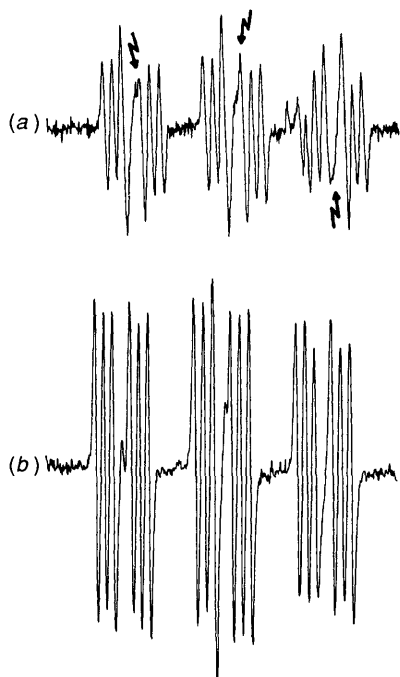
Fig. 3 EPR spectrum obtained 4 min after mixing a dichloromethane solution of (*a*) tetrabutylammonium succinimidate or (*b*) tetrabutylammonium tetramethylsuccinimidate and PBN with a solution of TBPA·⁺SbCl₆⁻ in dichloromethane. The sweep width is 5.0 mT. The feature marked with arrows in (*a*) becomes larger with an increase in water content and then constitutes a triplet of doublets, $a^N = 1.46$ and $a^H = 0.228$ mT, presumably originating from the hydroxyl spin adduct.
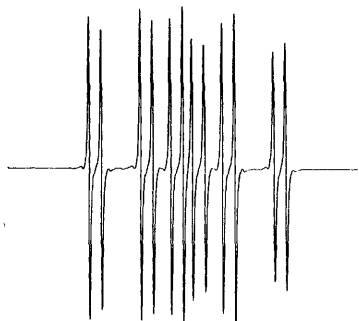

Fig. 4 EPR spectrum obtained 4 min after mixing a dichloromethane solution of triethyl phosphite and PBN with a solution of TBPA·⁺ SbCl₆⁻ in dichloromethane. The sweep width is 5.0 mT.
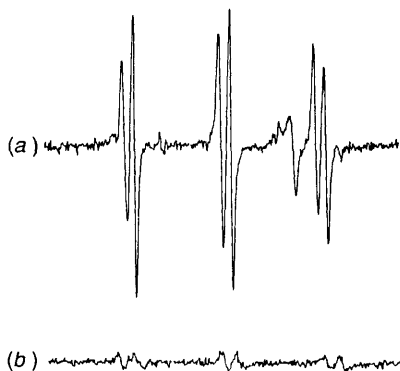

Fig. 5 EPR spectrum obtained (*a*) 4 min and (*b*) 12 h after mixing a dichloromethane solution of tetrabutylammonium hydrogendi(acetate) and PBN with a solution of TBPA·⁺SbCl₆⁻ in dichloromethane. The sweep width is 5.0 mT.

observed with $OsCl_6^-$ as the oxidant and ascribed to the spin adduct of $HOCOCH_2$ (or $^-OCOCH_2$), formed by homolytic decomposition of the acetoxy spin adduct to give a methyl

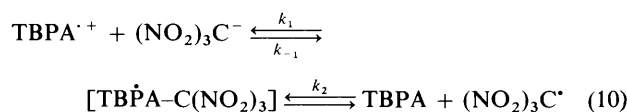radical, which then gave carboxymethyl radical by hydrogen abstraction from acetate ion [eqns. (8) and (9)].

$$\dot{P}BN–OCOCH_3 \longrightarrow PBN + CH_3^{·} + CO_2 \quad (8)$$

$$CH_3^{·} + H–CH_2CO_2^- \longrightarrow CH_4 + {^·}CH_2CO_2^- \quad (9)$$

This behaviour was seen also with tetrabutylammonium acetate as the source of acetate ion. Again, the acetoxy spin adduct decayed rather quickly ($k = 0.06 \pm 0.01$ min⁻¹) and the new one appeared with approximately the same rate ($k = 0.10 \pm 0.03$ min⁻¹).

The signal from hydrogenbispivalate ion was strong and stable for hours ($k = 0.018 \pm 0.04$ min⁻¹). On the other hand, benzoate ion gave a weak signal which disappeared rapidly ($\tau_{\frac{1}{2}} < 2$ min). Trifluoroacetate ion, of significantly lower nucleophilicity than any of the other carboxylates, gave no trifluoroacetoxy adduct but instead gave $PhCON(O^·)Bu^t$ in high concentration. Thus trifluoroacetate ion belongs to the same category as chloride, benzenesulfinate and nitrate ion with respect to the product formed, possibly for the same reason(s).

Bromide Ion.—As already mentioned, this ion undergoes electron transfer with TBPA·⁺ and thus is qualitatively different from cyanide, acetate and chloride ion.[12] Accordingly, one would expect that either or both of the following mechanisms would be feasible: (*i*) a strongly preferred pathway involving bromine-atom formation from the ET process between TBPA·⁺ and bromide, and (*ii*) a minor route leading to PBN·⁺ which, being a radical cation, would however also react by ET with bromide ion. Thus any PBN–Br· formed would originate from a spin trapping process proper.

In fact, no signal from this spin adduct or any other adduct was seen from the TBPA·⁺–PBN–Bu₄NBr system, as expected from the considerable difficulties involved in generating PBN–Br· by other means. It was eventually generated and detected by EPR spectroscopy in a continuously irradiated solution of bromine and PBN in benzene.[34] Upon discontinuation of the irradiation, PBN–Br· disappeared within two seconds.

Trinitromethanide Ion.—This ion has a redox potential of 1.9 V [23] and has recently [13] been shown to undergo electron transfer to TBPA·⁺. The kinetic behaviour of this reaction in dichloromethane showed saturation behaviour already at $[(NO_2)_3C^-] = 5$ mmol dm⁻³, consistent with the initial formation of a complex between TBPA·⁺ and $(NO_2)_3C^-$, followed by its slow homolytic decomposition [eqn. (10)]. This complex is probably identical with the cyclohexadienyl radical

$$TBPA^{·+} + (NO_2)_3C^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$$

$$[TB\dot{P}A–C(NO_2)_3] \overset{k_2}{\underset{}{\rightleftharpoons}} TBPA + (NO_2)_3C^{·} \quad (10)$$

of eqn. (2). From the kinetic data [23] at different $[(NO_2)_3C^-]_0$, k_2 was calculated to be 11 ± 1 min⁻¹ from the Michaelis–Menten equation. Knowing that the rate constant of the reaction between TBPA·⁺ and PBN is ≈ 6 min⁻¹, the reaction conditions for the TBPA·⁺–PBN–(NO₂)₃C⁻ system can be adjusted in a way that minimizes PBN oxidation. Even if it is most likely that PBN·⁺ will oxidize $(NO_2)_3C^-$ in the same way as TBPA·⁺ does, it is desirable to minimize the possibilities of misinterpretation as much as possible.

With concentrations that correspond to $k[(NO_2)_3C^-]/k$-(PBN) ≈ 4, a strong signal due to the trinitromethyl spin adduct was obtained. Even at a ratio of 20 a signal was obtained

and it is thus concluded that this case is an example of authentic spin trapping of a radical, generated *via* an oxidation process. Previous work of similar type,[18] involving anodic or chemical (perchloryl fluoride oxidation) generation of trinitromethyl radical from $(NO_2)_3C^-$ in acetonitrile gave similar results and identical conclusions were drawn.

Thiocyanate Ion.—This ion is oxidizable at even lower potential than bromide ion and thus should present the same mechanistic dichotomy. Anodic substitution by thiocyanate is formally known,[35] but only for phenols and anilines which are the only substrates that are reactive enough to react with anodically generated thiocyanogen. The system $TBPA^{\cdot+}$– $PBN-Bu_4NSCN$ indeed produced a weak EPR signal due to a new spin adduct with characteristics close to, but not identical with, those of the cyano adduct (Table 1). Previous attempts to study $PBN-SCN^{\cdot}$ utilized anodic oxidation of thiocyanate which apparently to some extent underwent desulfurization at the anode surface (platinum) and thus generated cyanide ion, opening the way for the radical cation mechanism of eqns. (1) and (2).[3e]

Azide Ion.—This ion is the most easily oxidizable one in Table 2 and would be expected to be mechanistically similar to bromide, thiocyanate and trinitromethanide ion, *i.e.*, spin trapping of azide radical formed by oxidation of azide ion should take place. Indeed the system $TBPA^{\cdot+}-PBN-Bu_4NN_3$ gave an EPR signal of the azide spin adduct, known from many other sources, among them anodic oxidation of azide ion in the presence of PBN.[3e]

Aliphatic Amines.—Aliphatic amines are easily oxidizable and thus should undergo electron transfer with radical cations. In agreement with this prediction, the reaction between 1,4-diazabicyclo[2.2.2]octane or tributylamine with $PBN-TBPA^{\cdot+}$ failed to give any spin adducts.

Conclusions

The most important conclusion from the data of Table 1 is that spin adducts are easily formed under oxidizing conditions by mechanisms other than the proper trapping of a radical by PBN. The oxidizing agent used, $TBPA^{\cdot+}$, is reactive enough to provide a low concentration of $PBN^{\cdot+}$ which can react with bond formation to nucleophiles which are resistant toward electron transfer oxidation. For $TBPA^{\cdot+}$, the borderline between bond formation and electron transfer is located somewhere between the carboxylate ions (where acetate ion is known to undergo electron transfer to an extent of $<10^{-3}\%$)[33] and bromide ion, which only undergoes electron transfer.[12] For nucleophiles more susceptible to oxidation than bromide, proper spin trapping, in all probability, takes place.

This simple pattern of reactivity is obscured by one important chemical property of the spin adduct, namely its reactivity in nucleophilic processes (S_N1 or S_N2 mechanism).[2] The series of carboxylates nicely demonstrates this complication.

R in RCO_2^-	$\tau_{\frac{1}{2}}$/min of spin adduct	pK of RCO_2H
CF_3	No adduct seen	0.5
Ph	<2	4.2
CH_3	12–25	4.8
$(CH_3)_3C$	38	5.0

As judged by the pK of RCO_2H, the leaving-group ability of RCO_2 should increase in the order $CF_3 < Ph < CH_3 < (CH_3)_3C$; this is the order of spin-adduct stabilities in this limited but uniform series of compounds. A second series is provided by the halide/pseudohalide ions.

Nu^-	$\tau_{\frac{1}{2}}$/min of spin adduct	pK of NuH
Br^-	<0.03 (Ref. 34)	−9
Cl^-	Not seen	−7
F^-	7	3.2
SCN^-	≈5	0.9
N_3^-	>60	4.7
CN^-	>500	9.2

The trend is similar, spin adducts with good leaving groups being unstable and only detectable under conditions of continuous generation (anodic, photochemical) or in low relative permittivity solvents, such as benzene. The failure to detect the chloro adduct under the conditions used here is thus easily understood.[3e,36]

The above results reinforce earlier warnings[3] about possible mechanistic complications of spin-trapping experiments under oxidizing conditions (and perhaps also sometimes reducing ones). These include photochemical experiments where the full realization and understanding of the electron-transfer aspects of photochemistry[6e,f] is of relatively recent date. Care must also be exercised with spin trapping in biological systems, since some redox enzymes are known to possess quite respectable potentials.[37] Since the experimental distinction between spin trap/ $Nu^{\cdot}$ and (spin trap)$^{\cdot+}/Nu^-$ pathways is not always as simple as in the cases presented here, much work will be required to substantiate or refute earlier proposals.

Experimental

Reactions.—These were performed by adding a saturated solution of tris(4-bromophenyl)aminium hexachloroantimonate (100–300 mm³ of a saturated solution in dichloromethane; ≈0.8 mmol dm⁻³) to a high-purity Ar-degassed solution of the nucleophile (0.03–0.08 mol dm⁻³) and PBN (0.1–0.3 mol dm⁻³) in dichloromethane (700 mm³) in the EPR tube. Final degassing/tuning was usually accomplished within 2 min. EPR spectra were recorded on a Bruker ER-200D SRC instrument. Electrochemical and kinetic experiments were performed with equipment described before.[23]

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