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SPIN TRAPPING OF INORGANIC RADICALS

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The use of nitrose compounds and nitrones as spin traps for the detection of short-lived inorganic radicals is discussed. To a certain degree nitrones and nitroso compounds are complementary. While nitroso compounds are superior with respect to spin trapping metal-centred radicals, nitrones form more persistent spin adducts with most small inorganic radicals.

Erroneous results may be obtained when hydrolysis and redox reactions involving the spin adducts are ignored. Spin trapping of pseudohalide radicals ($\cdot N_3$, $\cdot CN$, $\cdot SCN$) are discussed in more detail.

KEY WORDS: Spin trapping, inorganic radicals, metal-centred radicals, aminoxyl, nitrone, nitroso compound, pseudohalide.

INTRODUCTION

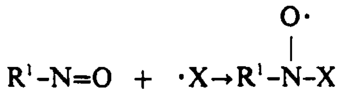
Unlike main group elements, transition metal compounds generally undergo redox reactions by single-electron transfer leading to inorganic radicals, e.g. oxidized/reduced counterions, ligand fragments and metal-centred radicals. In addition, metal-centred inorganic radicals may be formed by bond homolysis of dimeric metal-metal bonded coordination compounds or by cleavage of metal-ligand bonds.

Many inorganic radicals are not only short-lived but have also extremely short spin-lattice relaxation times due to their orbitally degenerate ground states. This effect, which operates for radicals such as $\cdot OH$, $\cdot SH$, $\cdot Br$, $\cdot Cl$ and others, causes severe line-broadening and makes direct ESR detection in fluid solutions impossible. In order to detect these radicals, cryogenic temperatures, very often as low as 4 K, are required.

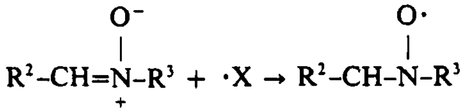
Furthermore, many inorganic radicals absorb light in the near UV region, i.e. the range where the precursor compounds very often absorb as well. Therefore, techniques based on the measurement of the light absorption, e.g. flash photolysis, appear to be less suitable.

Although inorganic radicals are structurally very different from organic radicals, they resemble each other with respect to their frontier orbitals. Hence, based on the concept of isolobal analogy[2], inorganic radicals such as $\cdot BH_3^-$, $\cdot Co(CN)_5^{3-}$, $\cdot Mn(CO)_5$ and $\cdot NH_2$ are expected to behave chemically like $\cdot CH_3$. Thus it is not very surprising that the spin trapping technique, originally designed for the detection of short-lived organic radicals,[3-5] may also be successfully applied to the detection of inorganic radicals.[6-8]

Despite the fact that more than 100 different compounds have been proven to be suitable spin traps, nitrones and nitroso compounds are the most commonly used spin traps. Both nitroso compounds and nitrones form persistent animoxyls (nitroxides) upon addition of radicals.



$$R^1\text{-}N{=}O \;+\; \cdot X \rightarrow R^1\text{-}\overset{\overset{\displaystyle O\cdot}{|}}{N}\text{-}X \qquad (1)$$

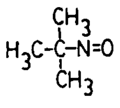


$$R^2\text{-}CH{=}\underset{+}{\overset{\overset{\displaystyle O^-}{|}}{N}}\text{-}R^3 \;+\; \cdot X \rightarrow R^2\text{-}CH\text{-}\overset{\overset{\displaystyle O\cdot}{|}}{N}\text{-}R^3 \qquad (2)$$

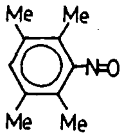
To a certain degree these spin traps are complementary with respect to trapping inorganic radicals, i.e. those radicals that are not trapped by nitrones form persistent spin adducts with nitroso compounds, and *vice versa*. An extensive compilation of ESR data for spin adducts has been published very recently.[9]

SPIN TRAPPING WITH NITROSO COMPOUNDS

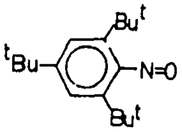
Both aliphatic and aromatic nitroso compounds are among the most commonly used spin traps for the detection of inorganic radicals. Typical examples are 2-methyl-2-nitrosopropane (MNP), 2,3,5,6-tetramethyl nitrosobenzene (nitrosodurene, ND), 2,3,6-tri-*tert*-butyl nitrosobenzene (BNB) and sodium 3,5-dibromo-4-nitrosobenzene sulphonate (SBNS).



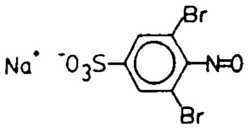
MNP



ND



BNB



SBNS

Many nitroso compounds form dimers in the solid state which, in general, do not react with radicals. In order to become spin traps, they have first to dissociate into monomers which makes kinetic experiments with nitroso spin traps rather difficult. However, BNB, due to steric hindrance by the bulky *tert*-butyl groups, exists exclusively as a monomer.

SBNS[10] and also its deuterated analogue appear to be particularly useful for the study of aqueous solutions, although only very few applications to inorganic radicals have been reported so far.

MNP is one of the most reactive spin traps. In addition, it is soluble in most solvents including water. On the other hand, MNP is very photosensitive both in the UV and in the red region forming di-*tert*-butyl aminoxyl which may mask the ESR signals of spin adducts. Although photostability has claimed for ND,[11] we have shown[12] that ND may indergo aryl-NO bond cleavage when irradiated with UV light. Dioxygen and transition metal complexes, however, were found to be efficient quenchers for the readtive excited state of ND. Therefore, the photosensitivity of ND seems to play a minor role when photoreaction of metal complexes are studied. It should be noted, however, that ND (and other nitroso compounds) may be readily reduced, e.g. by organometallic compounds, when in its electronically excited state.

Although nitroso compounds are less important spin traps for the detection of radicals with electronegative radicals centres, e.g. oxygen-centred radicals and halogen atoms, they have become increasingly attractive for the detection of metal-centred radicals (see Table I).

One of the most characteristic features of spin adducts of metal-centred radicals to nitroso compounds is that, unlike most other spin adducts of organic and inorganic radicals, the *g*-values vary over a wide range.

When electron-rich organometallic compounds are studied one should be aware of the fact that nitroso compounds may actually induce a radical process by electron transfer. In this case the ESR signal of the nitroso anion radical is also observed. Nitroso compounds may also be reduced by alkali metals. The formation of ion pairs between the nitroso anion radical and the corresponding cation has been monitored by ESR.[26]

As compared with nitrones, only relatively few spin adducts of radicals (other than metal-centred radicals) with nitroso compounds are known (see Table II).

Spin trapping of azidyl radicals ($\cdot N_3$) with nitroso compounds[38] deserves some further comments. The ESR spectrum of the ND spin adduct exhibits hyperfine splittings by three nitrogen nuclei, two of them being equivalent. By using ^{15}N-labelled azide it was shown[39] that the hyperfine splitting by the two equivalent nitrogen nuclei results from nitrosodurene and that only the third nitrogen splitting is caused by the azidyl radical which confirms the previously[36] assigned structure I for the spin adduct (see Scheme I). However, the question remained as to whether nitrosodurene dimers or monomers act as a spin trap. By using a mixture of ND and MNP it could be demonstrated[40] that the reaction sequence shown in Scheme I plays a role in spin trapping azidyl radicals. Since not only I but also the "mixed" spin

TABLE I

ESR parameters of spin adducts of metal-centred radicals with nitroso compounds[a]

Radical	Spin Trap	Solvent	a_N	a_M	*g*	Ref.
$\cdot Co(CN)_5^{3-}$	MNP	methanol	1.87	1.11 (^{59}Co)	2.0054	13
$\cdot Mo(CN)_7^{3-}$	ND	CH_2Cl_2	0.38	3.56 ($^{95,97}Mo$)	1.9823	14
$\cdot W(CN)_7^{3-}$	ND	CH_3CN	0.959			15
$\cdot Mo(CO)_3Cp$[b]	ND	CH_2Cl_2	1.45	0.40 ($^{95,97}Mo$)	2.005	16
$\cdot Re(CO)_5$	ND	CH_2Cl_2	1.403	3.80 ($^{185,187}Re$)	2.0098	17
$\cdot Re(CO)_4PPh_3$[c]	ND	CH_2Cl_2	1.39	3.43 ($^{185,187}Re$)	2.0087	17
$\cdot Mn(CO)_5$	ND	CH_2Cl_2	1.59	0.88 (^{55}Mn)	2.006	16
$\cdot Rh(CO)_2$	ND	CH_2Cl_2	1.60	0.42 (^{103}Rh)	2.012	18
$\cdot Fe(CO)_2CpMe_5$[d]	ND	benzene	1.708		2.0064	19
$\cdot Fe(CO)_2Cp$	ND	toluene	1.787		2.0052	19
$\cdot Cr(CO)_4Cl$	ND	CCl_4	0.83	1.86 (^{53}Cr)	1.9983	20
$\cdot UCp_3$	ND	THF	1.306		2.0076	21
$\cdot Ni(bipy)Et$[e]	ND	benzene	1.25		2.0130	22
$\cdot Zr(Cp)_2H$	MNP	benzene	1.37	0.43 (^{91}Zr)[f]		23
$\cdot Al(TPP)$[g]	BNB	benzene	1.20	0.19 (^{27}Al)	2.0049	24
$\cdot Pd(PPh)_3N_3$	ND	CH_2Cl_2	1.574	0.801 (^{105}Pd)[h]	2.0096	25

[a] coupling constants in mT, [b] *Cp* = cyclopentadienyl anion
[c] PPh_3 = triphenyl phosphine, additional splitting $a_P = 0.71$ (^{31}P)
[d] $CpMe_5$ = pentamethylcyclopentadienyl anion
[e] bipy = 2,2'-bipyridine, Et = ethyl
[f] additional splitting $a_H = 0.15$ (^1H)
[g] TPP = tetraphenylporphyrin dianion
[h] additional splitting $a_P = 0.432$ ^{31}P)

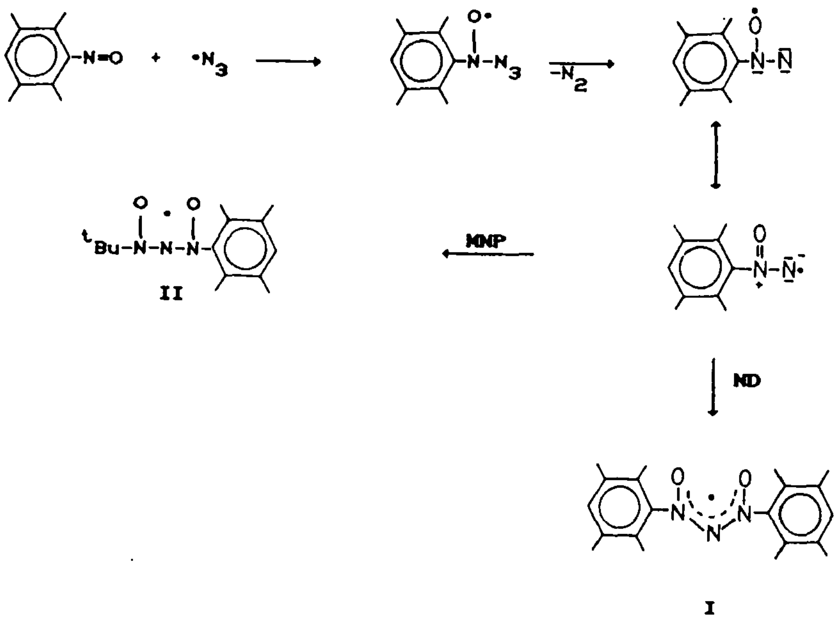
TABLE II
ESR parameters for spin adducts of inorganic radicals with nitroso compounds[a)]

Radical	Spin Trap	Solvent	a_N	a_X	g	Ref.
$\cdot PO_3^{2-}$	MNP	water	1.34	1.20 ($1^{31}P$)		27
$\cdot CN$[b)]	MNP	benzene	0.934	0.167 (1N)	2.0066	28
$\cdot BH_3^-$	MNP	benzene	1.30	1.28 (3H) 0.55 ($1^{11}B$) 0.18 ($1^{10}B$)	2.0059	29
$\cdot SO_2Cl$	MNP	benzene	1.17			30
$\cdot SO_2F$	MNP	benzene	1.24			30
$\cdot SO_2H$	MNP	MeOH/H_2O	1.47	0.46 ($1^{13}C$)	2.0055	31
$\cdot SO_2NH$	MNP	water	1.39		2.0055	32
$\cdot SO_2^-$	MNP	water	1.458		2.0054	32
$\cdot SO_3^-$	MNP	water	1.47		2.0054	32
$\cdot H$	MNP	water	1.441	1.391 (1H)		33
$\cdot D$	MNP	D_2O	1.40	0.22 (1D)		34
$\cdot AsO_2$ (or $\cdot AsO_3^{2-}$)	MNP	water	1.410	0.772 ($1^{75}As$)		35
$\cdot N_3$	ND	CH_2Cl_2	0.238	0.721 ($2^{14}N$)		36
$\cdot NCO$	ND	CH_2Cl_2	0.240	0.723 ($2^{14}N$)		37

[a)] all coupling constants in mT
[b)] Aminoxyl was formed by independent synthetic routes, not by spin trapping.

adduct II was formed in this reaction one may assume subsequent spin trapping by monomers. However, spin trapping by nitrosodurene dimers cannot be ruled out completely by these experiments.

Interestingly, the isoelectronic cyanatyl radical (·NCO) leads to the same spin adduct[37] confirming the correct assignment of I. However, it should be noted that, as far as we know, the behaviour of the azidyl and cyanatyl radicals is unique with



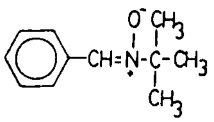
SCHEME I

respect to other pseudohalide radicals which apparently do not react with nitroso compounds to form persistent aminoxyls.

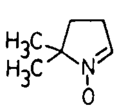
SPIN TRAPPING WITH NITRONES

Except for some platinum radicals[41] and some metal-centred radicals of group IV *b*[42–45], persistent spin adducts of metal-centred radicals with nitrones have not yet been described. On the other hand, many radicals that are not trapped by nitroso compounds form persistent spin adducts with nitrones.

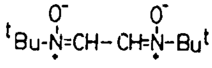
The structures of some typical nitrones used in spin trapping experiments are given below.



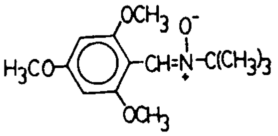
PBN



DMPO



GBBN



(MO)$_3$PBN

Due to their good solubility in both polar and non-polar solvents as well as their reasonable photochemical and thermal stability, PBN and DMPO are probably the most popular spin traps.

The use of DMPO as a spin trap for oxygen-centred radicals has been the subject of various excellent review articles[46–49] and will not be discussed here.

Usually, the ESR spectrum of a nitrone spin adduct exhibits hyperfine coupling of the unpaired election with the ^{14}N and the β-H nuclei which leads to a triplet of doublets. A compilation of hyperfine splitting constants observed in various spin adducts of inorganic radicals with PBN is given in Table III. Very often the influence of the solvent upon the hyperfine splitting exceeds that of the radical's structure.[64] Therefore, solvent effects have to be studied carefully before assigning spin adducts according to reference data found in the literature. However, it has been shown[65] that by introducing bulky methoxy groups into ortho-positions of the phenyl group of PBN the β-H coupling constants are much more affected by the nature of the trapped radical than in the unsubstituted analogue. On the other hand, the steric hindrance in (MO)$_3$PBN strongly reduces the spin trapping reactivity which, together with the weak solubility in polar solvents, renders (MO)$_3$PBN, in general, less suitable for the detection of inorganic radicals, although this spin trap appears to be extremely useful for some special cases (see below).

A significant improvement of the information content that may be extracted from spin adduct ESR data has been achieved by deuteration of PBN.[66] As can be seen from the azidyl spin adduct shown in Figure 1, deuteration of PBN leads to a dramatic decrease of linewidth which allows the resolution of hyperfine splitting by the γ- and δ-N nuclei.[67] It should be noted that long-range hyperfine couplings could also be detected in spin adducts of glyoxal bis(*tert*-butyl nitrone) (GBBN).[45] As compared with the fully deuterated PBN-d$_{14}$, this spin trap has the advantage of being less expensive. In addition, GBBN has been shown to give persistent spin adducts with bromine atoms.[52] The lifetime of this spin adduct was found to be about two orders of magnitude higher than for PBN.[54]

Interestingly, several inorganic radicals, e.g. $\cdot SO_3^-$, $\cdot PO_3^{2-}$ and $\cdot HPO_2^-$ (see Table

TABLE III
ESR hyperfine splitting constants for spin adducts of inorganic radicals to PBN[a)]

Radical	Solvent	a_N	a_H^{β}	a_X	Ref.
$\cdot H$	benzene	1.480	0.741 (2^1H)		50
$\cdot D$	CCl_4	1.47	0.73	0.11 (^2D)	51
$\cdot F$	benzene	1.22	0.118	4.56 (^{19}F)	52
$\cdot Cl$	CH_3CN	1.270	0.082	0.620 (^{35}Cl) 0.512 (^{37}Cl)	53
$\cdot Br$	benzene	1.13	–	3.49 (^{81}Br) 3.24 (^{79}Br)	54
$\cdot OH$	water	1.55	0.272	0.336 (^{17}O)	55
$\cdot OOH$	water	1.481	0.27	0.27 (^{17}O)	55
$\cdot N_3$	water	1.501	0.201	0.201 (^{14}N)	38
$\cdot NCO$	CH_3CN	1.509	0.315	0.184 (^{14}N)	56
$\cdot NCSSCN^-$	CH_3CN	1.444	0.109	0.368 (^{14}N)	57
$\cdot OSO_3^-$	CH_3CN	1.390	0.123		58
$\cdot SO_3^-$	water	1.495	0.197	0.034 (2^1H)	59
$\cdot CO_2^-$	water	1.580	0.452		59
$\cdot CN$	CH_3CN	1.504	0.198	0.985 (^{13}C)	56
$\cdot CONH_2$[b)]	water	1.553	0.320	0.050 (^{14}N) 0.050 (^1H)	60
$\cdot NC(O)^-$[b)]	CH_3CN	1.481	0.215	0.215 (^{14}N)	61
$\cdot NCHOSO_3$[c)]	CH_3CH/H_2O	1.485	0.082	0.1780 (^{14}N)	60
$\cdot OPO_3^{2-}$	water	1.546	0.184		62
$\cdot HPO_2^-$	water	1.608	0.317	1.603 (^{31}P) 0.184 (^1H) 0.027 (2^1H)	62
$\cdot PO_3^{2-}$	water	1.587	0.131	2.166 (^{31}P) 0.020 (2^1H)	62
$\cdot N(CN)_2$	water	1.587	0.291	0.151 (^{14}N)	63
$\cdot C(CN)_3$	CH_3CN	1.437	0.569		63
$\cdot NH_2$	water	1.614	0.354	0.123 (^{14}N) 0.054 (2^1H)	59

[a)] all coupling constants in mT, [b)] formed by hydrolysis of $\cdot CN$
[c)] formed by addition of $\cdot OSO_3^-$ radicals to cyanide

III), form spin adducts with normal, i.e. non-deuterated PBN, having an exceptional sharp linewidth which allows the resolution of small hyperfine splittings due to the ortho-protons of the phenyl ring adjacent to the nitrone function.

It is generally assumed that spin adducts are exclusively formed by addition of free radicals to the spin trap. However, alternative routes leading to spin adducts of nitrones should also be considered. One of these alternative routes, which is very common in inorganic spin trapping reactions,[68,69] is the hydrolysis of primary spin adducts leading to the hydroxyl spin adduct, although no *free* hydroxyl radicals are formed in the reaction (see Scheme II).

Using the spin trap $(MO)_3PBN$ it is possible to distinguish between hydroxyl spin adducts formed by hydrolysis and those formed by spin trapping free hydroxyl radicals since oxygen-centred radicals, unlike other radicals, preferably react with $(MO)_3PBN$ by hydrogen abstraction at the methoxy group (see Scheme III). The final aminoxyl IV (2H,3H-4,6-dimethoxy)benzo[b]furan-3-yl-*tert*-butyl aminoxyl) is formed by cyclisation (internal spin trapping) of the intermediate III. In addition, about 10 to 20% of the regular hydroxy spin adduct V, i.e. the spin adduct with a β-hydroxy group, are formed. The aminoxyl IV ($a_{\mathrm{N}} = 1.644$ mT, $a_{\mathrm{H}}^{\beta} = 0.150$ mT, $a_{\mathrm{H}}^{\gamma} = 0.123$ mT, in water) can be easily distinguished from the hydroxy

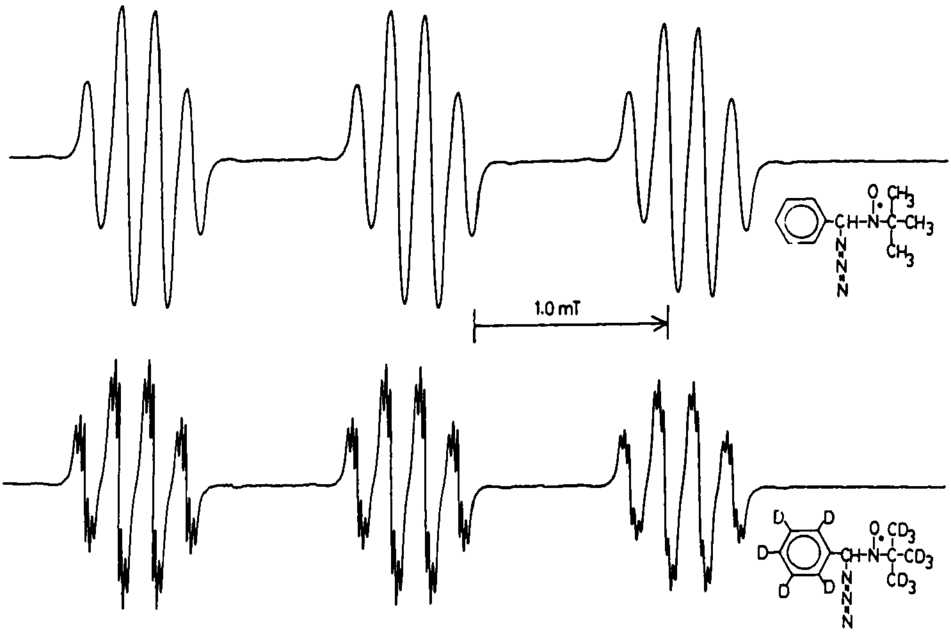
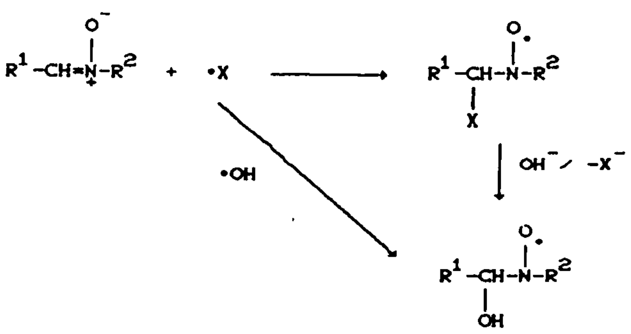


FIGURE 1 ESR spectra of the azidyl ($\cdot N_3$) spin adducts to PBN (top) as well as its deuterated analogue PBN-d_{14} (bottom). Azidyl radicals were generated by photolysis of the charge-transfer complex formed between CB_4 and $Bu_4N^+N_3^-$ in benzene solution. A high pressure xenon lamp equipped with a 350–500 nm band-pass filter was used as a source of radiation.

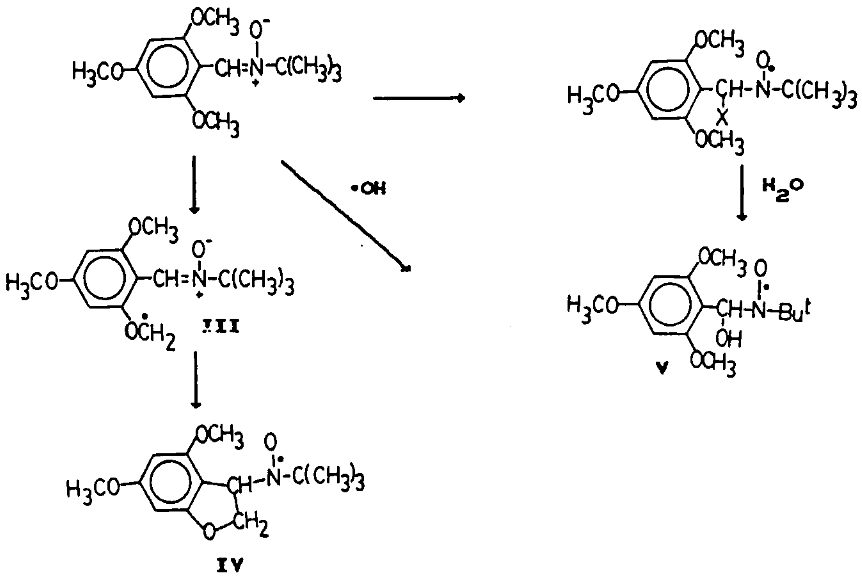


SCHEME II

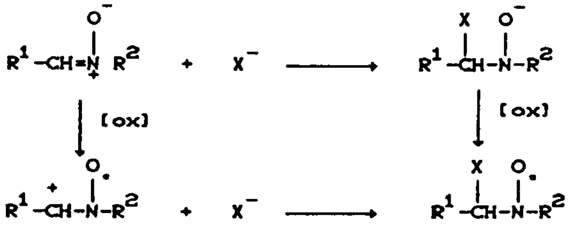
spin adduct V (a_N = 1.621 mT, $a^{\beta\text{-}H}$ = 0.885 mT) on the basis of the hyperfine coupling constants.

A second major problem in spin trapping experiments using nitrones arises from nucleophilic addition to yield a hydroxylamine anion, followed by oxidation of the latter (see Scheme IV).

Only mild oxidants are required to bring about oxidation of the hydroxylamine anion. The mechanismus given in Scheme IV plays an important role in the reaction of cyanide in aqueous solution.[70] However, recent spin trapping studies[61] on the oxidation of cyanide have created serious doubts about the possibility that cyanyl radicals can be spin-trapped in aqueous solutions at all. It is well established that[60] that the ultimate radical product of the one-electron oxidation of cyanide ions is the carbamoyl radical ($\cdot CONH_2$). If excess water is present, this is the only *free* radical



SCHEME III



SCHEME IV

that can be spin-trapped. If the amount of water is reduced, products of partial hydrolysis could also be detected. Apparently, the hydrolysis of cyanyl radicals is much faster than spin trapping by PBN.

According to Scheme IV, the alternative route, i.e. initial oxidation of the spin trap first, followed by addition of an anion, should be possible as well.[71] However, oxidation of nitrones requires very strong oxidants[56] which are not present under normal chemical conditions.

This situation may change dramatically when photolysis is involved since a molecule in its excited state is a much stronger oxidant (and reductant) than in its electronic ground state. Although it is quite common to avoid direct excitation of spin traps by the use of appropriate filters, one has to be aware that subsequent energy or electron transfer processes may occur. The energy of the lowest excited triplet state of PBN was measured[72] to be 16,200 cm^{-1}, and, for example, the rate constant for quenching the excited state of $[Ru(bipy)_3]^{2+}$ by PBN was determined[73] as about $3.3 \cdot 10^7$ $M^{-1} s^{-1}$. The resulting excited PBN molecule is easily oxidized to the cation radical which may react with even very weak nucleophiles to form an aminoxyl radical.[74]

It is usually assumed that free radicals react with nitrones by addition to the nitrone function. However, as already discussed for the reaction of oxygen-centred radicals with $(MO)_3$PBN this may not always be the case. Another example is the reaction of thiocyanatyl radicals (·SCN) with various nitrones.[57] While both ·SCN and ·NCSSCN$^-$ radicals are readily detectable by spin trapping with C-*tert*-butyl N-*tert*-butyl nitrone (BBN), only ·NCSSCN$^-$ radicals were trapped by PBN. If the PBN concentration is increased in order to compete with trapping of ·SCN by thiocyanate anions, a radical is formed which results from addition of ·SCN to the phenyl ring adjacent to the nitrone function of PBN. Similar behaviour was found for other nitrone spin traps containing phenyl groups as a constituent.

This provides a further example that despite many advantages offered by the use of popular spin traps such as PBN and DMPO one should try not to rely on a single spin trap. Instead, the use of a variety of spin traps is recommended, especially in the area of inorganic radical chemistry.

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