Direct Detection of the Cation Radical of the Spin Trap α-Phenyl-*N*-*tert*-butylnitrone†,[1]

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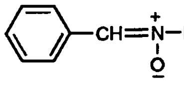
The radical cation PBN$^{\cdot +}$ **2** of the spin trap α-phenyl-*N*-*tert*-butylnitrone (PBN, **1**) was observed directly {$\lambda_{max}(H_2O)$/nm 410 [ε/dm^3 mol^{-1} cm^{-1} (5 ± 1) × 10^3]} and characterised by pulse radiolysis and laser flash photolysis absorption measurements in solvents of different polarity (water, CH_3CN, BuCl) as well as by low-temperature EPR. It was generated by direct two-photon ionisation of PBN, by electron-transfer from PBN to solvent cation radicals or to photoexcited triplet chloranil, and by reaction of PBN with the oxidising anion radical $SO_4^{\cdot -}$. The γ-irradiation of PBN in alkyl halide glasses at 77 K yielded green-coloured samples containing the stabilised radical cation PBN$^{\cdot +}$, whose EPR spectrum indicates the presence of aminoxyl-type radicals. PBN$^{\cdot +}$ reacts with a variety of nucleophiles to yield the corresponding stable aminoxyl radicals. Based on spectroscopic, kinetic and chemical evidence it is concluded that PBN$^{\cdot +}$ is an aminoxyl substituted phenylcarbenium ion.

The technique of spin trapping introduced[2] in 1967–1969 is a chemical method used in the study of the structure and reactivity of short-lived radicals which play a role in chemistry, biology and medicine.[3–7] Spin trapping is based on the addition of short-lived radicals (spins) to scavenger molecules (spin traps) which results in the formation of stable aminoxyl radicals (spin adducts) as is shown in eqn. (1) for the spin trap α-phenyl-*N*-*tert*-butylnitrone (PBN, **1**), as scavenger.



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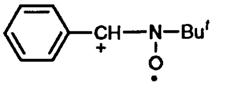

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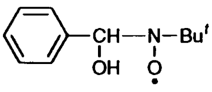
$$PBN + R^{\cdot} \longrightarrow PhC(R)H\text{-}N(O^{\cdot})\text{-}Bu^t \quad (1)$$

Complications in the interpretation of the reaction mechanism of spin trapping of radicals have arisen in radiation and photochemical studies,[4–6] in systems involving oxidants or reductants and in biological systems *in vivo* and *in vitro*.[4,6,7] In addition to the spin trapping reaction (1), the spin trap may be activated directly (*e.g.* through ionisation and excitation) or may be involved in chemical reactions with other solutes, as, for example, in electron-transfer processes.

In performing spin trapping studies it is therefore of prime importance to investigate all reaction channels which could be responsible for the formation of aminoxyl radicals. In particular, the formation of HO substituted aminoxyls in the presence of spin traps in chemical and biological systems should be critically analysed. This allows us to discriminate between radical-addition and electron-transfer mediated mechanisms and thus to identify the reaction sequences responsible for the production of primary radical or oxidising species.

Although the first observations[8] of aminoxyl **3** in the presence of PBN were made nearly 20 years ago, the supposed[8a] formation mechanism according to eqn. (2a), has not as yet been confirmed directly as the only reaction pathway. The possibility of reactions involving other functional groups in the spin trap molecule has not been taken into account.



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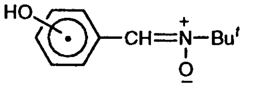

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$$PBN + HO^{\cdot} \longrightarrow 3 \quad (2a)$$

$$PBN + HO^{\cdot} \longrightarrow 4 \quad (2b)$$

Recently, we published the results from a pulse radiolysis study[9] of the reactions of HO$^{\cdot}$, e_{aq}^-, and H$^{\cdot}$ with the spin trap PBN. It was shown that HO$^{\cdot}$ radicals are scavenged by PBN preferably *via* addition to the aromatic ring, eqn. (2b), forming cyclohexadienyl type radicals **4**. For the originally expected spin trapping reaction of HO$^{\cdot}$ radicals, eqn. (2a), no indication could be found in steady-state and pulse radiolysis studies.[9,10] It seems now that only a small fraction of HO$^{\cdot}$ radicals could be trapped by PBN in the form of aminoxyl adducts **3**.

The trapping of solvated electrons by PBN in aqueous solutions was shown in the same study[9] to occur *via* the formation of the highly reactive intermediates $O^{\cdot -}$ and *N*-*tert*-butylbenzylideneimine (PhCH=N-Bu^t), eqns. (3) and (4), and not, as commonly believed,[8b] through an electron-addition reaction followed by protonation.

$$PBN^{\cdot} + e_{aq}^- \longrightarrow PhCH{=}N\text{-}Bu^t + O^{\cdot -} \quad (3)$$

$$PhCH{=}N\text{-}Bu^t + O^{\cdot -} \longrightarrow Ph\dot{C}H\text{-}N(O^-)\text{-}Bu^t \quad (4)$$

The imine Ph–CH=N–Bu^t and the anion radical $O^{\cdot -}$ form a benzylic type PBN anion radical PBN$^{\cdot -}$ [Ph$\dot{C}$H–N(O$^-$)–Bu^t] in an in-cage reaction (4). This was confirmed[9] by the fact that in the presence of CH_3OH the anion radical $O^{\cdot -}$ is converted into a $^{\cdot}CH_2OH$ radical which is subsequently trapped by the spin trap PBN.

The formation of intermediate cation radicals of nitrone spin traps has been postulated earlier[4,6] in order to interpret the appearance of spin adducts of unknown origin. It seems that deviating from the simple radical trapping mechanism, eqn. (1), cation radicals of the spin trap are also able to form aminoxyl

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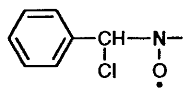
† *N*-Benzylidene-*tert*-butylamine *N*-oxide.

radicals. Thus, the oxidation of PBN to the cation radical $PBN^{\bullet+}$ **2** by $SO_4^{\bullet-}$ followed by nucleophilic addition of water, eqn. (5), has been suggested[11] to explain the appearance of the aminoxyl radical **3**.

$$PBN^{\bullet+} + H_2O \longrightarrow \mathbf{3} + H^+ \qquad (5)$$

Similarly, it has been proposed[12] that aminoxyl **5**, observed



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after oxidation of PBN by photoexcited arylonium salts in aqueous dioxane or in CH_2Cl_2 solutions, should be formed by nucleophilic addition of Cl^- to $PBN^{\bullet+}$, eqn. (6), and not by the

$$PBN^{\bullet+} + Cl^- \longrightarrow \mathbf{5} \qquad (6)$$

direct trapping of $Cl^\bullet$ according to eqn. (1). The formation of radical cations of various spin traps was proposed later also by other investigators and reviewed recently by Eberson,[13] who used this hypothesis to explain the formation of nucleophile derived spin adducts under oxidative spin trapping conditions (inverted spin trapping).

The present study is an extension of our previous work[9] in spin trapping chemistry, investigating the primary reactions of the spin trap PBN. Using the time-resolved techniques of pulse radiolysis and laser photolysis the main intention of this study was to search for possibilities of the direct detection of an intermediate PBN cation radical and to clear up any ambiguities in the PBN spin trapping mechanism.

Experimental

Pulse radiolysis and laser flash photolysis experiments were performed, except where otherwise noted, at room temp. in N_2 saturated solutions continuously flowing through the cell. Data processing and analysis were performed with programs developed at the Max-Planck-Group in Leipzig.

Pulse Radiolysis.—Experiments were performed with a pulse transformer type accelerator ELIT (Institute of Nuclear Physics, Novosibirsk, Russia) delivering 1 MeV, 16 ns electron pulses with a dose between 100–200 Gray. The optical detection system consisted of a pulsed 900 W Xenon lamp (XBO-900, Osram), a Spectra Pro-500 monochromator (Acton Research Corporation), a 1P28 (RCA) photomultiplier and a TDS 640 (500 MHz) Tektronics digitising oscilloscope.

Laser Photolysis.—Experiments were carried out with a perpendicular probe excitation arrangement. The solutions were photolysed in a quartz cell (0.3 × 0.3 cm) connected to a flow system (flow rate 150–200 $cm^3\ h^{-1}$) using the fourth (266 nm) or a third (355 nm) harmonic from a Quanta Ray GCR-11 Nd^{3+}:YAG laser (Spectra Physic Inc.). The pulse duration (fwhm) was measured to be 3 ns at $\lambda = 266$ nm and 5 ns at $\lambda = 355$ nm with a pulse energy $\leqslant 10$ mJ in the cell. The probe light of a pulsed 250 W Xenon lamp (XBO-250, Osram) passed through a Spectra Pro-275 monochromator (Acton Research Corporation) to a R955 photomultiplier tube (Hamamatsu Photonics). The output signals were captured using a Tektronix DSA 602 (600 MHz) digitising signal analyser in the 50Ω mode.

EPR Experiments.—First-derivative X band EPR spectra were measured on an ERS 300 (Berlin, ZWG) spectrometer with a data acquisition system. Solutions were degassed by the freeze–pump–thaw technique and sealed in a high-vacuum line. Irradiation was performed at 77 K in a ^{60}Co γ-ray source at doses of up to 5 kGray.

Chemicals.—PBN was synthesized and used as described earlier.[9] PBN solutions in the presence of $S_2O_8^{2-}$ were prepared immediately before irradiation. The experiments were performed within 20 min after solution preparation, guaranteeing that not more than 10% of the PBN was lost (UV-control). Absorption spectra were measured using a Shimadzu UV-2101 PC spectrophotometer. The aqueous solutions were prepared using water purified by a millipore milli-Q plus system. BuCl and Bu^tCl (both from Aldrich) was additionally purified as described in ref. 14. The following chemicals were used without further purification: acetonitrile (Chromasolv G, Riedel-deHaën), chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone, >99%, Fluka), potassium peroxidisulfate (99%, Merck) and Freon-113 (1,1,2-trichlorotrifluoroethane, 99%, Aldrich).

Results and Discussion

Radiolysis Studies.—*Pulse radiolysis of PBN solutions in* BuCl. In the radiolysis of BuCl, apart from radical species both solvated electrons and highly mobile positively charged holes ($h^{\bullet+}$) are formed,[14] eqn. (7). The electrons are scavenged immediately by solvent molecules, eqn. (8), forming $Bu^\bullet$ radicals and Cl^- anions.

$$BuCl \longrightarrow h^{\bullet+}, e^-_{solv} \qquad (7)$$

$$e^-_{solv} + BuCl \longrightarrow Bu^\bullet + Cl^- \qquad (8)$$

The positive holes move through the solvent in a charge-exchange mechanism[14,15] and are localized, eqn. (9), as BuCl molecular cations ($BuCl^{\bullet+}$) and butene radical cations ($But^{\bullet+}$) as the subsequent fragmentation products.

$$h^{\bullet+} + BuCl \longrightarrow BuCl^{\bullet+}, But^{\bullet+} \qquad (9)$$

The charge neutralization reaction [eqn. (10)] consumes the cations with the formation of molecular and radical products.

$$BuCl^{\bullet+}, But^{\bullet+} + Cl^- \longrightarrow \text{Products} \qquad (10)$$

In the presence of a solute with an ionisation potential (E_i) lower than that of the solvent, an efficient electron transfer from the solute to the solvent cation radicals proceeds,[14,15] eqn. (11), in competition with reactions (9) and (10).

The transient absorption spectrum obtained immediately after a 16 ns electron pulse in the pure solvent represents a superposition of the spectra of all solvent derived positively charged species, and displays a broad absorption maximum near 550 nm in agreement with earlier published data.[14]

In the pulse radiolysis of solutions of the spin trap PBN in BuCl we observed (Fig. 1) the formation of a new species with an absorption band at $\lambda_{max} = 420$ nm and a weak shoulder at 640 nm in the course of decay of the BuCl positive species. The formation of the absorption at $\lambda_{max} = 420$ nm occurs parallel in time with the decay of those of the BuCl positively charged species (see inserts in Fig. 1 with formation at $\lambda = 420$ nm and decay kinetics at $\lambda = 530$ nm).

The lifetime of the 420 nm intermediate decreased when the PBN concentration was increased. This indicates that this species reacts with the parent PBN molecule in an ion–molecule reaction as is shown in eqn. (14). At a PBN concentration of 3.3×10^{-3} mol dm^{-3} the 420 nm species decayed with a halflife of about 20 ns (see Fig. 2 and inserts). Two small and overlapping peaks at $\lambda = 380$ and 360 nm are observed in the course of the decay (Fig. 2), and are tentatively assigned to the

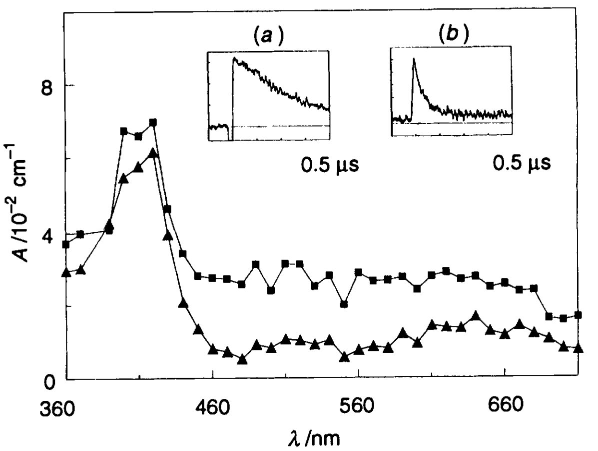


Fig. 1 Absorption spectra recorded 26 and 85 ns after the 16 ns electron pulse of a solution of PBN (5.5×10^{-4} mol dm^{-3}) in BuCl: (■), 26.5; (▲) 85.2 ns. Inserts show time profiles for PBN$^{\bullet+}$ at (a) 420 nm and BuCl cations at (b) 530 nm.

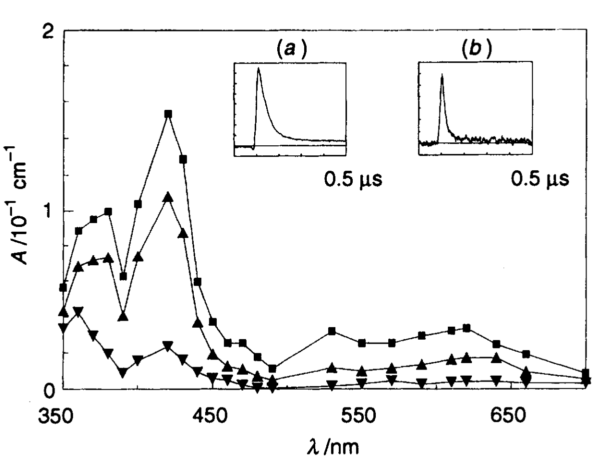


Fig. 2 Absorption spectra recorded 10, 20 and 100 ns after the 16 ns electron pulse of a solution of PBN (3.3×10^{-3} mol dm^{-3}) in BuCl: (■), 10.5; (▲), 20; (▼), 100 ns. Inserts show time profiles for PBN$^{\bullet+}$ at (a) 420 and BuCl cations at (b) 550 nm.

reaction products. Increasing the PBN concentration to 10^{-2} mol dm^{-3}, only the 420 nm species and decay products could be seen immediately after the pulse.

In view of the low E_i of the PBN molecule* we assign the 420 nm transient to the PBN cation radical **2** formed by the electron-transfer reaction (11) in competition with other decay channels of the solvent cations.

$$\mathrm{PBN} + (\mathrm{h}^{\bullet+}, \mathrm{BuCl}^{\bullet+}, \mathrm{Bu}^{t\bullet+}) \longrightarrow \mathrm{PBN}^{\bullet+} + (\mathrm{BuCl, butene}) \qquad (11)$$

The decay of the BuCl cations analysed in the wavelength range of 490–540 nm has been found to be pseudo-first order with respect to the PBN concentration. The observed decay rate, k_{obs}, can be expressed by eqn. (12) where a is a term

$$k_{obs} = a + k_{11}[\mathrm{PBN}] \qquad (12)$$

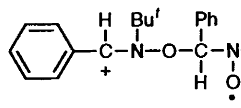
describing the decay of solvent cations in reactions (9) and (10) in the absence of PBN. With $a = 1.1 \times 10^7$ s^{-1} and measurements of k_{obs} at various PBN concentrations [Fig. 3(a)] k_{11} was determined to be 2.2×10^{10} dm^3 mol^{-1} s^{-1}.

The cation radical PBN$^{\bullet+}$ decayed, eqn. (14), with a pseudo-first-order rate constant (analysed at 420 nm) proportional to the PBN concentration. From measurements [eqn. (13)] of k_{obs}

$$k_{obs} = b + k_{14}[\mathrm{PBN}] \qquad (13)$$

for the PBN$^{\bullet+}$ decay at varied PBN concentrations the rate constant for reaction (14) was determined to be $k_{14} = 8.0 \times 10^9$ dm^3 mol^{-1} s^{-1} [Fig. 3(b)]. Term b in eqn. (13) is equal to 2.5×10^6 s^{-1} [from intercept in Fig. 3(b)] and describes the decay of PBN$^{\bullet+}$ at low PBN concentration. Under our experimental conditions the decay of PBN$^{\bullet+}$ was always exponential, and therefore a marked contribution from the recombination of PBN$^{\bullet+}$ with Cl$^-$ anions, reaction (6), could be excluded.

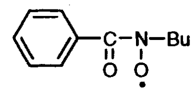
Since we have not found any spectroscopic evidence for the formation of dimeric cation radicals as observed in the pulse radiolysis of aromatics,[17] we believe that reaction (14) most probably proceeds as a result of a Coulombic attraction,† forming a metastable addition product **6**.



6

$$\mathrm{PBN} + \mathrm{PBN}^{\bullet+} \longrightarrow \mathbf{6} \qquad (14)$$

Intermediate **6** could have the structure of a distonic radical cation in which the positively charged carbon and the (aminoxyl) radical centre are formally separated by five bonds. It seems that the short-lived absorption band at λ = 380 nm which appeared in the course of the PBN$^{\bullet+}$ decay (Fig. 2) may belong to **6**. For its rapid decay we suggest the formation of imine PhCH=NBu^t and a benzoyl-*tert*-butylaminoxyl radical **7** as formulated in eqn. (15).



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$$\mathbf{6} \longrightarrow \mathbf{7} + \mathrm{PhCH{=}N{-}Bu}^t + \mathrm{H}^+ \qquad (15)$$

The weak shoulder in the absorption observed at λ = 360 nm after the decay of PBN$^{\bullet+}$ at high PBN concentrations (Fig. 2) may belong to one of these products, namely to the stable aminoxyl **7**. As reported in ref. 19, the aminoxyl radical **7** has an absorption peak at λ = 360 nm (ε/dm^3 mol^{-1} cm^{-1} 230).

Earlier, the aminoxyl radical **7** was detected by steady-state EPR spin trapping studies[20] of γ-radiolysis of CCl_4 and other alkyl halides in the presence of PBN. Based on our pulse radiolysis data, PBN$^{\bullet+}$ should be formed in the γ-radiolysis of PBN solutions in alkyl halides. Thus, spin trapping results[20] support our proposal for the decay mechanism of the cation radical PBN$^{\bullet+}$ *via* reactions (14) and (15).

EPR Spin Trapping Studies.—For a deeper insight into the structure of PBN$^{\bullet+}$, low temperature EPR spin trapping studies were performed of the paramagnetic products of γ-radiolysis of PBN dissolved in glass-forming matrices of Bu^{t}Cl and

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* The E_i of PBN is not known. In this work we assume, that PBN has nearly the same E_i (8.01 eV) as the nearest PBN analogue *N*-benzylidene-*N*-methylamine *N*-oxide.[16a] It is known[16b] that for other nitrones E_i lies near the value of 8–8.5 eV.

† The dipole moment of PBN molecule (3.56 D) indicates a negatively charged oxygen atom.[18]

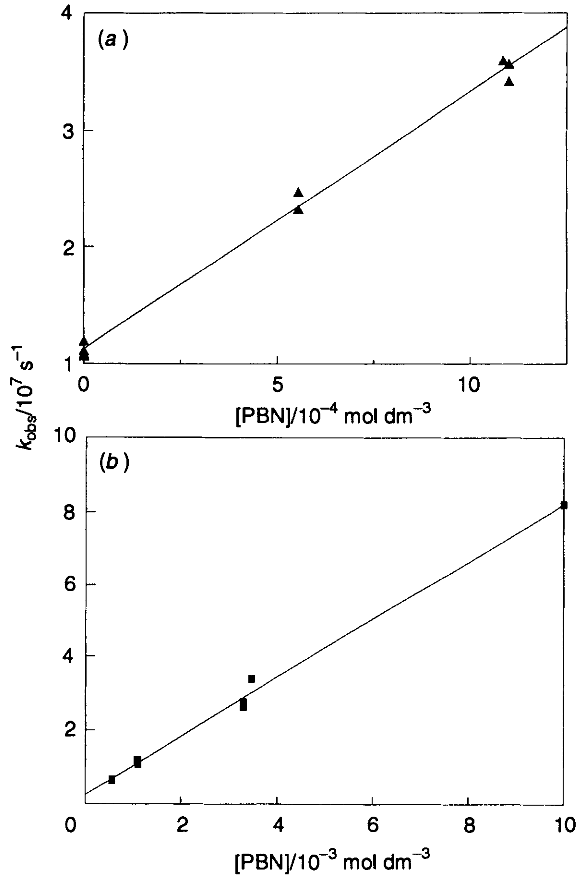


Fig. 3 Dependence of k_{obs} for the decay (*a*) of BuCl positive charged species and (*b*) PBN$^{\cdot+}$ on PBN concentration measured by pulse radiolysis

$CF_2ClCFCl_2$ (Freon-113). The solvents used are internal electron scavengers and therefore enable the study of molecular cationic transients stored in the highly viscous low-temperature glasses.[21]

In Freon-113 as well as in Bu^{i}Cl, similar ionic processes take place[21,22] as those described for BuCl [*cf.* eqns. (7)–(10)]. In both matrices secondary electrons are converted in Cl^- and corresponding matrix derived radicals (Bu$^{i\cdot}$ and $CF_2ClCFCl^{\cdot}$). In the presence of PBN an electron-transfer reaction as described by eqn. (11) should take place, giving rise to the cation radical of PBN.

After irradiation of frozen, glassy solutions of PBN (at 77 K), both matrices were intensely green in colour due to the formation of PBN$^{\cdot+}$. The EPR spectra of irradiated frozen PBN solutions are shown in Figs. 4(*a*) and (*b*). In the Freon-113 matrix, where the EPR signal of the matrix derived radical $CF_2ClCFCl^{\cdot}$ is very weak because of anisotropic broadening, the EPR spectrum after irradiation is only due to PBN$^{\cdot+}$ [*cf.* Fig. 4(*a*)]. It shows an asymmetric line with parallel transitions similar to those from ^{14}N, indicating an aminoxyl-type radical.[23] Assuming an axial symmetry, the anisotropic coupling constant $A_{\parallel}$ = 27.5 G and $g_{\parallel}$ = 2.0037 of PBN$^{\cdot+}$ could be determined. In an Bu^{i}Cl matrix, the combined EPR spectra of PBN$^{\cdot+}$ and of the solvent derived Bu$^{i\cdot}$ radicals were observed [Fig. 4(*b*)].

No changes in the EPR spectra shown in Figs. 4(*a*) and (*b*) were found at 77 K during 1–2 h after irradiation. However, after slow warming of the matrices until discolouration took place, a change in the EPR spectra was observed [Figs. 4(*c*) and (*d*)]. In both matrices studied the signal from PBN$^{\cdot+}$ disappeared, and instead of it an EPR signal from the chloro-substituted aminoxyl radical **5** with the characteristic ^{14}N parallel transition $A_{\parallel}$ of 32.4 G and $g_{\parallel}$ = 2.0038 appeared. The overall radical concentration during the discolouration showed not more than a 20% decrease (within the limits of EPR measurements). Hence, the decay of the cation radical PBN$^{\cdot+}$ results in a nearly quantitative formation of aminoxyl radical **5**.

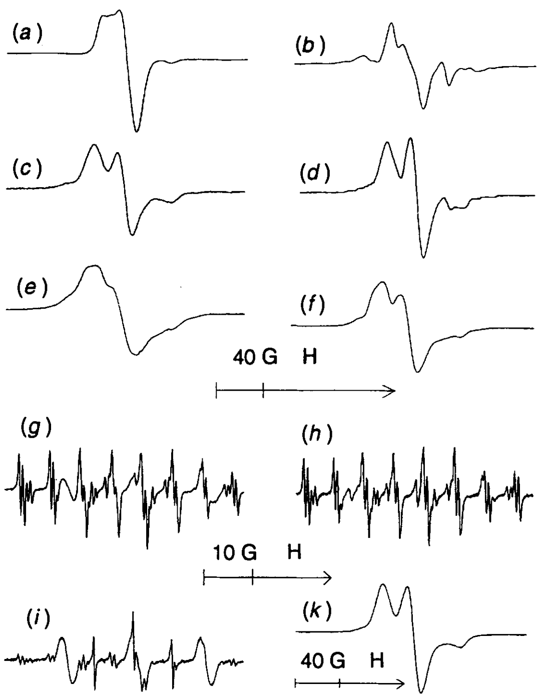
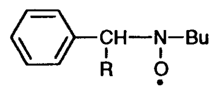


Fig. 4 EPR spectra of γ-irradiated PBN (0.05 mol dm^{-3}) solution in Freon-113 (*a, c, e, g, i*) and Bu^{i}Cl (*b, d, f, h, k*) recorded (*a–f, k*) at 77 K, (*g–h*) at 240 K and (*i*) at room temp.

The EPR spectra observed after further slow warming of each matrix up to the melting point are shown in Figs. 4(*e*) and (*f*). The overall radical concentration dropped down to about 20% of its initial value. This is not surprising, because the spin trapping of radicals, eqn. (1), in a glassy matrix during melting cannot efficiently compete with the decay of radicals (including aminoxyls) in disproportionation and recombination reactions.[24]

Well-resolved EPR spectra at 240 K in solutions [see Figs. 4(*g*) and (*h*)] allow us to identify aminoxyls **5** [a_N = 12.24 G, $a(^{35}Cl)$ = 6.38 G, $a(^{37}Cl)$ = 5.52 G and a_H = 0.69 G (*cf.* refs. 20 and 25)] in both systems studied as well as PBN spin adducts **8** and **9** with the matrix derived radicals.



8 R = $CF_2ClCFCl$
9 R = Bu^i

The observed relative amount of adduct **8** (triplet with a_N = 14.0 G) in the case of Freon-113 is equal to 40% [see Fig. 4(*g*)]. In Bu^{i}Cl spin adduct **9** is present only in a minor amount [Fig. 4(*h*)]. In this case after recooling the samples to 77 K we recorded a pure spectrum of aminoxyl **5** [Fig. 4(*k*)]. Comparing the latter spectrum with those shown in Figs. 4(*c*) and (*d*), it is clear that aminoxyl **5** is the main radical observed after the decay of PBN$^{\cdot+}$.

The observed yields of aminoxyls in solution depend strongly on the annealing temperature, *i.e.* on the rate of secondary decay reactions in each solvent. In the case of the Freon-113 spectrum shown in Fig. 4(*i*) observed after 10 min annealing at room temp., it is possible to identify spin adduct **8** and aminoxyl **7**

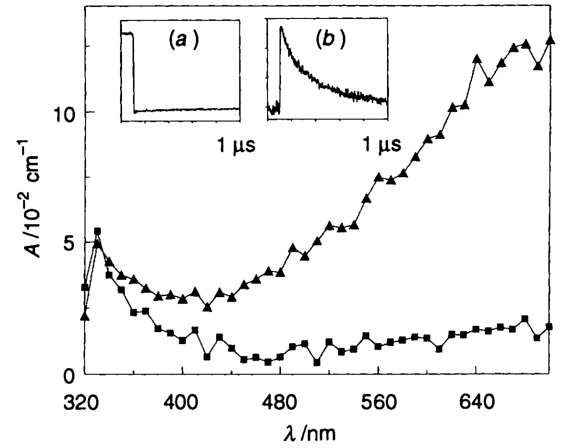


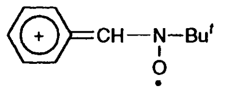
Fig. 5 Absorption spectra recorded after a 3 ns laser (266 nm) pulse in a solution of PBN (2×10^{-4} mol dm^{-3}) in H_2O: (▲), 7.46; (■), 739 ns. Inserts shows bleaching of PBN absorbance at (*a*) 305 nm during the pulse and decay of e_{aq} at (*b*) 600 nm.

(triplet with $a_N = 7.9$ G). Under the same conditions in the case of Bu^{t}Cl only very small amounts of the spin adduct **9** and also the aminoxyl **7** were observed (spectra not shown).

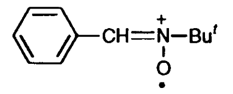
Thus, the main radical product observed after decay of the cation radical PBN$^{\cdot+}$ during warming of both matrices up to discolouration is chloro-substituted aminoxyl **5**.

It might be argued that aminoxyl **5** could be formed if Cl$^{\cdot}$ atoms were trapped by PBN according to eqn. (1) as was proposed earlier.[20] We can exclude this reaction because in the radiolysis of hydrogen-containing alkyl chlorides, no Cl$^{\cdot}$ atoms will be formed.[14,15] Cl$^{\cdot}$ Atoms in γ-irradiated Freons were also not detected.[21,22] Therefore, we conclude that aminoxyl **5** results from a nucleophilic addition reaction (6) of Cl$^-$ to the cation radical PBN$^{\cdot+}$. Cl$^-$ are formed in both matrices in reactions similar to eqn. (8).

From these various observations we deduce that PBN$^{\cdot+}$ is a stable aminoxyl radical cation, with the positively charged carbon attached directly to the aminoxyl group as is shown in the mesomeric structure **2**. Based on the observation that the aminoxyl group in PBN$^{\cdot+}$ is not involved in reactions with nucleophiles, we conclude that PBN$^{\cdot+}$ is an α-aminoxylcarbenium ion which may be represented by mesomeric structures **2**, **2a** and **2b**. PBN$^{\cdot+}$ may be considered as a typical phenylcarbenium ion[26] with an aminoxyl group as substituent.



2a



2b

The positive charge in **2** is stabilised by the resonance with the aromatic π-system[26] and by overlapping of the vacant π-orbital on carbon with the nitrogen lone pair of electrons. The fact that aminoxyl groups are also involved in the stabilization of positive charge is evident from EPR data for the cation radical PBN$^{\cdot+}$. The parallel transition coupling constant $A_{\parallel}$ for aminoxyl **2** is smaller than those for dialkylaminoxyls[5,23] and chloro-substituted aminoxyls **5** (see above) and similar to that of *tert*-butylaminoxyls with electron-withdrawing substituents. This indicates a decreased spin density on the nitrogen atom in **2**.

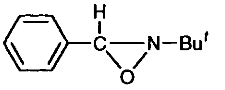
The formation of α-nitroxylcarbenium ions as primary oxidation products may be typical also for other nitrones. Therefore, a mechanism of their formation should be discussed. In view of the low[16] E_i of PBN, it seems likely that the oxidation of PBN proceeds by the removal of one π-electron from the nitrone moiety. The nitrone moiety, [$>$C=N$^+$(O$^-$)–], has an entire 'allylanion-type' molecular orbital with four π-electrons in the three atomic 2p-orbitals.[18]

The removal of one electron from these orbitals should result in a primary metastable allyl-type cation radical. Taking into account the higher electron affinity of the oxygen atom, we believe that this primary structure will relax to the energetically more favourable α-aminoxylcarbenium ion **2** (stabilisation energy[27] for aminoxyl is about 30 kcal mol^{-1}).*

Laser Flash Photolysis Studies.—Photoionisation of PBN by laser photolysis at 266 nm. The transient absorption spectra of intermediates appearing immediately after a 3 ns laser pulse of aqueous solutions of PBN are shown in Fig. 5. The absorption at λ_{max} near 720 nm may be unambiguously assigned to the solvated electron. The decay rate of e_{aq}^- increased strongly in the presence of the electron scavenger 2-chloroethanol (1%, v/v) or when the solution was saturated with oxygen. Hence, photoionisation, eqn. (16), of PBN takes place. The observed yield of e_{aq}^- increased with the laser power in a manner typical for biphotonic processes[28] as shown in eqn. (16).

$$\mathrm{PBN} \xrightarrow{2h\nu} \mathrm{PBN}^{\cdot+} + e_{aq}^- \qquad (16)$$

In the UV range of the transient spectrum, at $\lambda < 320$ nm, a strong bleaching of the PBN absorbance during the laser pulse was observed (see insert at 305 nm in Fig. 5) accompanied by a short-lived fluorescence. We explain this effect by the known[29] photoisomerisation, eqn. (17), of PBN into phenyl-*N*-*tert*-butyloxazirane **10**, which proceeds *via* the singlet excited state.



10

$$^{1}\mathrm{PBN} \longrightarrow \mathbf{10} \qquad (17)$$

In contrast to PBN, oxazirane **10** has only a minor absorption[30] at $\lambda > 260$ nm and therefore cannot be characterised directly. From the evaluation of PBN bleaching in the course of the laser pulse it was estimated that up to 30–50% of the initial PBN concentration will be converted in oxazirane **10**. Increasing the laser power results in a saturation of the yield of **10** at the 50% level.

The concentration of oxazirane **10** formed by the laser pulse is essentially larger than that of e_{aq}^- and the ratio depends strongly on the laser power. Thus, in the spectrum shown in Fig. 5, immediately after the pulse the ratio [**10**] : [e_{aq}^-] is about 20. At lower laser power e_{aq}^- was not observed, while nearly 30% of PBN was converted into oxazirane **10**.

As a photoionisation product, the cation radical PBN$^{\cdot+}$ was expected to be observed immediately after the pulse. A weak absorption shoulder at $\lambda = 410$ nm superimposed with the strong absorption band of e_{aq}^- was observed (Fig. 5), and tentatively assigned to PBN$^{\cdot+}$. In deaerated solutions, e_{aq}^- decays with a pseudo-first-order rate constant proportional to the initial PBN concentration. As already mentioned, PBN traps e_{aq}^- forming[9] a benzylic type anion radical PBN$^{\cdot-}$ with $\lambda_{max} = 360$ nm. After the decay of e_{aq}^- this species appears in the spectrum (Fig. 5) as a weak shoulder. The in-cage reaction mechanism responsible for PBN$^{\cdot-}$ formation is given in eqns. (3) and (4) (*cf.* also ref. 9). Oxazirane **10** is known[31] as a highly efficient oxidant and, therefore, it should also scavenge e_{aq}^- with

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* 1 kcal = 4.184 kJ.

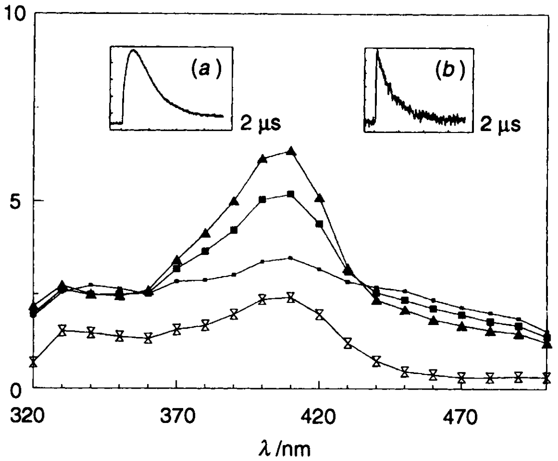

Fig. 6 Absorption spectra recorded after 3 ns laser pulse (266 nm) of a solution of PBN (1 × 10^{-3} mol dm^{-3}) in 0.16 mol dm^{-3} $K_2S_2O_8$ in H_2O: (■), 4; (■), 40; (▲), 89; (⧖), 686 ns. Inserts show time profiles for $PBN^{\bullet+}$ at (*a*) 410 nm and $SO_4^{\bullet-}$ at (*b*) 500 nm.

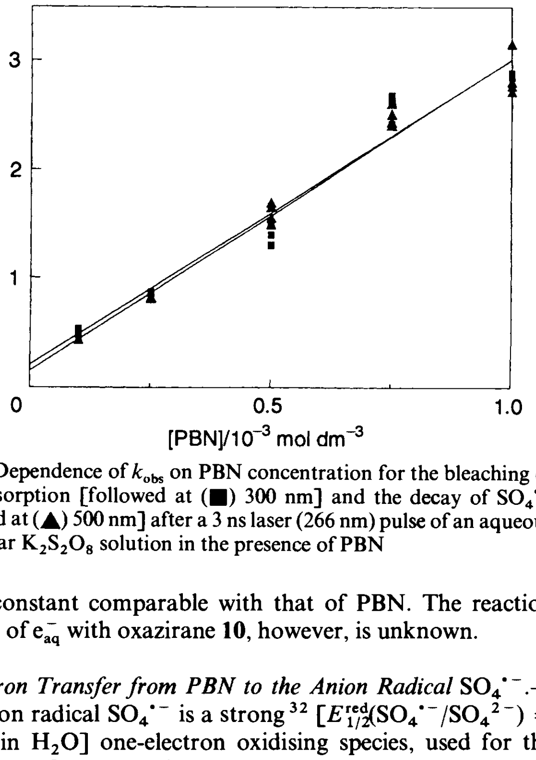

Fig. 7 Dependence of k_{obs} on PBN concentration for the bleaching of PBN absorption [followed at (■) 300 nm] and the decay of $SO_4^{\bullet-}$ [followed at (▲) 500 nm] after a 3 ns laser (266 nm) pulse of an aqueous 0.16 molar $K_2S_2O_8$ solution in the presence of PBN

a rate constant comparable with that of PBN. The reaction product of e_{aq}^- with oxazirane **10**, however, is unknown.

Electron Transfer from PBN to the Anion Radical $SO_4^{\bullet-}$.—The anion radical $SO_4^{\bullet-}$ is a strong[32] [$E_{1/2}^{red}(SO_4^{\bullet-}/SO_4^{2-})$ = 2.43 V in H_2O] one-electron oxidising species, used for the generation of cation radicals from electron donor molecules in aqueous solutions.[33] PBN has an oxidation potential $E_{1/2}^{ox}(PBN/PBN^{\bullet+})$ of 1.47 V (determined[34] in CH_3CN) and, therefore, may be oxidized by $SO_4^{\bullet-}$. The $SO_4^{\bullet-}$ anion radicals were produced by 266 nm laser excitation of $Na_2S_2O_8$ in aqueous solution with subsequent homolysis, eqn. (18), proceeding with a quantum yield[35] of about 1.

$$S_2O_8^{2-} \xrightarrow{h\nu} 2SO_4^{\bullet-} \qquad (18)$$

Immediately after the 3 ns laser pulse we observed the spectrum of $SO_4^{\bullet-}$ with a broad peak at λ 445 nm (ε/dm^3 mol^{-1} cm^{-1} 1367, ref. 35) and a pronounced plateau at $\lambda < 380$ nm.[33,35] Fig. 6 shows the transient absorption spectra taken after 3 ns laser pulsing of an aqueous solution containing $S_2O_8^{2-}$ and PBN. Immediately after the pulse the spectrum of $SO_4^{\bullet-}$ is observed as well as a bleaching of the PBN absorption at $\lambda < 310$ nm due to photoisomerisation, eqn. (17), of PBN. Because under our experimental conditions PBN absorbs a part of the excitation light (*cf.* refs. 30, 31), three primary parallel processes could take place—formation of $SO_4^{\bullet-}$, photoisomerisation of PBN and its photoionisation. The subsequently described experiments were performed using low laser power that excludes the photoionisation of PBN.

The oxidation of PBN by $SO_4^{\bullet-}$ could be monitored as a function of time after the pulse, as indicated in the transient spectra as well as in the absorption time profiles given as inserts in Fig. 6. The $PBN^{\bullet+}$ absorption band with λ_{max} at 410 nm similar to that detected in pulse radiolysis experiments in BuCl can be seen clearly from the spectral changes shown in Fig. 6. A blue shift by about 10 nm of λ_{max} of $PBN^{\bullet+}$ in aqueous solutions (comparing with λ_{max} = 420 nm in BuCl) may be explained by the higher polarity of the aqueous solution. Two isosbestic points at 360 and 435 nm speak for the direct connection between the $SO_4^{\bullet-}$ decay and the $PBN^{\bullet+}$ formation as formulated in eqn. (19).

$$SO_4^{\bullet-} + PBN \longrightarrow PBN^{\bullet+} + SO_4^{2-} \qquad (19)$$

An estimate for the extinction coefficient of $PBN^{\bullet+}$ at λ_{max} = 410 nm gives (5 ± 1) × 10^3 dm^3 mol^{-1} cm^{-1}. The decay of $SO_4^{\bullet-}$ (analysed at 500 nm) and the depletion of PBN (analysed at 290–310 nm) after the pulse were exponential, with the same pseudo-first-order rate constant proportional to the PBN concentration. In this manner reaction (19) could be followed from the side of both reactants $SO_4^{\bullet-}$ as well as PBN. From a plot of the observed rate constants, k_{obs}, for the $SO_4^{\bullet-}$ decay and for the depletion of PBN absorption *vs.* PBN concentration (Fig. 7), the rate constant for reaction (19) was determined to be k_{19} = 3.0 × 10^9 dm^3 mol^{-1} s^{-1}. In aqueous CH_3CN (1:1, v/v) solutions this constant is three times smaller at 8.9 × 10^8 dm^3 mol^{-1} s^{-1}, thus indicating[36] an outer-sphere electron transfer *via* reaction (19).

The observed kinetic behaviour of the transients as well as the solvent influence on the electron transfer rate constant allows us to exclude a radical addition of $SO_4^{\bullet-}$ to PBN with the formation of a spin adduct in the manner shown in reaction (1) (*cf.* ref. 37).

The cation radical $PBN^{\bullet+}$ decayed with a pseudo-first-order rate constant equal to 2 × 10^6 s^{-1} (analysed at 410 nm) without any dependence on PBN concentration up to 10^{-3} mol dm^{-3}. Therefore, the $PBN^{\bullet+}$ decay channels *via* reactions (14) and (15) could be excluded, and the decay of $PBN^{\bullet+}$ proceeds *via* reaction with water molecules, eqn. (5), forming aminoxyls **3** with k_5 = 3.6 × 10^4 dm^3 mol^{-1} s^{-1}. This indicates a relatively low reactivity of the cation radical $PBN^{\bullet+}$ towards water molecules.

From early[11,38] and also more recent[37] steady-state spin trapping studies, it is known that aminoxyl **3** is often detected in the course of photochemical or thermal homolysis of aqueous $S_2O_8^{2-}$ in the presence of PBN. Taking into account the fact that $HO^\bullet$ cannot be formed under such conditions,[33] it is clear that aminoxyl **3** must be formed in a nucleophilic addition reaction of H_2O to $PBN^{\bullet+}$ as is shown in eqn. (5). This conclusion supports the earlier proposal[11] regarding the formation mechanism of aminoxyl **3** from the cation radical $PBN^{\bullet+}$, and not in the spin trapping reaction according to eqn. (2a).

Electron Transfer to Chloranil Triplet.—Chloranil (CA) in the triplet excited state (^{3}CA) is an efficient one-electron oxidising species and has been shown to react rapidly with various electron donor molecules.[39] According to Rehm and Weller[40] in the case of PBN the expected electron-transfer reaction is exothermic by about 0.8 eV and, therefore, a nearly diffusion controlled electron transfer rate constant should be expected. In accordance with the literature,[39,41] on laser irradiation at λ =

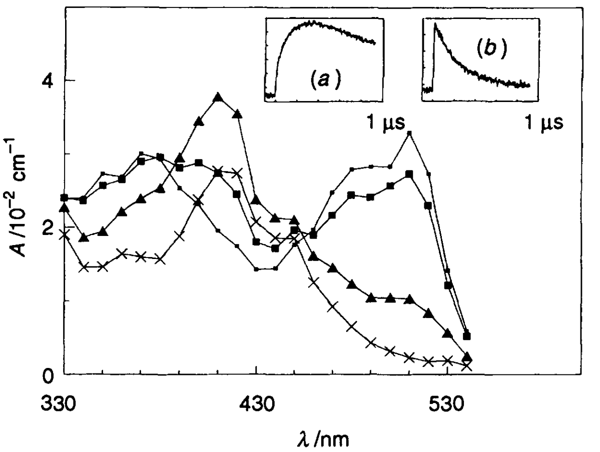

Fig. 8 Absorption spectra recorded after laser pulsing (5 ns, 355 nm) of a solution of chloranil (5×10^{-3} mol dm^{-3}) and PBN (5×10^{-4} mol dm^{-3}) in CH_3CN (5% H_2O, v/v): (■), 8.46; (■), 60.8; (▲), 301; (×), 842 ns. Inserts show time profiles for $PBN^{•+}$ at (*a*) 410 nm and ^3CA at (*b*) 520 nm.

355 nm of the CA solution in CH_3CN (5% H_2O, v/v) immediately after the 5 ns pulse we have observed triplet–triplet absorption bands of ^3CA at $\lambda_{max} = 510$ nm (ε/dm^3 mol^{-1} cm^{-1} 7570) and 370 nm and a shoulder at $\lambda = 480$ nm. The chloranil triplet ^3CA is known to be formed with a quantum yield of about 1. In CH_3CN (5% H_2O, v/v) ^3CA decayed presumably by H atom abstraction from CH_3CN as shown in eqn. (20), producing[39] the chloranil semiquinone radical ($CAH^•$) with λ_{max} at 435 nm (ε/dm^3 mol^{-1} cm^{-1} 7700).

$$^3CA + CH_3CN \longrightarrow CAH^• + {}^•CH_2CN \qquad (20)$$

The rate constant for this reaction was determined (following the decay of ^3CA absorption at $\lambda = 520$ nm) to be $k_{20} = 2 \times 10^4$ dm^3 mol^{-1} s^{-1}, lying in the range expected for H atom abstraction reactions by quinone triplets.[39]

On laser excitation of such a solution containing different concentrations of PBN, immediately after the pulse the ^3CA absorption was observed (see Fig. 8). PBN has practically no absorption at $\lambda = 355$ nm and hence may not be excited directly. ^3CA Decays generating a species with λ_{max} at 410 nm as shown in Fig. 8 (*cf.* also inserted time profiles taken at 410 and 520 nm). In view of the experiments described above, we assign this species to be cation radical $PBN^{•+}$.

The kinetics of the electron-transfer reaction, eqn. (21), can be

$$^3CA + PBN \longrightarrow CA^{•-} + PBN^{•+} \qquad (21)$$

seen clearly by a growth in absorption at 410 and 450 nm, a decrease at 510 nm, and an isosbestic point near 455 nm as shown in Fig. 8. Based on the results reported in refs. 39 and 41 we attribute the 450 nm species to the chloranil anion radical ($CA^{•-}$) as the counter ion of $PBN^{•+}$.

The anion radical $CA^{•-}$ is known to have a strong absorption[39,41] band at $\lambda_{max} = 450$ nm (ε/dm^3 mol^{-1} cm^{-1} 9700) with a shoulder[39] at 420 nm and could interfere with the formation kinetics of $PBN^{•+}$ at 410 nm. Therefore, we performed experiments in CH_3CN containing 5% H_2O (v/v), where the anion radical $CA^{•-}$ is protonated rapidly by water molecules resulting in $CAH^•$. Under conditions shown in Fig. 8 the dominating absorption at 410 nm is due to $PBN^{•+}$ and only a third of the absorbance at 410 nm could be ascribed to other species. An estimate for the extinction coefficient of $PBN^{•+}$ gives $(5 \pm 1) \times 10^3$ dm^{-3} mol^{-1} cm^{-1}. This is consistent with estimation made from the $SO_4^{•-}$ oxidation of PBN.

The decay of ^3CA in the presence of PBN was found to be exponential with a pseudo-first-order rate constant proportional to the PBN concentration. From measurements of the ^3CA decay (followed at 520 nm) at varied PBN concentrations the rate constant was determined to be $k_{21} = 8.1 \times 10^9$ dm^3 mol^{-1} s^{-1}.

The decay of $PBN^{•+}$ analysed at 410 nm was found to be exponential with a pseudo-first-order rate constant of 4.5×10^5 s^{-1}.

It is reasonable to assume that $PBN^{•+}$ decays in the reaction with water, eqn. (5), as was described above. An estimate for the $PBN^{•+}$ decay in reaction with water (using k_5 measured above) gives 1.5×10^5 s^{-1} for the pseudo-first-order rate constant. This indicates that in CH_3CN containing 5% H_2O a further decay reaction channel exists, *i.e.*, the ion-molecule reaction (14) with PBN. An estimate for k_{14} in this case gives 6×10^8 dm^3 mol^{-1} s^{-1}.

From earlier spin trapping studies[42,43] it is known that in steady-state photolysis of aqueous or alcoholic solutions of quinones (benzoquinone, anthraquinone and chloranil) in the presence of PBN, aminoxyl **3** and analogous RO-substituted aminoxyl radicals are formed. Based on such experiments an oxidation of water and alcohols by triplet excited quinones was proposed. From our studies it can be concluded that instead of H_2O or ROH, the spin trap PBN will be oxidised by the triplet quinones. Subsequently $PBN^{•+}$ reacts with the nucleophiles H_2O or ROH in reactions such as eqn. (5), producing the corresponding aminoxyls.

Conclusions

We have been able to generate PBN cation radicals under various experimental conditions in solutions and frozen matrices, giving us the opportunity to investigate the kinetic properties of $PBN^{•+}$, its structure and stability. The radical cation $PBN^{•+}$ was detected directly as a primary kinetically distinguishable intermediate after: (*i*) electron transfer to solvent cation radicals, eqn. (11); (*ii*) direct biphotonic ionisation, eqn. (16); (*iii*) oxidation by the anion radical $SO_4^{•-}$, eqn. (20), and by triplet excited chloranil ^3CA, eqn. (21).

The radical cation $PBN^{•+}$ is an α-aminoxylcarbenium ion **2** and reacts with nucleophiles forming substituted aminoxyl radicals. In this work we use both the term α-aminoxylcarbenium ion and cation radical to describe $PBN^{•+}$. Indeed, the species in question is a stable cation radical, because it is generated as a result of electron transfer from the molecular spin trap PBN. EPR data give us structural information and show that this species is an aminoxyl radical. The chemical behaviour speaks for the phenylcarbenium ion.

Briefly, we have concluded that two parallel reaction channels exist for the formation of aminoxyls by spin trapping studies in oxidative conditions: (*i*) true spin trapping as formulated in eqn. (1); and (*ii*) electron-transfer mediated nucleophile trapping by the α-aminoxylcarbenium ion, derived from the nitrone spin trap. Additionally, PBN plays the role of a nucleophile and reacts with $PBN^{•+}$ in an ion–molecule reaction (14), followed by eqn. (15), forming aminoxyl **7** and imine PhCH=N-Bu^t.

Furthermore, the nucleophilic substitution in aminoxyl radicals at the carbon atom attached directly to the aminoxyl group, [eqn. (22)], observed earlier[6] may be expected to proceed with the α-aminoxylcarbenium ion **2** as an intermediate.

$$\begin{aligned}&\text{Ph–C(X)H–N(O}^•\text{)–Bu}^t + \text{Nu} \longrightarrow \\ &\qquad \text{Ph–C(Nu)H–N(O}^•\text{)–Bu}^t + \text{X}^- \qquad (22)\end{aligned}$$

$$X = Cl;\ Nu = CH_3OH, \text{pyridine}, PBN$$

Reaction (22) could be responsible for the secondary transformation reactions in spin trapping applications.

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