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Spin Trapping of Inorganic Radicals

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1 Introduction

About 30 years ago it was demonstrated by both American[1] and a group of Hungarian and Russian[2] researchers that nitroso compounds add organic free radicals to form persistent aminoxyls which are readily detectable by EPR spectroscopy. This work was extended by Dutch[3] and Japanese[4] workers, the latter showing that aminoxyls are also formed by addition of short-lived free radicals to nitrones. Shortly after this, the importance of this reaction as an analytical tool for detection and identification of short-lived radicals was recognized by Janzen[5] and, independently, by Lagercrantz[6] in Sweden, Perkins[7] in the U.K., de Boer[8] in the Netherlands, Leaver and Ramsay[9] in Australia and Terabe and Konaka[10] in Japan. Later Janzen and Blackburn[11] coined the expression *spin trapping* for a reaction where a short-lived radical $^{\bullet}R$ is scavenged by a diamagnetic compound S to form a persistent radical adduct $R\text{–}S^{\bullet}$, equation 1.

$$^{\bullet}R + S \longrightarrow R\text{–}S^{\bullet} \qquad (1)$$

In this reaction the diamagnetic scavenger S is called the *spin trap*, and the resulting persistent radical $R\text{–}S^{\bullet}$ is named the *spin adduct*. Unlike many short-lived radicals $^{\bullet}R$, the spin adduct $R\text{–}S^{\bullet}$ is readily detectable by EPR even in liquid solution at higher temperatures.

Although more than 100 different compounds have proven to be suitable spin

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[1] A K Hoffman and A T Henderson, *J Am Chem Soc*, 1961, **86**, 4671

[2] F Tudos, I Kende, T Berezsnich, S Szolodovnikov, and V Vojevodskij, *Magy Kem Foly*, 1963, **69**, 371, F Tudos, I Kende, T Berezhnykh, S P Solodovnikov, and V V Voevodskii, *Kinet Katal*, 1965 **6**, 203

[3] A Mackor, Th A J W Wajer, J D W van Voorst, and Th J de Boer, *Tetrahedron Lett*, 1966, 2115, Th A J W Wajer, A Mackor, Th J de Boer, and J D W van Voorst, *Tetrahedron*, 1967, **23**, 4021

[4] M Iwamura and N Inamoto, *Bull Chem Soc Jpn*, 1967, **40**, 702, 703

[5] E G Janzen, *Chem Eng News*, 1965, **43**, 50, E G Janzen and J L Gerlock, *Nature*, 1967, **222**, 867, E G Janzen and B J Blackburn, *J Am Chem Soc*, 1968, **90**, 5909

[6] C Lagercrantz, *J Phys Chem*, 1971, **75**, 3466, C Lagercrantz and S Forshult, *Nature*, 1968, **218**, 1247, C Lagercrantz and K Torssell, *Acta Chem Scand*, 1968, **22**, 1935

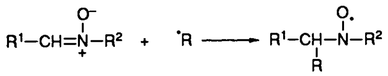
[7] M J Perkins, in 'Essays on Free-radical Chemistry', Special Publication No 24, The Chemical Society, London 1970, p 97, G R Chalfont, M J Perkins, and A Horsfield, *J Am Chem Soc*, 1968, **90**, 7141

[8] Th J de Boer, *Can J Chem*, 1982, **60**, 1602 and references therein

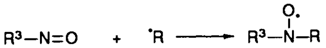
[9] I H Leaver and G C Ramsay, *Tetrahedron*, 1969, **25**, 5669

[10] S Terabe and R Konaka, *J Am Chem Soc*, 1969, **91**, 5655

[11] E G Janzen and B J Blackburn, *J Am Chem Soc*, 1969, **91**, 4481



$$R^1\text{–}CH\text{=}\overset{O^-}{\underset{+}{N}}\text{–}R^2 + {}^{\bullet}R \longrightarrow R^1\text{–}\underset{R}{CH}\text{–}\overset{O^{\bullet}}{N}\text{–}R^2 \qquad (2)$$



$$R^3\text{–}N\text{=}O + {}^{\bullet}R \longrightarrow R^3\text{–}\overset{O^{\bullet}}{N}\text{–}R \qquad (3)$$

traps, nitrones and *C*-nitroso compounds, which both give persistent aminoxyls upon radical addition (equations 2 and 3), are preferred by most researchers.

The spin trapping technique has been successfully applied to EPR detection of organic free radicals.[12] Applications in biochemistry and medicine[13] and in various areas of chemistry such as gas phase reactions,[14] electrochemistry,[15] and photochemistry[16] have also been reviewed. An extensive compilation[17] of spin adduct EPR data have been published recently. Although the spin trapping was originally designed for the detection of short-lived organic radicals, many inorganic radicals have also been shown to form persistent spin adducts with both nitroso compounds and nitrones. This is of particular importance since 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 ${}^{\bullet}$OH, ${}^{\bullet}$SH, ${}^{\bullet}$Br, ${}^{\bullet}$Cl, and others, causes severe line-broadening and makes direct EPR detection in fluid solutions impossible. In order to detect those radicals, cryogenic temperatures, very often as low as 4 K, are required. Moreover, many inorganic radicals absorb light only in the near UV region, *i.e.* the range where the precursor compounds usually also exhibit high absorbance. Therefore techniques based on the measurement of the light absorption, *e.g.* flash photolysis, are unsuitable.

In some previous publications[18] particular reference has been made to

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[12] E G Janzen, *Acc Chem Res*, 1971, **4**, 31, M J Perkins, *Adv Phys Org Chem*, 1980, **17**, 1, R Kh Freidlina, I I Kandror, and R G Gasanov, *Usp Khim*, 1978, **47**, 508, V E Zubarev, V N Belevskij, and L T Bugaenko, *Usp Khim*, 1979, **48**, 1361, D Rehorek, *Z Chem*, 1980, **20**, 325, I Rosenthal and P Riesz, *Radiat Phys Chem*, 1987, **30**, 381, P Riesz and S Rustgi, *Radiat Phys Chem*, 1979, **13**, 21

[13] E G Janzen, in 'Free Radicals in Biology', ed W A Pryor, Vol 4, Academic Press, New York 1980, 115, P J Thornalley, *Life Chem Rep*, 1986, **4**, 57, G M Rosen, *Adv Free Radical Biol Med*, 1985, **1**, 345, E G Janzen, H J Stronks, C M DuBose, J L Poyer and P B McCay, *Environ Health Perspect*, 1985, **64**, 151, E Albano, A Tomasi, K H Cheeseman, V Vannini, and M U Dianzani, in 'Free Radicals in Liver Injury', ed G Poli, K H Cheeseman, M U Dianzani, and T F Slater, IRL Press, Oxford, 1985, p 7, P B McCay, T Noguchi, K-L Fong, E K Lai, and J L Poyer, in 'Free Radicals in Biology', ed W A Pryor, Vol 4, Academic Press, New York, 1980, p 155

[14] E G Janzen, *Creat Detect Excited State*, 1976, **4**, 83

[15] T H Walter, E E Bancroft, G L McIntire, E R Davis, L M Gierasch, H N Blount, H J Stronks, and E G Janzen, *Can J Chem*, 1982, **60**, 1621

[16] J R Harbour and M L Hair, *Adv Colloid Interface Sci*, 1986, **24**, 103, D Rehorek and H Hennig, *Can J Chem*, 1982, **60**, 1565, D Rehorek, S Di Martino, T J Kemp, and H Hennig, *J Inf Rec Mat*, 1989, **17**, 469

[17] G R Buettner, *Free Radical Biol Med*, 1987, **3**, 259

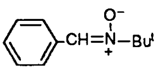
[18] M C R Symons, *Philos Trans R Soc London B*, 1985, **311**, 451, D Rehorek, *Proc 10th Conf Coord Chem, Smolenice/CSSR 4 7th June 1985*, p 329, D Rehorek, H Hennig, C M DuBose, T J Kemp, and E G Janzen, *Free Rad Res Commun*, 1990, **10**, 75, R P Mason and C Mottley, in 'Electron Spin Resonance', Vol 10B, ed M C R Symons, A Specialist Periodical Report, The Royal Society of Chemistry, London, 1987, p 185

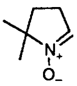
problems arising from spin trapping inorganic radicals. Possible pitfalls in the course of spin trapping have also been pointed out by various workers.[19–21] Here we will discuss problems specific for spin trapping inorganic and organometallic radicals.

2 Spin Trapping using Nitrones

Except for some platinum radicals[22] and metal-centred radicals[23] of Group IVB, persistent spin adducts of metal-centred paramagnetic species with nitrones have not yet been described. On the other hand, many inorganic radicals and atoms 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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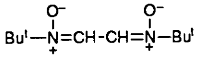
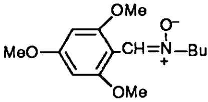
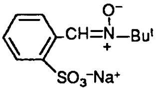
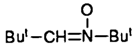

GBBN


(MO)$_3$PBN


2-SSPBN


$Bu^t-CH=\overset{O}{N}-Bu^t$

DBN

As a result of their high 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.

Usually the EPR spectrum of a nitrone spin adduct exhibits hyperfine coupling of the unpaired electron with nuclear spins of the ^{14}N and the β-H which leads to a triplet of doublets. However, if the centre of the trapped radical has a magnetically active nucleus, *i.e.* a nucleus with a spin $I > 0$, additional splitting may be seen. The size of the β-H and ^{14}N hyperfine splittings (and, in some cases, other hyperfine splittings) in the spin adduct may serve as a diagnostic tool for the identification of the trapped radical $^{\bullet}$R. EPR hyperfine splittings for inorganic spin adducts to PBN are summarized in Table 1. Very often the influence of the

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[19] C. Mottley and R. P. Mason, *Biol. Magn. Reson.*, 1989, **8**, 489; K. Stolze and R. P. Mason, *Biochem. Biophys. Res. Commun.*, 1987, **143**, 941; C. Mottley, B. Kalyanaraman, and R. P. Mason, *FEBS Lett.*, 1981, **130**, 12; J. M. Coxon, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1981, 329.

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

[21] H. Chandra and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1986, 1301.

[22] H. C. Clark and C. S. Wong, *J. Am. Chem. Soc.*, 1975, **95**, 7073.

[23] P. Rivière, S. Richelme, M. Rivière-Baudet, J. Satgé, M. J. S. Cynane, and M. F. Lappert, *J. Chem. Res. (M)*, 1978, 2801; *J. Chem. Res. (S)*, 1978, 218; P. Riviere, S. Richelme, M. Riviere-Baudet, J. Satgé, P. I. Riley, M. F. Lappert, J. Dunogues, and R. Calas, *J. Chem. Res. (S)*, 1981, 130; *J. Chem. Res. (M)*, 1981, 1663; A. Alberti, R. Leardi, G. F. Pedulli, A. Tundo, and G. Zanardi, *Gazz. Chim. Ital.*, 1983, **113**, 869; H. Chandra, I. M. T. Davidson, and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1982, 1353.

Table 1 *EPR hyperfine splitting constants for spin adducts of inorganic radicals to PBN*

Radical	*Solvent*	a_N/mT	a_H/mT	a_X/mT	*Ref*
$^{\bullet}$H	benzene	1 480	0 741 (2H)		57
$^{\bullet}$D	CCl_4	1 47	0 73	0 11 (^{2}D)	58
$^{\bullet}$F	benzene	1 22	0 118	4 56 (^{19}F)	30
$^{\bullet}$Cl	CH_3CN	1 270	0 082	0 620 (^{35}Cl)	
				0 512 (^{37}Cl)	59
$^{\bullet}$Br	benzene	1 13	—	3 49 (^{81}Br)	
				3 24 (^{79}Br)	31
$^{\bullet}$OH	water	1 55	0 272	0 336 (^{17}O)	60
$^{\bullet}$OOH	water	1 481	0 27	0 27 (^{17}O)	60
$^{\bullet}N_3$	water	1 501	0 201	0 201 (^{14}N)	28
$^{\bullet}$NCO	CH_3CN	1 509	0 315	0 184 (^{14}N)	15
$^{\bullet}$NCSSCN	CH_3CN	1 444	0 109	0 368 (^{14}N)	38
$^{\bullet}OSO_4$	CH_3CN	1 390	0 123		61
$^{\bullet}SO_3$	water	1 495	0 197	0 034 (2H)	62
$^{\bullet}CO_2$	water	1 580	0 452		63
$^{\bullet}$CN	CH_3CN	1 504	0 198	0 985 (^{13}C)	15
$^{\bullet}CONH_2$	water	1 553	0 320	0 050 (^{14}N)	
				0 050 (^{1}H)	25
$^{\bullet}$NC(OH) [a]	CH_3CN	1 481	0 215	0 215 (^{14}N)	26
$^{\bullet}NCHOSO_3$ [b]	CH_3CN/H_2O	1 485	0 082	0 170 (^{14}N)	25
$^{\bullet}OPO_3^{2}$	water	1 546	0 184		63

[a] Formed by hydrolysis of CN [b] Formed by addition of OSO_3 radicals to cyanide

solvent on the hyperfine splitting exceeds that of the radical structure[24] Therefore solvent effects have to be studied carefully before literature data are used for assigning spin adducts When a bulky methoxy group is introduced into the *ortho*-position of the phenyl ring 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 poor 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 as will be shown below

In addition to the ^{14}N coupling and hyperfine splittings due to magnetically active nuclei in β-position, long-range hyperfine splittings may be observed for some radicals Examples are spin adducts of $^{\bullet}SO_3$, $^{\bullet}PO_3^{2}$, and $^{\bullet}HPO_2$ radicals to PBN which exhibit additional splittings due to the two *ortho*-protons of the phenyl ring adjacent to the nitrone function In the case of the $^{\bullet}HPO_2$ spin adduct to PBN, hyperfine splitting by the proton attached to the phosphorus nucleus could also be resolved

Long-range hyperfine couplings are also observed in the carbamoyl ($^{\bullet}CONH_2$) spin adduct to PBN In inorganic reactions carbamoyl radicals are formed by

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[24] E G Janzen G A Coulter U M Oehler and J P Bergsma *Can J Chem* 1982 **60** 2725

either stepwise hydrolysis of cyanyl radicals ($^{\bullet}CN$) or $^{\bullet}OH$ radical addition to cyanide ions [25] The spin adduct of the intermediate radical $^{\bullet}N{=}COH^{-}$ could also be detected [26]

It was shown by Janzen *et al* [27] that deuteration of PBN leads to sharpening of the EPR lines which allows the resolution of splittings caused by magnetically active nuclei in the γ-position, *e g* proton splittings in the spin adduct of $^{\bullet}CH_3$ and $^{\bullet}CH_2CH_3$, respectively Using $^{2}H_{14}$-PBN as a spin trap, the hyperfine splitting caused by ^{14}N nuclei in γ- and δ-positions, respectively, could be observed in the spin adduct of the $^{\bullet}N_3$ radical confirming the previous assignment [28] of the $^{\bullet}N_3$ spin adduct

Interestingly, well-resolved ESR spectra with long-range hyperfine couplings could be obtained with the spin trap glyoxal-bis(t-butyl nitrone) (GBBN) [29] This spin trap also turned out to be very useful, since spin adducts of bromine atoms are easily detectable during photolysis of carbon bromides [30] The lifetime of the $^{\bullet}Br$ spin adduct to GBBN is about two orders of magnitude higher than with PBN [31] However, no spin adducts of iodine atoms have been reported so far

Although PBN is one of the most popular spin traps, other spin traps may be recommended for special purposes Thus, 5,5-dimethyl-pyrroline-1-oxide (DMPO) [32] is widely used for studies in aqueous systems The use of DMPO as a spin trap for oxygen-centred radicals has been the subject of various excellent review articles [33] and will not be discussed here

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 quite common in inorganic spin trapping reactions,[34] 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 1) Thus, chlorine atoms [35] and $^{\bullet}OSO_3^{-}$ radicals [26] were shown to react according to Scheme 1 Using the spin trap $(MO)_3PBN$ [36] it is possible to distinguish between hydroxyl spin adducts formed by hydrolysis (a), and those formed by spin trapping free hydroxyl radicals (b), since oxygen-centred radicals, unlike other radicals, preferentially

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[25] D Rehorek and E G Janzen, *Z Chem*, 1985, **25**, 69

[26] D Rehorek, T J Kemp, and E G Janzen, to be submitted for publication

[27] E G Janzen, U M Oehler, D L Haire, and Y Kotake, *J Am Chem Soc* 1986 **108** 6858

[28] D Rehorek, P Thomas, and H Hennig, *Inorg Chim Acta*, 1979 **32** L1

[29] D Rehorek and E G Janzen, *J Prakt Chem*, 1985, **327**, 969

[30] E G Janzen, D Rehorek, and H J Stronks, *J Magn Reson* 1984, **56**, 174

[31] D Rehorek and E G Janzen, *Z Chem*, 1984 **24**, 441

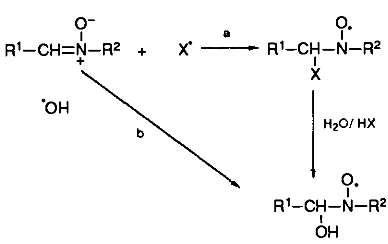
[32] E G Janzen and J I -P Liu, *J Magn Reson*, 1973 **9** 510

[33] E Finkelstein G M Rosen, and E J Rauckman, *Arch Biochem Biophys* 1980, **200** 1 G M Rosen and E Finkelstein *Adv Free Radical Biol Med* 1985 **1** 345, G M Rosen and E J Rauckman *Methods in Enzymology*, 1984, **105**, 198 G R Buettner in 'Superoxide Dismutase Vol II ed L W Oberley, CRC Press, Boca Raton, Florida, 1982, p 63

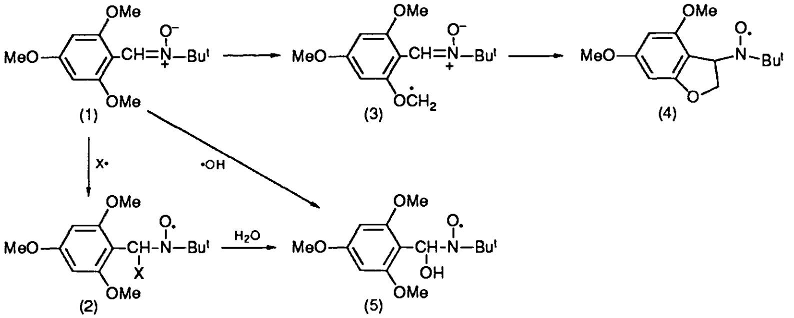
[34] D Rehorek C M DuBose, and E G Janzen *Inorg Chim Acta*, 1984 **83** L7 *Z Chem* 1984 **24** 188

[35] D Rehorek, E G Janzen, and Y Kotake, *Can J Chem*, in press

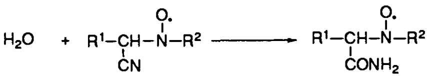
[36] K Sommermeyer and W Seiffert *Z Naturforsch B*, 1975, **30**, 807, C M DuBose Spin trapping with alpha-2 4 6-trimethoxyphenyl N-tert-butyl nitrone, Ph D Thesis, University of Georgia Athens U S A 1985 E M Janzen C M DuBose and Y Kotake *Tetrahedron Lett* 1990 **31** 7395



Scheme 1



Scheme 2

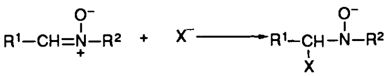


$$H_2O + R^1\text{-}\underset{CN}{CH}\text{-}\overset{O\cdot}{N}\text{-}R^2 \longrightarrow R^1\text{-}\underset{CONH_2}{CH}\text{-}\overset{O\cdot}{N}\text{-}R^2 \qquad (4)$$

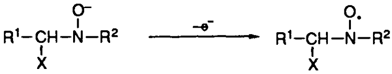
react with $(MO)_3PBN$ by hydrogen abstraction at the methoxy group (see Scheme 2). The final aminoxyl (4), 2*H*,3*H*-(4,6-dimethoxy)benzo[*b*]furan-3-yl t-butyl aminoxyl, is formed by cyclization (internal spin trapping) of the intermediate (3). In addition, about 10 to 20% of the regular hydroxy spin adduct (5), *i.e.* the spin adduct with an α-hydroxy group, are formed. The aminoxyl (4) ($a_N = 1.644$ mT, $a_H^1 = 0.150$ mT, $a_H^2 = 0.123$ mT, in water) can be easily distinguished from the hydroxy spin adduct (5) ($a_N = 1.621$ mT, $a_H = 0.885$ mT) on the basis of the hyperfine coupling constants.

In addition to the reaction sequence shown in Scheme 2 *partial* hydrolysis of the spin adduct may also occur. Thus, cyanyl spin adducts (and probably also the corresponding hydroxylamine) undergo hydrolysis to form eventually the carbamoyl spin adduct, equation 4.

Reaction is more pronounced for 2-SSPBN than for PBN. However, in both cases hydrolysis of the spin adduct is rather slow ($k = 5 \times 10^{-3}\,s^{-1}$) and does not compete with hydrolysis of the cyanyl radical leading also to the carbamoyl spin adduct. Hence, unambiguous discrimination between hydrolysis of cyanyl spin adducts and spin trapping of *free* carbamoyl radicals should be possible. The spin trap 2-SSPBN, which is commercially available, has been introduced[37]

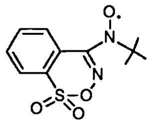


$$R^1{-}CH{=}\overset{O^-}{\underset{+}{N}}{-}R^2 + X^- \longrightarrow R^1{-}\underset{X}{CH}{-}\overset{O^-}{N}{-}R^2 \qquad (5)$$



$$R^1{-}\underset{X}{CH}{-}\overset{O^-}{N}{-}R^2 \xrightarrow{-e^-} R^1{-}\underset{X}{CH}{-}\overset{O\cdot}{N}{-}R^2 \qquad (6)$$

because it is a very water-soluble spin trap. This spin trap should be used with caution, however, since it readily undergoes nucleophilic addition of a number of inorganic anions, followed by oxidation of the thus formed hydroxylamine anion, equations 5 and 6. Since only mild oxidants are required in order to bring about oxidation of the hydroxylamine anion, aminoxyl radicals are detectable in the reaction mixture even when no short-lived *free* radicals are formed in the course of the reaction, *e.g.* fairly intense EPR signals of hypophosphite radical spin adducts ($a_N = 1.574$ mT, $a_H^1 = 0.370$ mT, $a_H^2 = 0.251$ mT, $a_P = 2.011$ mT) were recorded simply upon addition of sodium hypophosphite to an air-saturated aqueous solution of 2-SSPBN. A similar behaviour was reported[20] for PBN in some cases. Fortunately, for most reactions PBN is far less reactive towards nucleophilic addition. Thus, contrasting the observation made by Forrester and Hepburn[20] at lower pH, cyanide ions lead only to traces of cyanyl and carbamoyl spin adducts at pH 9—10. Although additional problems arise from the enhanced photosensitivity of 2-SSPBN which results in the formation of various persistent aminoxyls upon photolysis,[26] this spin trap, nevertheless, may be of particular interest for specific applications. Thus, 2-SSPBN appears to be unique with respect to spin trapping of some radicals formed during oxidation of cyanide ions. A triplet of triplets ($a_N^1 = 1.175$ mT, $a_N^2 = 0.347$ mT) assigned to the aminoxyl (6) has been detected[26] when cyanide ions are oxidized by Cu^{II} ions.



(6)

Apparently, the SO_3^- group is involved in the formation of the final spin adducts. It is noteworthy, that (6) is also formed when $^{\cdot}N_3$ and $^{\cdot}NCO$ radicals react with 2-SSPBN, suggesting the mechanism shown in Scheme 3.

Participation of other groups than the nitrone function in the formation of the final spin adduct has also been observed[38] for reaction of $^{\cdot}SCN$ and $^{\cdot}NCSSCN^-$ radicals with PBN where cyclization involving the phenyl ring occurs, leading to quite complicated EPR spectra. On the other hand, *C*-alkyl nitrones such as di-t-butyl nitrone (DBN) that do not have phenyl rings adjacent to the nitrone

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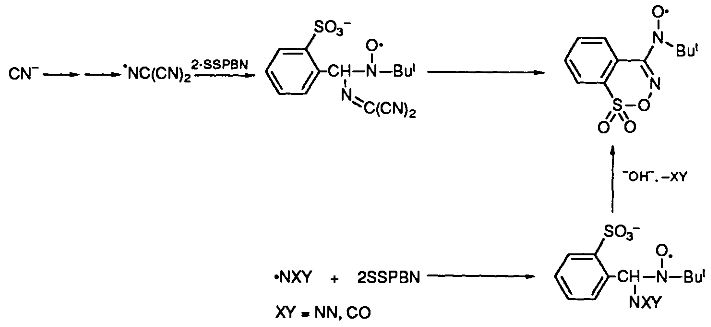
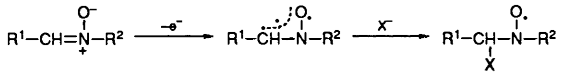
[37] E. G. Janzen and R. V. Shetty, *Tetrahedron Lett.*, 1979, 3229.

[38] D. Rehorek and E. G. Janzen, *Inorg Chim. Acta*, 1986, **118**, L29.



Scheme 3

 (7)

$$R^1\text{–CH=}\underset{+}{\overset{O^-}{N}}\text{–}R^2 \xrightarrow{-e^-} R^1\text{–}\dot{C}H\text{–}\overset{O\cdot}{N}\text{–}R^2 \xrightarrow{X^-} R^1\text{–}\underset{X}{CH}\text{–}\overset{O\cdot}{N}\text{–}R^2 \quad (7)$$

function have been proven to be excellent spin traps for both $^{\bullet}SCN$ and $^{\bullet}NCSSCN^-$ radicals.

Distinguishing clearly between spin adducts formed by true radical addition and those formed by 'non-radical' processes is an important problem when using the spin trapping technique, and this problem becomes particularly relevant when dealing with inorganic radicals, since their formation requires either strong oxidants or polar solvents or strongly nucleophilic precursors. All these conditions are unfavourable for spin trapping using nitrone spin traps. In addition to the reaction (a) shown in Scheme 1, the presence of strong oxidants may lead to the formation of short-lived nitrone radical-cations as reported by Chandra and Symons[21] which may eventually yield aminoxyls, equation 7.

However, oxidation of nitrones requires very strong oxidants[15] which are not present under usual chemical conditions. This situation may change dramatically when photolysis is involved. Although it is quite common to avoid direct excitation of spin traps by using appropriate filters, one has to be aware that energy or electron transfer processes may occur. Thus, Baumann *et al.*[39] have shown that electronically excited organic dyestuffs may transfer their energy to nitrones. The resulting excited nitrone is easily oxidized to the cation radical which may react with even weak nucleophiles to form the corresponding aminoxyl. For PBN the energy for the lowest excited triplet state was measured[40] as $16\,200\,cm^{-1}$. The rate constant for quenching the excited state of $[Ru(bipy)_3]^{2+}$ by PBN was found[41] to be about 3.3×10^7 dm^3 mol^{-1} s^{-1}. The

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[39] H. Baumann, U. Dertel, H. J. Timpe, V. E. Zubarev, N. V. Fok, and M. J. Mel'nikov, *Z. Chem.*, 1984, **24**, 182.

[40] A. P. Darmanyan and G. Moger, *J. Photochem.*, 1984, **26**, 269.

[41] D. Rehorek and H. Knoll, unpublished results.

resulting excited PBN molecule is easily oxidized to the cation radical which may react with even very weak nucleophiles to form an aminoxyl radical.

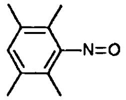
A somewhat different situation arises when sensitizers are used which absorb in the high energy region, say below 400 nm. Since a molecule in its excited state is a much stronger oxidant (and reductant) than in its electronic ground state, electron transfer between the excited molecule and the spin trap may occur. This has been proven[42] to be the case for 9,10-dicyanoanthracene, which is known[43] to be a powerful oxidant in its excited singlet state capable of oxidizing a large variety of inorganic anions. Lifetime quenching experiments with PBN gave a good Stern–Volmer plot with $k_q = (7.00 \pm 0.14) \times 10^9$ dm^3 mol^{-1} s^{-1}. In the presence of inorganic anions, spin adducts of both sensitizer anion and inorganic radicals were observed. The latter are, however, formed by addition of anions to PBN^+.

3 Spin Trapping using Nitroso Compounds

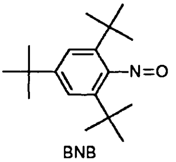
Next to nitrones, aliphatic and aromatic nitroso compounds are the most commonly used spin traps. Typical examples for nitroso spin traps are 2-methyl-2-nitrosopropane (MNP),[7] 2,3,5,6-tetramethylnitrosobenzene (nitrosodurene, ND),[44] 2,4,6-tri-t-butylnitrosobenzene (BNB),[45] and sodium 3,5-dibromo-4-nitrosobenzene sulphonate (SBNS).[46]

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

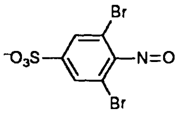
MNP



ND



BNB



SBNS

Unlike nitrones, many nitroso compounds are dimers in the solid state. In order to act as spin traps, dissociation into monomers has to occur. This may lead to some difficulties in kinetic spin trapping experiments. However, because of steric hindrance by the bulky t-butyl groups, BNB exists exclusively as a monomer.

SBNS[46] and 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. Attempts to detect cyanyl-free radicals formed by catalytic reaction of hydrogen peroxide in the presence of horseradish peroxidase[47] have failed. It was found that persistent spin adducts of $^{\bullet}SO_3^-$ radicals to SBNS may be formed by decomposition of SBSN.[47,48]

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[42] A. Schleitzer, *Diplomarbeit*, University of Leipzig 1991; D. Rehorek, A. Schleitzer, H. Knoll, and T. J. Kemp, *J. Photochem. Photobiol. A: Chemistry*, submitted for publication.

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Table 2 *EPR parameters for spin adducts of inorganic radicals with C-nitroso compounds*

Radical	*Spin trap*	*Solvent*	a_N/mT	a_H/mT	a_X/mT	*g*	*Ref.*
$^{\bullet}CN$	MNP	water	0.964		0.178 (1N)		47
$^{\bullet}BH_3^-$	MNP	benzene	1.39		1.26 (3H) 0.55 ($1^{11}B$) 0.18 ($1^{10}B$)	2.0059	64
$^{\bullet}SO_2F$	MNP	benzene	1.24				65
$^{\bullet}SO_2Cl$	MNP	benzene	1.17				65
$^{\bullet}SO_2H$	MNP	$MeOH/H_2O$	1.47		0.46 ($1^{13}C$)	2.0055	66
$^{\bullet}SO_2NH_2$	MNP	water	1.39			2.0055	67
$^{\bullet}SO_3^-$	MNP	water	1.47			2.0054	67
$^{\bullet}H$	MNP	water	1.441		1.391 (1H)		68
$^{\bullet}D$	MNP	D_2O	1.40		0.22 (1D)		69
$^{\bullet}PO_3^{2-}$	MNP	water	1.34		1.20 (1P)		70
$^{\bullet}AsO_2$	MNP	water	1.410		0.772 (1As)		71
$^{\bullet}N_3$	ND	CH_2Cl_2	0.238		0.721 (2N)		49
$^{\bullet}NCO$	ND	CH_2Cl_2	0.240		0.732 (2N)		51
$^{\bullet}HPO_2^-$		water	1.608	0.317	1.603 (^{31}P) 0.184 (^{1}H) 0.027 ($2^{1}H$)		63
$^{\bullet}PO_3^{2-}$		water	1.587	0.313	2.166 (^{31}P) 0.020 ($2^{1}H$)		63
$^{\bullet}N(CN)_2$		water	1.587	0.291	0.151 (^{14}N)		63
$^{\bullet}C(CN)_3$		CH_3CN	1.437	0.569			63
$^{\bullet}NH_2$		water	1.614	0.354	0.123 (^{14}N) 0.054 ($2^{1}H$)		63

[a] Formed by hydrolysis of $^{\bullet}CN$. [b] Formed by addition of $^{\bullet}OSO_3^-$ radicals to cyanide.

MNP is one of the most reactive of spin traps; it is also 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-t-butyl aminoxyl which may mask the ESR signals of spin adducts.

Nitroso compounds add free radicals directly to the N=O bond. Therefore, spin adducts of nitroso compounds exhibit more line-rich ESR spectra, and the identification of the trapped radicals is more straightforward. There are, however, only relatively few inorganic free radicals which lead to persistent aminoxyls upon addition to nitroso compounds (see Table 2).

Among those radicals that form persistent spin adducts with *C*-nitroso compounds are azidyl radicals ($^{\bullet}N_3$). This reaction deserves some comment. $^{\bullet}N_3$ radicals produced by photolysis of either $[Co(NH_3)_5N_3]^{2+}$ [28] or CBr_4/N_3^-,[49,50] may add to both nitroso monomers and dimers leading to a triazene-1,3-dioxyl radical which exhibits hyperfine splitting by three ^{14}N nuclei. The same spin

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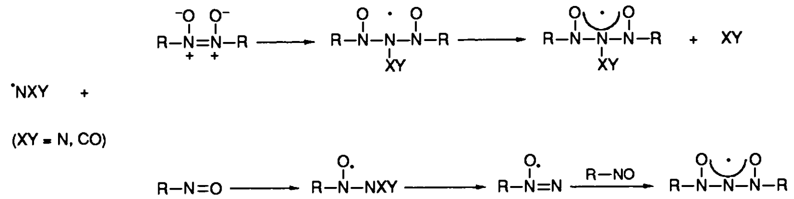
[49] D. Rehorek and E. G. Janzen, *Z. Chem.*, 1984, **24**, 68.

[50] H. Knoll, D. Rehorek, and D. J. Stufkens, *Z. Chem.*, 1990, **30**, 220.



Scheme 4

adduct has been observed when cyanate is oxidized.[51] The mechanism shown in Scheme 4 has been proposed for the formation of azidyl and cyanatyl spin adducts.

On the other hand, many short-lived paramagnetic fragments of coordination compounds (metallo radicals, organometallic radicals) form fairly persistent aminoxyls upon addition to nitroso compounds. Spin trapping of short-lived metallo radicals formed during photolysis of organometallic compounds was first demonstrated by Hudson *et al.*[52] While the *g*-values for spin adducts of simple inorganic radicals to nitroso compounds do not vary markedly with the nature of the radical trapped, the *g*-values of spin adducts of organometallic radicals very often are strongly influenced by the metallo fragment (see Table 3).

Therefore, many metal-centred radical adducts to nitroso compounds should be regarded as paramagnetic metal complexes with organic nitroso ligands rather than metallo nitroxides. In some cases adducts between nitroso compounds and metallo fragments are formed spontaneously by ligand replacement.[53] When using nitroso compounds as spin traps for organometallic radicals, one should be aware that nitroso compounds readily undergo electron-transfer reactions with electron-rich organometallic compounds and that nitroso anion radicals are therefore common by-products in spin trapping reactions.

Spin trapping using nitroso compounds has recently been proven[54] for the detection of a Rh-centred metallo radical formed during sonolysis of an organometallic rhodium compound. Surprisingly, spin traps are not decomposed by ultrasonic irradiation to a great extent which renders this a promising technique for studying radical processes initiated by ultrasound.

Electron transfer between the organometallic complex and the nitroso compound may also be achieved photochemically as we have shown[55] recently for the reaction of triply bonded organometallic Cr and Mo compounds with both aliphatic and aromatic nitroso compounds. In addition, spin adducts of

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[51] D. Rehorek and E. G. Janzen, *Can. J. Chem.*, 1984, **62**, 1598.

[52] A. Hudson, M. F. Lappert, P. W. Lednor, and B. K. Nicholson, *J. Chem. Soc., Chem. Commun.*, 1974, 966; A. Hudson, M. F. Lappert, and B. K. Nicholson, *J. Chem. Soc., Dalton Trans.*, 1977, 551.

[53] E. Dinjus, D. Walther, R. Kirmse, and J. Stach, *J. Organomet. Chem.*, 1980, **198**, 215.

[54] D. Rehorek, S. Di Martino, S. Sostero, D. Traverso, and T. J. Kemp, *Inorg. Chim. Acta*, 1990, **178**, 1.

[55] D. Rehorek, S. Di Martino, S. Sostero, O. Traverso, and T. J. Kemp, *J. Prakt. Chem.*, in press.

Table 3 *EPR hyperfine coupling constants and g-values of spin adducts of metal-centred radicals with nitroso compounds*

Radical	*Spin trap*	*Solvent*	a_N/mT	a_M/mT	*g*	*Ref*
$^{\bullet}Co(N)_5^{2}$	MNP	methanol	1 87	1 11 (^{59}Co)	2 0054	72
$^{\bullet}Mo(CN)_7^{2}$	ND	CH_2Cl_2	0 38	3 56 ($^{95\ 97}$Mo)	1 9823	73
$^{\bullet}W(CN)_7^{2}$	ND	CH_2Cl_2	0 959			74
$^{\bullet}Mo(CO)_3Cp^{a}$	ND	CH_2Cl_2	1 45	0 40 ($^{95\ 97}$Mo)	2 005	52
$^{\bullet}Re(CO)_5$	ND	CH_2Cl_2	1 403	3 80 ($^{185\ 187}$Re)	2 0098	75
$^{\bullet}Re(CO)_4PPh_3{}^{b}$	ND	CH_2Cl_2	1 39	3 43 ($^{185\ 187}$Re)	2 0087	75
$^{\bullet}Mn(CO)_5$	ND	CH_2Cl_2	1 59	0 88 (^{55}Mn)	2 006	52
$^{\bullet}Rh(CO)_2$	ND	CH_2Cl_2	1 60	0 42 (^{103}Rh)	2 012	76
$^{\bullet}Fe(CO)_2CpMe_5{}^{c}$	ND	benzene	1 708		2 0064	77
$^{\bullet}Fe(CO)_2Cp$	ND	toluene	1 787		2 0052	77
$^{\bullet}Cr(CO)_4Cl$	ND	CCl_4	1 83	1 86 (^{53}Cr)	1 9983	78
$^{\bullet}UCp_3$	ND	THF	1 306		2 0076	79
$^{\bullet}Ni(bipy)Et^{d}$	ND	benzene	1 25		2 0130	80
$^{\bullet}ZrCp_2H$	MNP	benzene	1 37	0 43 (^{91}Zr)^{e}		81
$^{\bullet}Al(TPP)^{f}$	BNB	benzene	1 20	0 19 (^{27}Al)	2 0049	82
$^{\bullet}Pd(PPh_3)N_3$	ND	CH_2Cl_2	1 574	0 801 (^{105}Pd)^{g}	2 0096	83

[a] Cp = cyclopentadienyl anion [b] PPh_3 = triphenyl phosphine additional splitting a_P = 0 71 mT (^{31}P) [c] $CpMe_5$ = pentamethylcyclopentadienyl anion [d] bipy = 2 2 bipyridine Et = ethyl [e] Additional splitting a_H = 0 15 mT [f] TPP = tetraphenylporphyrin dianion [g] Additional splitting a_P = 0 432 mT

metallo radicals to nitroso compounds may undergo photolytic cleavage of the metal–N bond forming nitroso anion radicals

The main disadvantage of using nitroso compounds as spin traps in photoreactions is their photochemical instability [56] Symmetric aminoxyls are formed by NO–carbon bond cleavage and subsequent addition of the alkyl (or aryl) radical to the intact nitroso compounds Owing to their high stability, symmetric aminoxyls have very intense EPR signals which may mask weaker signals of other spin adducts Therefore, direct excitation of the nitroso spin trap should be avoided by using band-pass filteres As discussed above for nitrone spin traps, nitroso compounds may also react with electronically excited sensitizers Thus, reductive quenching of zinc porphyrins and oxidative quenching of 9,10-dicyanoanthracene by ND has been observed [42]

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