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The Use of Spin-trapping in the Study of the Mechanisms of Radical Processes

V.E.Zubarev, V.N.Belevskii, and L.T.Bugaenko

The review is devoted to the spin-trapping method developed in recent years and used to identify short-lived radicals (mainly in liquid phase) and to investigate the mechanisms of their reactions. Unstable radicals are accepted by a spin-trapping agent with formation of a fairly stable free radical which carries information about its short-lived precursor. The EPR spectra of the resulting spin adducts can be recorded in the liquid phase and are as a rule well resolved. The properties of various spin-trapping agents are described in detail and tables of the parameters of the EPR spectra of the adducts of spin-trapping agents with the trapped radicals are presented. The application of the spin-trapping method in the study of the mechanisms of radical processes in various fields of chemistry is considered.
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I. INTRODUCTION

The free radicals arising in the course of chemical reactions usually have very short lifetimes, which precludes their detection in the chemical reaction zone by the usual EPR method, since the steady-state concentrations of the radicals are below the sensitivity of modern EPR spectrometers. In order to detect short-lived radicals, special research techniques have therefore been developed: (1) stabilisation of radicals in the solid phase at low temperatures; (2) flow methods in the liquid phase with the radicals generated by means of Fenton's reagent or the titanium reagent in an acid medium; (3) recording of EPR spectra (or optical absorption spectra) under continuous irradiation by an electron beam or light in the liquid phase directly in the resonator; (4) stabilisation of radicals on the surface; (5) the method of chemically induced dynamic nuclear polarisation (CIDNP). These methods yielded much information about the radicals and the mechanisms of radical reactions. However, they suffer from many significant limitations. Owing to the high rate of radical reactions, it is usually impossible to detect the primary radicals. Analysis of the EPR spectra of solid specimens is in most cases difficult because of the broadening of the lines and the superposition of the spectra of several radicals. Flow methods are suitable only for a limited number of chemical reactions and involve the consumption of a large amount of reagents. Considerable technical and methodological difficulties arise also when the CIDNP method or a spectrometer irradiated by an electron beam are used. The majority of radical reactions occurring in the liquid phase cannot be investigated by the methods enumerated above.

The spin-trapping method, developed in recent years, has significantly greater possibilities and permits the investigation of short-lived radicals in liquid, solid, and gaseous phases. It is based on the acceptance by compounds (spin-trapping agents) of short-lived radicals with formation of fairly stable radical adducts having a characteristic EPR spectrum. Extensive information about short-lived radicals arising in photolysis, radiolysis, electrolysis, gas discharge, oxidation, thermal decomposition, rearrangement, and polymerisation has been obtained with the aid of the spin-trapping method. The aim of the present review is to demonstrate the possibilities of the method and the prospects for its utilisation in the study of the mechanisms of radical reactions. Earlier reviews[1-3] present data published up to 1971†. Since then the number of studies involving the use of spin trapping agents has greatly increased, new spin-trapping agents have become available, and new fields of their application have arisen.

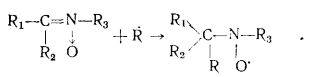
II. SPIN-TRAPPING AGENTS

Mainly nitroso-compounds and nitrones are used as spin-trapping agents. In the study of the mechanism of the photolysis of 't-nitrosobutane' and nitrosobenzene it was observed[4] that these compounds react with the intermediate radicals arising as a result of the photolysis of the nitroso-compounds, forming stable nitroxy-radicals. Iwamura and Inamoto[5,6] were the first to use nitrones for the synthesis of stable radicals. It was shown subsequently that many nitroso-compounds and nitrones combine with unstable radicals, forming long-lived radicals. Table 1 presents a list of the main spin-trapping agents.

Nitroso-t-butane and *C*-phenyl-*N*-t-butylnitrone are most frequently employed. The unstable radical adds to the N–O fragment of the nitroso-compound:

$$R_1\text{—NO} + \dot{R} \rightarrow R_1\text{—N}(\dot{O})\text{—R} \quad .$$

Radicals add to the double bond of nitrones:



Nitroxy-radicals, which belong to the large class of stable radicals whose properties have been thoroughly investigated[7,8], are formed in both cases.

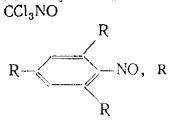
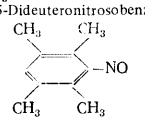
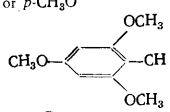
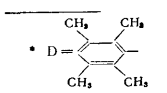
Apart from nitroso-compounds and nitrones, certain other compounds containing multiple bonds or heteroatoms are used as spin-trapping agents (see Table 1).

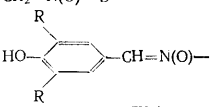
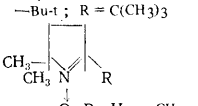
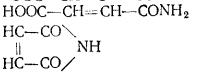
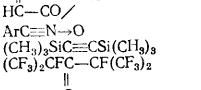
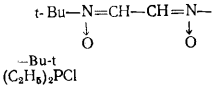
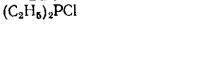
1. Nitrosoalkanes

The majority of nitroso-compounds exist in the forms of dimers which dissociate into monomers in solution. Only the monomeric form reacts with radicals. Mainly t-nitrosobutane and related compounds are used as spin trapping agents.

t-Nitrosobutane (TNB, t-BuNO). The simplest and most convenient method of synthesising TNB has been described by Stowell[9] (oxidation of t-$BuNH_2$ with hydrogen peroxide in the presence of Na_2WO_4), but other methods of synthesis are also available[10]. Solid TNB is a colourless dimer, which dissociates in solution with the appearance of a characteristic blue colour. The dimer–monomer equilibrium constants in CCl_4, methanol, heptane, and toluene have been determined[9,11-14].

Table 1. The spin-trapping agents investigated.

Spin-trapping agent	References
t-BuNO(TNB)	(see Table 2)
$(CF_3)_2CNO$	21, 22
$(CD_3)_2CNO$	23—25
$(CH_3)_2C(NO)C(O)CH_3$	2, 18
$PhCH(NO)CH_3$	15
Nitrosocyclohexane	15
CCl_3NO	31
	41—43
(BNB), CH_3O, CH_3OCO, Cl	(see also Table 4)
C_6H_5NO	19
C_6F_5NO	41
3,5-Dideuteronitrosobenzene	19
	41
	(see also Table 3)
N,N-Dimethyl-*p*-nitrosoaniline	154
PhCH = N(O)-Bu-t (PBN)	(see also Table 5)
p-$XC_6H_4CH{=}N(O){-}$Bu-t X=NO_2, Cl, CH_3, CH_3O	5,68
$PhCH{=}N(O)Ph$	152
$PhCH{=}N(O)C_6H_4X$, X=*p*-Cl, *p*-OCH_3, *p*-CH_3, or *m*-Cl	152
$Ph_2C{=}N(O)Ph$	152
$X{-}C_6H_4CH{=}N(O)Ph$, X=*p*-NO_2 or *p*-CH_3O	152
	156
	

Spin-trapping agent	References
$PhCH{=}N(O)CH_2Ph$	152
$Ph_2C{=}N(O)CH_2Ph$	152
$X{-}C_6H_4CH{=}N(O)CH_2Ph$, X = *p*-$NO_2$, or *p*-$C(CH_3)_3$	152
$PhN(NO){-}C(O)CH_3$	153
$CH_2{=}N(O)$–Bu-t; (MH)	33, 69
$CH_2{=}N(O)$–D*	41
	62
	64—68
$CH_2{=}NO_2^-$	76—79
$^-OOC{-}CH{=}CH{-}COO^-$	74, 75
$HOOC{-}CH{=}CH{-}CONH_2$	74, 75
	74, 75
	73
$(CH_3)_3SiC{\equiv}CSi(CH_3)_3$	81
$(CF_3)_2CFC(O)CF(CF_3)_2$	82
$(CH_3)_3C{-}C(O){-}C(CH_3)_3$	151
	99
	5
–Bu-t $(C_2H_5)_2PCl$	80

The monomeric form of TNB in solution has an optical absorption maximum at 667 nm (ϵ = 18.2 litre $mole^{-1}$ s^{-1} in methanol[12]), while the dimer absorbs at 294 nm ($\epsilon = 5.7 \times 10^3$ litre $mole^{-1}$ s^{-1} in heptane[14]). The photolysis of liquid TNB solutions by visible light results in the formation of stable t-Bu_2NO radicals[4,15] and the solution cannot therefore be stored in the light. These radicals are also formed on heating TNB solutions[16]. In frozen solutions the monomeric form of TNB is resistant to the action of light[17], while the dimer dissociates under these conditions to the monomer under the influence of light[17,18]. It has been suggested that the photolysis of TNB in solution proceeds via the following mechanism:

$$\text{t-BuNO} \xrightarrow{h\nu} \text{t-BuNO}^* \rightarrow \text{t-Bu}^\cdot + \text{NO}, \qquad (1)$$

$$\text{t-Bu}^\cdot + \text{t-BuNO} \rightarrow \text{t-Bu}_2\text{NO}^\cdot, \qquad (2)$$

†See also the review by R. Kh. Freidlina, I. I. Kandror, and R. G. Gasanov, Uspekhi. Khim., 47, 508 (1978) [Russian Chemical Reviews, 47, No. 3 (1978)].

or

$$t\text{-BuNO}^* + t\text{-BuNO} \rightarrow t\text{-Bu}_2\dot{N}O + NO. \quad (3)$$

$t\text{-Bu}_2\dot{N}O$ radicals are also formed in the radiolysis of TNB solutions in benzene and toluene at 20°C as a result of the transfer of excitation energy from aromatic compounds to TNB.[13]

It has been shown[18] that TNB is stable in the presence of oxidants such as $Pb(AcO)_4$ and Ce^{4+} and over a wide pH range[18]. However, it was later observed[19] that alkyl hydroperoxides and dimethyl sulphoxides react with nitroso-compounds to form nitroxy-radicals:

$$R'OOH + R''NO \rightarrow \underset{\underset{OOR'}{|}}{R''\text{—}N\text{—}OH} \rightarrow R'\dot{O} + \underset{\underset{O\cdot}{|}}{R''\text{—}N\text{—}OH} \xrightarrow{+R''NO} \underset{\underset{O\cdot}{|}}{R'\text{—}O\text{—}N\text{—}R''}. \quad (4)$$

Nitroso-compounds react readily with certain anions [polystyrene, poly(methyl methacrylate), nitromethane, acetate, and cyanide anions][20], forming amino-oxyanions, which are oxidised either by the nitroso-compound itself or by "traces" of O_2 to nitroxy-radicals:

$$R^- + t\text{-BuNO} \rightarrow t\text{-Bu}\underset{\underset{O^-}{|}}{\text{—}N\text{—}R} \xrightarrow{t\text{-BuNO}} R\text{—}\underset{\underset{O\cdot}{|}}{N}\text{—Bu-t}. \quad (5)$$

Table 2. Parameters of the EPR spectra of the TNB radical adducts.

Radical	Solvent	T, °C	a_N, G	a^H_β, G	a^H_γ, G	Refs.
$\dot{H}$	Methanol	−50	13.5	13.5	—	27
$\dot{H}$	Benzene	+20	13.6	12.9	—	28—30
$\dot{C}H_3$	CH_2Cl_2	−70	15.5	12.9	—	18
$\dot{C}H_3$	DMSO + H_2O	+20	16.0	13.2	—	31, 32
$\dot{C}H_3$	Benzene	+20	15.2	11.3	—	33
$CH_3\dot{C}H_2$	CH_2Cl_2	−40	14.9	10.4	0.5	18
$CH_3\dot{C}H_2$	DMSO + H_2O	+20	15.7	11.3	0.3	32
$C_5H_{11}\dot{C}H_2$	Water	+20	15.0	10.4	0.5	32
$C_2H_5(CH_3)\dot{C}H$	CH_2Cl_2	−40	15.3	2.2	—	18
$(CH_3)_2\dot{C}H$	CH_2Cl_2	−40	14.7	1.66	0.3	18
$\dot{P}h$	Benzene	+20	12.3	$a^H_o = a^H_p = 2.0$	$a^H_m = 0.9$	33
$Ph\dot{C}H_2$	Toluene	+20	14.2	7.5	—	30, 33
$CH_3\dot{O}$	Methanol	−80	29.5	1.54	—	11, 35, 12
$C_2H_5\dot{O}$	Ethanol	−80	29.1	1.1	—	11, 12
n-$C_3H_7\dot{O}$	1-Propanol	−80	29.4	1.2	—	11
iso-$C_3H_7\dot{O}$	2-Propanol	−80	29.4	—	—	11
t-$BuO\dot{}$	Benzene	+20	26.6	—	—	33
$\dot{C}H_2OH$	Methanol	−80	14.4	4.0	—	11, 35
$\dot{C}H_2OH$	Methanol	+20	14.2	4.8	—	33
$CH_3\dot{C}HOH$	Ethanol	−80	14.5	2.0	—	11
$C_2H_5\dot{C}HOH$	1-Propanol	+20	14.1	1.8	—	33
R—$\dot{C}O$	Benzene	−20	8.0	—	—	34
H—$\dot{C}O$	$CHBr_3$	−20	7.0	1.4	—	25, 38
$CH_3\dot{S}$	CH_3SH	−103	18.9	1.2	—	36
$C_3H_7\dot{S}$	C_3H_7-SH	−85	17.8	—	—	36
$Ph\dot{C}HCHO$	Benzene	+40	14.6	3.7	1.3	39
$CH_3CO\dot{C}H_2$	Acetone	120	14.8	8.3	—	31
$CH_3\dot{C}HCOCH_3$	Ketone	+20	14.6	2.5	—	31
$\dot{C}H_2COOH$	Water	+20	16.1	8.4	—	37
$PhCO\dot{C}H_2$	$PhCOCH_3$	+25	14.4	7.9	—	31
$HOC(CH_3)_2\dot{C}H_2$	t-Butyl alcohol	+30	15.4	11.0	—	40
$Et_2N\dot{C}HCH_3$	Et_3N	+20	14.3	4.06	—	30
t-Bu	Methanol	+20	16.0	—	—	18, 32
$\dot{C}F_3$	CH_2Cl_2	−60	12.2	$a_F = 12.5$	—	31
$\dot{C}Cl_3$	$CHCl_3$	+20	12.5	$a_{Cl} = 2.2$	—	33
$\dot{O}H$	Water	+20	28.0	$a^H_{OH} = 4.4$	—	66

The interpretation of data on the trapping of TNB radicals in the presence of oxidants and in electron-donating media must therefore be approached with caution.

2-Methyl-2-nitroso-3-butanone is similar to TNB as regards its chemical properties and the EPR spectra of radical adducts[2,18] and is sometimes a more effective radical acceptor. When this compound is acted upon by ultraviolet light, acyl radicals are formed and then trapped.

Fully fluorinated t-nitrosobutane is also used to trap unstable radicals[21,22].

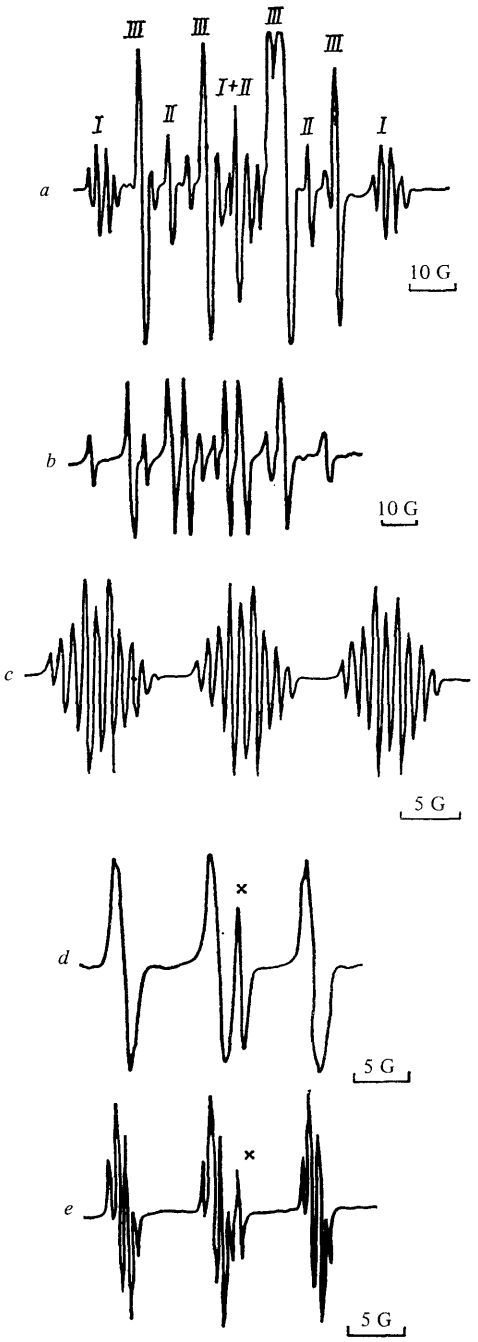
The EPR spectra of the radical adducts of TNB and 2-methyl-2-nitroso-3-butanone have a triplet due to splitting by the nitrogen atom of the nitroso-group and additional hyperfine structure arising as a result of the interaction with the magnetic nuclei of the trapped radical. Splitting by the t-butyl group is not observed. The trapped radical can be identified on the basis of the nature of the additional hyperfine structure, the constants for splitting by nitrogen atoms (a_N) or β-hydrogen (a^H_β), and in certain cases γ-hydrogen (or heteroatoms). Table 2 presents the splitting constants for the most characteristic TNB radical adducts. The values of a_N are different for different classes of organic radicals: a_N = 26–29 G for RO· radicals, 14–16 G for alkyl radicals, and 7–8 G for acyl radicals. Definite regularities in the variation of the constants for splitting by hydrogen and heteroatoms, associated with the structure of the trapped radical, have been observed. In polar solvents, the splitting constants can increase by 1–2 G relative to non-polar solvents and comparative measurements must therefore be performed in identical solvents. One must note that, owing to the broadening of the EPR lines due to the influence of the t-butyl group, a splitting smaller than 0.3 G is not resolved in the spectra.

An appreciable improvement of the resolution of the EPR spectra can be achieved by employing fully deuterated t-nitrosobutane $(CD_3)_3CNO$, whose synthesis has already been described[24]. The adducts of this trapping agent give rise to very narrow lines in EPR spectra, which makes it possible to observe additional splitting due to γ-protons or radicals with heteroatoms, which cannot be resolved in the case of the usual TNB. In addition, the signal to noise ratio is improved[23–26]. For example, splitting by the protons of the CH_3 group due to the hyperfine (HF) interaction via the carboxy-group has been observed for the adduct of $(CD_3)_3CNO$ with the radical $CH_3O\dot{C}O$ (Figs. *d* and *e*)

2. AROMATIC NITROSO-COMPOUNDS

(a) Nitrosobenzene

The disadvantages of TNB described above (sensitivity to light, oxidants, strong acids, and certain anions as well as instability of many adducts) limit the application of this trapping agent. Nitrosobenzene has some advantages compared with TNB[19]. It is readily available, exists in solution largely in the active monomeric form, and is not sensitive to light at wavelengths in excess of 360 nm. Only ultraviolet light with $\lambda < 310$ nm leads to the formation of the diphenylnitroxy-radical. Spin adducts with nitrosobenzene are usually stable at 20°C and their EPR spectra contain very narrow lines, so that very small splittings are resolved in the latter. The main disadvantage of nitrosobenzene is difficulty of analysing its EPR spectra, because addition HFS lines due to the benzene ring protons arise ($a^H_o = a_p = 2.5$ G, $a^H_m = 0.9$ G). The spectra simplify when 3,5-dideuteronitrosobenzene is used instead of nitrosobenzene, but the replacement itself leads to a broadening of the lines due to an unresolved HFS caused



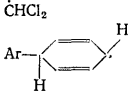
EPR spectra of the adducts of t-nitrosobutane (TNB) with trapped radicals: *a*) irradiation of methanol with electrons having an energy of 3 MeV at −45°C directly in the resonator[30] [I) $CH_3O-N(\dot{O})-t-Bu$: II) $HOCH_2-N(\dot{O})-Bu-t$; III) $H-N(\dot{O})-Bu-t$]; *b*) adducts of TNB with the $\dot{C}H_3$ radical in benzene, obtained on decomposition of acetyl peroxide[15,33]; *c*) adduct of TNB with the phenyl radical in benzene at 20°C (thermal decomposition of benzoyl peroxide)[147]; *d*) adduct of TNB with the $CH_3O\dot{C}O$ radical; *e*) adduct of perdeutero-t-nitrosobutane with the $CH_3O\dot{C}O$ radical (in contrast to case *d*, the lines due to the CH_3 group are evidently resolved); the cross denotes one of the lines due to the adduct with the t-Bu$\dot{O}$ radical.

by the influence of the deuterium nuclei[19]. Substituted nitrosobenzene derivatives, which are free from the disadvantages of nitrosobenzene, have been used as spin-trapping agents[41-43].

(b) Nitrosodurene (2,3,5,6-tetramethylnitrosobenzene)[41]

Nitrosodurene (ND), synthesised by the method of Smith and Taylor[44], is a colourless dimer in the crystalline state; even in solutions it exists largely in the dimeric form. On heating, the degree of dissociation of the dimer increases and a greenish colour appears. Nitrosodurene is appreciably soluble in $CHCl_3$ and methylene chloride; in aromatic hydrocarbons its solubility is about 0.003 M and in other solvents it is even smaller. However, in consequence of the high trapping rate constants, such nitrosodurene concentrations are sufficient to trap short-lived radicals. The main advantages of nitrosodurene as a spin-trapping agent are simplicity of the EPR spectra of its spin adducts and the large amount of information contained in them, insensitivity to ultraviolet light, and high stability of radical adducts at 20°C. The EPR spectra exhibit hyperfine splitting by the nitrogen atom of the NO group and by the protons of the trapped radical.

Table 3. Parameters of the EPR spectra of the adducts formed as a result of the capture of radicals by nitrosodurene in benzene at 20°C.[41]

Radical	*g*-Factor	a_N, G	a_β^H, G	Splitting by other atoms
$\dot{C}H_3$	2.0060	13.7	12.17	
$\dot{C}H_3$	2.0061	14.4	13.6	(t-Butyl alcohol (Ref.40))
$\dot{C}_2H_5$	2.0061	13.68	10.97	—
$PhCH_2\dot{C}H_2$	2.0060	13.59	10.87	—
$CH_2{=}CH{=}\dot{C}H_2$	2.0060	13.57	10.20	—
$Ph\dot{C}H_2$	2.0061	13.61	7.93	—
$PhO\dot{C}H_2$	2.0062	12.00	4.84	—
$P\dot{h}$	2.0057	10.11	$a_o^H=a_p^H=2.78$ $a_m^H=0.95$	—
$\dot{C}_6H_4OH$-*p*	2.0050	11.80	$a_o^H=3.25$; 2.75 $a_m^H=a_m^H=0.83$	—
$\dot{C}H_2OH$	2.0059	13.91	7.71	—
$C_2H_5\dot{C}HOH$	2.0060	13.75	3.39	—
t-BuO	2.0054	25.18	—	—
t-Bu	2.0061	13.6	—	—
$\dot{C}Cl_3$	2.0071	10.73	—	$a_{Cl}=1.31$
$\dot{C}HCl_2$	2.0068	11.13	1.14	$a_{Cl}=3.01$
	—	13.5	8—14	161

The splitting by the *para*-protons and the protons of the CH_3 groups is not resolved, but the lines are broadened owing to the interaction with these protons. The HFS lines of the radical adducts of deuterated nitrosodurene [2,3,5,6-tetrakis(trideuteromethyl)nitrosobenzene] are appreciably narrowed, but splitting by the *para*-protons is manifested (a = 0.34 G).[41] The parameters of the EPR spectra of the nitrosodurene adducts are presented in Table 3. All alkyl radicals, including tertiary radicals, add to nitrosodurene via the nitrogen atom and do not form anilino-radicals. The presence of electronegative groups reduces a_N and increases the g-factors. The values of

a_{β}^{H} depend greatly on the structure of the trapped radical. The disadvantages of nitrosodurene include poor solubility in many compounds, the broadening of the lines, and lability of adducts with RO· radicals.

(c) 2,4,6-tri-t-butylnitrosobenzene (BNB)[42,43,45]

Compared with other spin-trapping agents, BNB has a number of advantages. 1. It dissolves readily in many solvents and exists in the active monomeric form in both the solid state and in solution. 2. The spin adducts of BNB have simple, satisfactorily resolved EPR spectra, but the latter show splitting due to *meta*-protons. 3. BNB is a bifunctional trapping agent: radicals can add both to the nitrogen atom, forming nitroxy-radicals, and to the oxygen atom of the nitroso-group with formation of *N*-alkoxy-anilino-radicals (the reaction pathway is determined by the structure of the precursor radical):

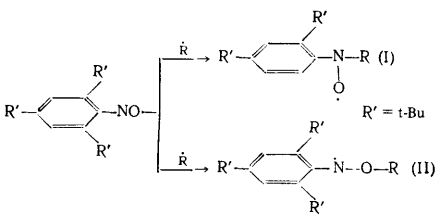


Table 4. Parameters of the EPR spectra of the radical adducts of 2,4,6-tri-t-butylnitrosobenzene.

Radical	Type of adduct	Solvent	*g*-Factor	a_N, G	a_{β}^{H}, G	a_m^H, G	Splitting by other atoms
H·	I	Benzene	2.0061	11.65	—	1.03	12.96 (α-H)
H·	I	Methanol	2.0062	12.7	—	0.9	15.0 (α-H)
ĊH$_3$	I	Benzene	2.0060	13.03	12.33	0.81	—
ĊH$_3$	I	*t*-Butyl alcohol	2.0061	14.2	13.4	0.9	—
Ċ$_2$H$_5$	I	Benzene	2.0060	13.46	17.99	0.83	—
n-Ċ$_4$H$_9$	I	Benzene	2.0061	13.44	17.97	0.78	—
(CH$_3$)$_2$CHĊH$_2$	I	Benzene	2.0061	13.57	18.27	0.84	—
(CH$_3$)$_2$ĊH	I	Benzene	2.0061	13.29	22.19	0.76	0.38 (6-γ-H)
C$_2$H$_5$(CH$_3$)ĊH	I	Benzene	2.0061	13.33	22.25	0.76	0.39 (5-γ-H)
CH$_2$=CH—ĊH$_2$	I	Benzene	2.0060	13.40	16.42	0.84	—
Ph·	I	Benzene	2.0057	9.88	—	0.63	2.86 (2-*o*-H) 2.61 (1-*p*-H) 0.92 (2-*m*)-H
PhĊH$_2$	I	Benzene	2.0061	13.62	14.75	0.83	—
ĊH$_2$OH	I	Methanol	2.0062	13.9	13.9	1.0	—
CH$_3$ĊHOH	I	Ethanol	2.0060	12.60	14.4	0.96	0.12 (12H)
CH$_3$Ȯ	I	Methanol	2.0054	24.0	2.0	0.9	—
Ċ$_2$H$_5$Ȯ	I	Ethanol	2.0052	24.0	2.7	0.9	—
ĊH$_2$(CH$_3$)$_2$COH	II	*t*-Butyl alcohol	2.0040	11.7	—	2.1	2.1 (2-R-H)
(CH$_3$)$_2$ĊH	II	Benzene	2.0040	11.01	—	1.82	1.82 (1-R-H)
Ċ$_6$H$_{11}$	II	Cyclohexane	2.0040	10.95	—	1.79	1.79 (1-R-H)
t-Bu·	II	Benzene	2.0040	10.26	—	1.90	—
Si(C$_2$H$_5$)$_3$	II	Benzene	2.0040	10.33	—	1.96	—
CH$_3$COĊH$_2$	I	Acetone	2.0060	13.47	14.93	0.82	—
PhOĊH$_2$	I	Anisole	2.0064	12.23	9.85	0.82	—

*Here I = nitroxy-radical and II = anilino-radical.

The EPR spectra of *N*-alkoxyanilino-radicals can be readily distinguished from the spectra of nitroxy-radicals, because their *g*-factor and the constant for splitting by the nitrogen atom (Table 4) are smaller and the line width is greater than for nitroxy-radicals. 4. The majority of BNB adducts are stable in non-polar solvents at 20°C. 5. BNB is not photolysed in solution, which makes it possible to use it in the study of photochemical reactions.

Primary alkyl radicals react with BNB, forming exclusively nitroxy-radicals. Tertiary alkyl radicals add only to the O atom with formation of anilino-radicals. Secondary alkyl radicals add to both N and O atoms. Like tertiary alkyl radicals, triethylsilyl and triethylstannyl add to the oxygen atom. Certain radicals with heteroatoms (t-BuȮ, the phenoxy-radical, ĊCl$_3$, the *N*-methylanilino-radical, Ṡ–Ph, etc.) are either ineffectively trapped or do not form stable adducts with BNB. However, BNB is perhaps the best spin-trapping agent for alkyl radicals, since the EPR spectra of their spin adducts are the most sensitive to changes in the structure of the radicals. Among other substituted nitrosobenzenes, the following compounds may be noted.

2,4,6-Trimethoxycarbonylnitrosobenzene[41] is a colourless dimer in the solid state, but dissociates almost completely in solution. In terms of the nature of the spin adducts, this nitroso-compound resembles nitrosodurene, but is a more convenient spin-trapping agent because of its high solubility and the very small width of the lines due to the spin adducts.

2,4,6-Trimethoxynitrosobenzene[41] has properties similar to those of nitrosodurene and the spectra of the spin adducts are simple and have narrow HFS lines. The compound itself is resistant to photolysis but is poorly soluble in many solvents.

2,4,6-Trichloronitrosobenzene[41] largely dissociates in solution but is not photolysed.

Pentafluoronitrosobenzene[41] is a monomer even in the crystalline state, is not photolysed in solution, but has been little investigated as a spin-trapping agent.

3. NITRONES

When the radicals Ṙ are trapped by nitrones having the general formula R′–CH=N(O)–R″, the products are the nitroxy-radicals R′–CH(Ṙ)–N(Ȯ)–R″, whose EPR spectra consist in most cases of a triplet of doublets (splitting by the nitrogen atoms and β-hydrogen atoms). The HFS due to the trapped radicals is usually not resolved and special mention shall be made of the exceptions to this rule. Nitrones can be used conveniently as spin-trapping agents, because of their high reactivity, ready solubility in many compounds, the simplicity of their EPR spectra, and the stability of the spin adducts.

(a) *C*-Phenyl-*N*-t-butylnitrone (PBN)

The majority of workers have synthesised PBN by Emmons' method[46]. The spectrum of PBN in solution in ethanol has an absorption band with a maximum at 294 nm (ϵ_{294} = 16 700 litre mole^{-1} s^{-1}) at 20°C.[46] The compound is stable and relatively insensitive to light, O_2, and water vapour, and dissolves readily in the majority of solvents (its solubility ranges from 0.1 to 1.0 M). Many adducts with PBN are stable at room temperature. In a highly acidic medium PBN hydrolyses with formation of hydroxylamine and benzaldehyde[46]. In the presence of oxidants [Cl_2, Br_2, NO_2, nitrosyl chloride, t-butyl nitrite, $KMnO_4$, and $Pb(AcO)_4$] the stable benzoyl-t-butylnitroxy-radical is formed[47–50] (triplet with a_N = 7.5–8 G).

The data concerning the resistance of PBN to ultraviolet light are contradictory. After prolonged photolysis of solid PBN, the formation of an unidentified radical (triplet in EPR spectra with a_N = 15.2 G) was noted[51]. However, radicals were not detected after ultraviolet irradiation of PBN solutions in methanol, ethanol, and benzene. On the other hand, photolysis of methanol in the presence of PBN led to the observation of the EPR spectrum of an adduct with $\dot{C}H_2OH$ radicals, while irradiation through a filter containing 0.5 M PBN does not lead to the appearance of radicals[55]. It is believed that the photoexcited PBN molecule is capable of abstracting a hydrogen atom from the solvent molecule.

The formation of the radical Ph–C(O)–N(Ȯ)–Bu-t was observed after intense ultraviolet irradiation of PBN solutions in benzene. A possible mechanism of the formation of this radical is based on the intermediate formation of the oxazirane Ph–C(H)(O)–N–Bu-t.[52,53] The contradictory nature of the data of different workers on the photochemical stability of PBN can be attributed not only to the complexity of the processes taking place but also to the purity of the reagent as well as the presence of oxygen in solution. It is noteworthy that no stable radicals are formed during the preparation of PBN solutions in daylight in alcohols and hydrocarbons.

Like other nitrones, PBN is an effective trapping agent not only for radicals but also for certain anions (nitromethane, phthalimide, benzyl cyanide, and styrene anions), the trapping process resulting in the formation of the corresponding nitroxy-radicals. The presence of traces of air increases the yield of these radicals[20,56]. Nitrones readily enter into the 1,3-dipolar addition reaction, which limits their use as spin-trapping agents. Examples of this are provided by the addition of HCN[20] and acetates[47]. At 20°C in the absence of light both $Pb(AcO)_4$ in benzene solution and CH_3COOK in acetic acid[20,47] react with PBN to form a spin adduct (a_N = 12.8 G, a_β^H = 1.73 G) indistinguishable from the adducts of PBN with the radical $CH_3COO\dot{}$:

$$Ph{-}CH{=}\overset{+}{N}{-}Bu\text{-}t + Pb(OAc)_4 \rightarrow Ph{-}CH(O^-){-}N{-}Bu\text{-}t$$

$$\rightarrow Ph{-}CH(AcO){-}N(OPb(OAc)_3){-}Bu\text{-}t \xrightarrow{em} Ph{-}CH(AcO){-}N(O\cdot){-}Bu\text{-}t$$

Slow oxidation of this adduct with air leads to the appearance of the benzoyl-t-butylnitroxy-radical.

Caution is necessary in the interpretation of the mechanism of the formation of the spin adducts of PBN with the radicals $CH_3COO\dot{}$ and $PhCOO\dot{}$, arising in the thermal decomposition of acetates and benzoates, since the same spin adducts can appear also in the nucleophilic addition of acetate and benzoate ions to PBN[20,49].

PBN reacts readily with Grignard reagents and organometallic compounds of sodium, potassium, etc., the process being accompanied by the intermediate formation of the hydroxyamide anion, which oxidises in air to the corresponding nitroxy-radical[47,56]:

$$LiR + PhCH{=}N(O){-}Bu\text{-}t \rightarrow Ph{-}CH(R){-}N(OLi){-}Bu\text{-}t \xrightarrow{O_2} Ph{-}CH(R){-}N(O\cdot){-}Bu\text{-}t$$

This property of nitrones is used for the "specific synthesis" of nitroxy-radicals in order to identify them.

The EPR spectra of the PBN radical adducts Ph–CH(R)–N(O·)–Bu-t consist of a triplet of doublets (as a result of splitting by the nitrogen atom and the β-proton) with small differences in the splitting constants a_N and a_β^H. As stated above, splitting by the nuclei of the trapped radical $\dot{R}$ is not manifested with the exception of adducts with H atoms and inorganic radicals (Table 5). In order to identify the trapped radicals, a very accurate (to within 0.03G) measurement of the hyperfine splitting constants is necessary (for comparison with the available literature data). The solvent has an appreciable influence on the splitting constants: they increase in more polar systems. The "specific synthesis" of nitroxy-radicals in the same solvent is necessary for identification in many instances. The measurement of the width of the line due to adducts may be of some assistance in identification. For example, the adducts of PBN with the radicals $CH_3O\dot{}$ and $\dot{C}H_2OH$ have lines with widths of 0.5 and 1.2 G respectively[57,58]. This difference is associated with the unresolved HFS due to the protons of the $\dot{C}H_2OH$ radical. Thus the EPR spectra of PBN adducts with trapped radicals contain much less information about the nature of the trapped radicals than in the case of nitroso-compounds.

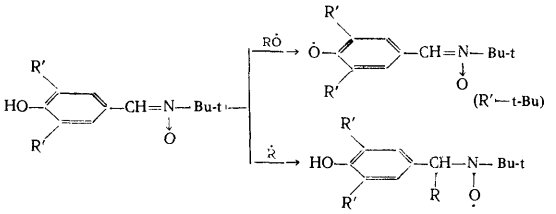
Table 5. Parameters of the EPR spectra of the radical adducts of *C*-phenyl-*N*-t-butylnitrone (PBN).

Radical	Solvent	*T*, °C	a_N, G	a_β^H, G	Splitting by other atoms	Refs.
$\dot{H}$	Benzene	+25	14.8	7.4	—	61
$\dot{H}$	Alcohols	−30	15.8	8.3	—	57, 58
$\dot{C}H_3$	Benzene	+25	14.2	3.45	—	47
$\dot{C}_2H_5$	Benzene	+25	13.9	3.2	—	47
$Ph\dot{}$	Benzene	+25	13.8	2.1	—	47, 67
$Ph\dot{}$	Alcohols	+25	15.25	3.14	—	136
$PhC\dot{H}_2$	Toluene	120	13.9	2.3—2.45	—	47
$\dot{C}H_2OH$	Methanol	+20, +30	15.5	3.75	—	57—59
$CH_3\dot{C}HOH$	Ethanol	+20	15.44	3.6	—	57—59
$CH_3O\dot{}$	Methanol	+20, −30	14.5	2.8	—	57—59
$C_2H_5O\dot{}$	Ethanol	+20	14.49	2.67	—	59
$(CH_3)_2CHO\dot{}$	2-Propanol	+20	14.52	2.18	—	59
$(CH_3)_2\dot{C}OH$	2-Propanol	+20	15.36	3.59	—	59
F·	Benzene	+25	12.2	1.18	a (F)=45.6	1
Cl·	Benzene	+25	12.1	0.75	6.05 (^{35}Cl); 4.88 (^{37}Cl)	1
$CH_3COO\dot{}$	Benzene	+20	12.8—13.03	1.73—1.92	—	47
$PhCOO\dot{}$	Benzene	+20	12.6—12.85	1.29—1.48	—	46
$\dot{C}N$	Benzene	+20	14.4	5.5	a_γ^N=1.2	160
$\dot{C}H_2CN$	Acetonitrile	+20	14.9	3.9	a_γ^H=0.65	160
$\dot{C}H_2CN$	Benzene	+20	14.7	3.7	a_γ^H=0.6	160
$\dot{C}H(CN)_2$	$CH_2(CN)_2$	+20	14.8	5.0	a_γ^H=0.68	160
$\dot{C}H(CN)_2$	Benzene	+20	14.5	3.9	a_γ^H=0.65	160

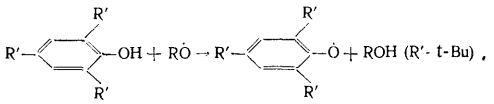
(b) Bifunctional Trapping Agents

Among other nitrones, the attention of investigators has been drawn to bifunctional trapping agents. α-(3,5-Di-t-butyl-4-hydroxyphenyl)-N-t-butyl-nitrone has been described[62]. Oxygen-containing radicals ($R\dot{O}$, $Ac\dot{O}$, $PhCOO\dot{}$, etc.) react with the nitrone by abstracting the phenolic hydrogen with formation of stable phenoxy-radicals; the solution is then coloured blue. Radicals with the unpaired electron at a carbon atom add to the β-carbon

atom of the nitrone, forming nitroxy-radicals, which colour the solution yellow-orange. The EPR spectrum of the phenoxy-radical (a_N = 5.05 G, a_β^H = 2.1 G, a_m^H = 1.7 G) differs strongly from the spectrum of the nitroxy-radical (a_N = 13.5–15.5 G, a_β^H = 2.3–4.2 G). The formation of oxygen-containing radicals in the system can be readily established on the basis of EPR and optical absorption spectra[62]:

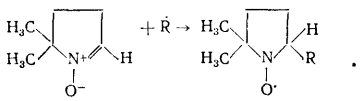


Together with this nitrone, an equimolar mixture of more readily available substances, PBN and 2,4,6-tri-t-butylphenol, can be used with equal success as a bifunctional trapping agent[63]. The PBN and phenol concentrations can be varied, the EPR spectral line of the phenoxy-radical formed is narrower than in the case of the preceding trapping agent, and the satellites due to the 13C atom of the phenoxy-radical are not superimposed on the weaker lines of the nitroxy-radicals:



(c) Cyclic Nitrones

The addition of short-lived radicals to five-membered nitrones of the pyrrolidine series has been studied[64–68]. Among them, 5,5-dimethylpyrroline 1-oxide (DMPO) is of greatest interest[64–68]:

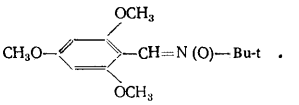


All radicals with the unpaired electron localised mainly at a carbon atom react with DMPO to form adducts whose EPR spectra consist of a triplet of doublets but the splittings by the β-proton are significantly greater than by nitrogen (in contrast to PBN). For adducts with hydroxyalkyl radicals (with the exception of $\dot{C}H_2OH$), the splitting by β-protons is greater by 2–3 G than in the case of alkyl radicals, while for adducts with acyl, benzoyl, and $\dot{C}F_3$ radicals, it is smaller by several gauss.

In the EPR spectra of DMPO adducts with oxy-radicals (RȮ, AcȮ, BzȮ, etc.) there is additional splitting due to one of the γ-protons and the splitting by β-protons is smaller almost by a factor of 3 than for adducts with alkyl radicals (Table 6). The EPR lines of the adducts with RȮ radicals can therefore be readily distinguished from the spectra of other adducts.

The spin adducts of DMPO are stable at 20°C, have narrow lines in the EPR spectra, and the trapping agent itself exhibits a high efficiency in the trapping of radicals (Table 7) and can be conveniently used to trap oxy-radicals.

N-(2,3,5,6-Tetramethylphenyl)nitrone and methyl-*N*-(2,3,5,6-tetramethylphenyl)nitrone[41] as well as 2,4,6-trimethoxy-PBN[156] have been proposed for the trapping of oxy-radicals:



The adducts of these nitrones with oxy-radicals are stable and have EPR parameters which differ markedly from those of other radicals.

Table 6. Parameters of the EPR spectra of the radical adducts of DMPO[64–68].

Radical	Solvent	a_N, G	a_β^H, G	a_γ^H, G	Refs.
Ḣ	Water	16.7	22.4	—	66
ȮH	Water	15.0	15.0	—	66
$\dot{C}H_3$	Benzene	14,3	20.52	—	64
n-$\dot{C}_4H_9$	Benzene	14.24	20.41	—	64
$Ph\dot{C}H_2$	Benzene	14.16	20.66	—	64
Pḧ	Benzene	13.76	19.22	—	64
$\dot{C}H_2OH$	Benzene	14.66	20.67	—	64
$CH_3\dot{C}HOH$	Benzene	15.03	22.53	—	64
$(CH_3)_2\dot{C}OH$	Benzene	14.58	23.91	—	64
$CH_3\dot{C}{=}O$	Benzene	14.03	17.87	—	64
$Ph\dot{C}{=}O$	Benzene	13.99	15.57	—	64
$NH_2\dot{C}{=}O$	Benzene	15.23	18.56	—	64
$\dot{C}F_3$	Benzene	13.22	15.54	1.01 (3-F)	64
$CH_3\dot{O}$	Benzene	13.58	7.62	1.85 (1-H)	64
$C_2H_5\dot{O}$	Benzene	13.11	7.93	1.97 (1-H)	64
t-BuȮ	Benzene	12.24	9.63	0.87 (2-H)	64

Table 7. The rate constants for the trapping of radicals by spin-trapping agents.

Radical	Spin-trapping agent	Matrix	T, °C	k, litre mole^{-1} s^{-1}	Refs.
t-BuȮ	t-BuNO	Benzene	+25	$1.6\cdot10^8$	68
t-Bu̇	CH_2 = N(O)-Bu-t	Benzene	+25	$3.5\cdot10^8$	68
t-Bu̇	PBN	Benzene	+25	$5.5\cdot10^8$	68
t-Bu̇	p-NO_2-PBN	Benzene	+25	$9.0\cdot10^8$	68
t-Bu̇	p-Cl-PBN	Benzene	+25	$6.5\cdot10^8$	68
t-Bu̇	p-CH_3-PBN	Benzene	+25	$3.4\cdot10^8$	68
t-Bu̇	p-CH_3O-PBN	Benzene	+25	$5.5\cdot10^8$	68
t-Bu̇	DMPO	Benzene	+25	$5.0\cdot10^8$	68
$\dot{C}F_3$	CF_3NO	Benzene	+25	$5.8\cdot10^7$	68
t-BuOC̈O	TNB	Benzene	+40	$1.1\cdot10^8$	95
Pḧ	PBN	Benzene + alcohol	+20	$1.2\cdot10^7$	135
PhCOȮ	PBN	Benzene + alcohol	+20	$4.0\cdot10^7$	135
$CH_3\dot{O}$	PBN	Methanol	+20	$1.2\cdot10^8$	58
$CH_3\dot{O}$	TNB	Methanol	−45	$1.3\cdot10^8$	157
$C_2H_5\dot{O}$	PBN	Ethanol	+20	$2.0\cdot10^8$	139

(d) t-Butylmethylenenitrone

t-Butylmethylenenitrone (MN) CH_2=N(O)=Bu-t has been proposed[33,69] as a spin-trapping agent and its application in radiation chemistry has been described[40,70]: MN is synthesised by the reaction of TNB with diazomethane[71,72].

This nitrone is readily soluble in water, alcohols, and many organic solvents. It is not photolysed by light with a wavelength in excess of 300 nm, but light with shorter wavelengths leads to the formation of the radical t-Bu–CH_2–N(Ȯ)–Bu-t (a_N = 13.1 G, a_β^H = 7.0 G). The splitting by β-protons in the spectra of radical adducts of MN depends greatly on the nature of the trapped radical and there is also splitting by the nuclei of the added radical $\dot{R}$. The EPR spectra of the adduct of MN with the radical $\dot{R}$ have the same parameters as the spectra of the adducts of TNB with the radicals $R\dot{C}H_2$ (where R is an H atom or a radical group):

$$\dot{H} + CH_2{=}N(O){-}Bu\text{-}t \rightarrow CH_3{-}N(\dot{O}){-}Bu\text{-}t \leftarrow t\text{-}BuNO + \dot{C}H_3 ,$$
$$\dot{C}_6H_5 + CH_2{=}N(O){-}Bu\text{-}t \rightarrow C_6H_5CH_2{-}N(\dot{O}){-}Bu\text{-}t \leftarrow t\text{-}BuNO + C_6H_5\dot{C}H_2 .$$

4. OTHER SPIN-TRAPPING AGENTS

Apart from nitroso-compounds and nitrones, organic compounds of other classes have been used as spin-trapping agents (Table 1). The *N*-oxides of aromatic nitriles trap unstable radicals, forming fairly stable iminoxy-radicals[73], and no less information is obtained about the structure of the trapped radical than in the case where nitroso-compounds are used:

$$Ar{-}C{\equiv}N{\rightarrow}O + \dot{R} \rightarrow \begin{matrix} Ar \\ R \end{matrix}\!\!>\!C{=}N{-}\dot{O} .$$

For example, the spectra of adducts with the radicals $R{-}\dot{C}O$ show splitting by the group R.[73] A deficiency of these trapping agents is that the geometrical isomers of the same iminoxy-radical have different EPR spectra, which complicates analysis.

The formation of adducts of certain organophosphorus compounds with radicals t-BuȮ has been observed.[80] The formation of radicals of this type can be of interest for organophosphorus chemistry:

$$\text{t-Bu}\dot{O} + (C_2H_5O)_2PCl \rightarrow (C_2H_5O)_2\dot{P}Cl(O{-}Bu\text{-}t) .$$

Substituted acetylenes[81] (for example, $CF_3{-}C{\equiv}C{-}CF_3$, $C_6H_5{-}C{\equiv}C{-}C_6H_5$) can be used as spin-trapping agents. The trapping process involves the formation of 1,2-disubstituted or trisubstituted vinyl radicals, the lifetimes of certain radicals at 20°C exceeding 1 h.

The ability to trap unstable radicals with formation of stable radical adducts is also possessed by perfluoroketones $(CF_3)_2CF{-}\underset{\underset{O}{|}}{C}{-}CF(CF_3)_2$[82] and di-t-butyl selenoketone[151].

5. SPIN-TRAPPING AGENTS IN AQUEOUS SOLUTIONS

Poor solubility frequently limits the application of spin-trapping agents in aqueous solutions. For example, DMPO, PBN, and TNB dissolved in water to an extent less than 0.1 M.[66] An exception is MN, which readily dissolves in water (see above).

In order to investigate the radicals arising in aqueous solutions, maleate and fumarate anions[74] as well as the amides and imides of maleic acid have been used[75]. These trapping agents can be employed particularly to trap ȮH radicals and H atoms.

Many inorganic and aromatic radicals arising in the radiolysis of aqueous solutions and in the reactions of ȮH radicals and $SO_4^{\dot{-}}$ radical-ions (generated, for example, in the photolysis of H_2O_2 and persulphate) with inorganic anions and aromatic compounds[83-86] have been identified[76-79] with the aid of nitromethane in the *aci*-form $CH_2{=}NO_2^-$ in an alkaline medium. Two types of reaction take place with the nitromethane anion: the addition of the inorganic radical $\dot{X}$ to the C=N bond with formation of the adduct $X\dot{C}H_2\dot{N}O_2^-$ and electron transfer from $CH_2{=}NO_2^-$ to the inorganic anion with formation of $\dot{C}H_2NO_2$, which also adds to the nitromethane anion. The constants for hyperfine splitting by the nitrogen atom and methylene protons in the radical-anion $X\dot{C}H_2\dot{N}O_2^-$ depend greatly on the nature of the trapped radicals; splitting due to the trapped radicals sometimes appears in the spectrum ($X = C\dot{N}$, $H\dot{P}O_2^-$).

The radical adducts with the nitromethane anion have short lifetimes (less than a second) and their detection requires the continual generation of radicals in the resonator (under an electron beam or with the aid of a flow technique). Direct detection of the majority of inorganic radicals in aqueous solution under an electron beam (without spin-trapping agents) is impossible[86], because the radicals themselves have shorter lifetimes by several orders of magnitude.

6. STABILITY OF RADICAL ADDUCTS AND THEIR SECONDARY REACTIONS

The stability of nitroxy-radicals is determined by the possibility of tautomeric transformations[7,8], the type of substituent at the nitrogen atom, temperature, and the solvent. Certain nitroxy-radicals can react with one another to form diamagnetic compounds[87-89]. It has been shown in the study of the reactions of dialkyl- and diaryl-nitroxy-radicals that the rate constants for the destruction of these radicals depend on the nature of the solvent[87]. For example, in isopentane the rate constant for the destruction of nitroxy-radicals is 40 times greater than in water. The formation of hydrogen bonds and complexes of nitroxy-radicals with a polar solvent is well known[8]. The solvation of the radical centre as well as other groups (for example, OH groups) alters the reactivity of the radical. For example, the adducts of TNB and PBN with the radicals RȮ are appreciably less stable than the adducts with the radicals $R\dot{C}HOH$.[12,57,58] The increased stability of the adducts of $R\dot{C}HOH$ has been explained by the formation of a hydrogen bond with the solvent and also an intramolecular hydrogen bond[12,58,70].

The PBN adducts are much more stable than the TNB adducts with the analogous radicals, which is due to the stabilising influence of the phenyl groups. For example, the adducts of TNB with alkyl radicals can be observed in the liquid phase either at a low temperature or under the conditions of continuous generation of radicals[18,27,32,33,90], while the analogous adducts with PBN are observed under steady-state conditions at 20°C (including the adduct with H atoms)[57,58,91,92].

In order to avoid an error in the interpretation of the mechanisms of the formation of radicals, account must be taken of the possibility of rapid secondary reactions of spin adducts with one another and with the spin-trapping agent. For example, the adduct of TNB with the radical $\dot{C}Cl_3$ is transformed as a result of secondary reactions into an adduct of TNB with the radical $Cl\dot{C}O$.[38] The absence of an adduct of TNB with the radical $\dot{C}H_2OH$ in γ-irradiated methanol has been explained[35] by the fact that $\dot{C}H_2OH$ is a secondary radical and appears in the reaction of $CH_3\dot{O}$ with methanol. The use of another trapping agent (PBN) showed that in radiolysis both radicals are primary species[57,58,92].

Nitroxy-radicals with a mobile β-hydrogen atom disproportionate with formation of hydroxylamine and a nitrone[87,88,93]:

$$2\left(\text{—CH}_2\text{—N—R}\right) \rightarrow \text{—CH=N—R} + \text{—CH}_2\text{—N—R}$$

(O· / O / OH)

The reaction between the adducts of TNB with H atoms and the radicals $\dot{C}H_2OH$ proceeds via the same mechanisms[12]:

$$\text{t-BuN(}\dot{\text{O}}\text{)H} + \text{HOCH}_2\text{—N(}\dot{\text{O}}\text{)—Bu-t} \rightarrow$$
$$\rightarrow \text{t-BuN(OH)H} + \text{HOCH=N(O)—Bu-t}\ .$$

Both radical adducts are detected with the aid of EPR spectra only under an electron beam and rapidly disappear after the beam is switched off, although the TNB adduct with the $\dot{C}H_2OH$ radical is itself stable at 20°C.[12,94]

The adduct of TNB with the radicals t-Bu$\dot{O}$ decomposes (the decomposition rate constant in benzene[95] at 40°C is 1.1×10^{-3} s^{-1}) with formation of the radicals t-Bu, which add to the TNB molecule, forming the stable radical t-$Bu_2N\dot{O}$:[95]

$$\text{t-BuON(}\dot{\text{O}}\text{)—Bu-t} \rightarrow \text{t-BuNO}_2 + \text{t-Bu} \xrightarrow{\text{t-BuNO}} \text{t-Bu}_2\text{N}\dot{\text{O}}\ .$$

The adducts of t-Bu$\dot{O}$ radicals with nitrosodurene[40] and probably with other trapping agents decompose analogously.

The nitroxy-radicals arising in the trapping of unstable radicals by nitrones and nitroso-compounds can trap yet another radical with formation of a diamagnetic compound:

$$\dot{R} + \text{R—NO} \rightarrow \text{R—N—R} \xrightarrow{\dot{R}} \text{R—N—R}\ .$$

(O· / OR)

The rate constants for the reactions of nitroxy-radicals with solvated electrons, H atoms, and the radicals $\dot{O}H$ and $\dot{C}H_3$ reach 10^9–10^{10} litre $mole^{-1}$ s^{-1} [8,96,158] and those for the reactions with R$\dot{C}$HOH radicals reach 10^8 litre $mole^{-1}$ s^{-1}. This property of nitroxy-radicals has served as a basis for their employment as radical counting agents[8,97], which must be taken into account in the determination of the amount of unstable radicals captured by the spin-trapping agent, because one molecule of the spin-trapping agent can capture two radicals. In the case of nitrones the first radical adds to the carbon atom of the nitrone group and the second adds to the oxygen atom[98].

In addition, it has been noted[1,99,100] that, as a result of the trapping of unstable radicals by nitrones, the hydrogen atom in the radical adduct becomes readily mobile and can be abstracted by certain radicals and the nitrone formed in this case can capture radicals:

$$\text{Ph—CH—N—Bu-t} \xrightarrow{\dot{R}} \text{Ph—C=N—Bu-t} + RH\ .$$

(R / O· / R / O)

For example, in the study of the radical adducts of PBN with chlorine and fluorine atoms, two types of nitroxy-radicals were detected in the EPR spectra[1,101]: Ph–CH(Cl)–N(Ȯ)–Bu-t and Ph–CCl_2–N(Ȯ)–Bu-t.

III. THE APPLICATION OF SPIN-TRAPPING AGENTS IN THE STUDY OF RADICAL PROCESSES

1. THE MECHANISMS OF ORGANIC REACTIONS

(a) Oxidation of Organic Compounds

In the majority of studies carried out with the aid of spin-trapping agents, the formation of radicals in the interaction of various oxidants with organic compounds of many classes has been investigated. Nitrosobenzene and TNB have been used to study the mechanism of the oxidation of aromatic compounds by nickel peroxide dispersed in benzene[19,102]. The aromatic hydrocarbons $ArCHR_2$ or Ar_2CHR with mobile methylene hydrogen atoms are oxidised with formation of radicals of the benzyl type if the substituents R are phenyl, cyano-, acyl, acyloxy-, alkoxy-, or allyl groups. The radicals formed in the oxidation of aromatic amines and phenols[19], diphenylacetonitrile, carbazole, acetonylacetone, and acetamide[102] by nickel peroxide have also been investigated.

Lead tetraacetate and Ce^{4+} ions oxidise 1,3-dicarbonyl compounds, for example acetylacetone and it is suggested that the first stage of the process is electron transfer from the ketone to the oxidant cation. Adducts with radicals of the type R–CO–$\dot{C}$H–CO–R have been observed in the presence of TNB.[18,32] On excitation with ultraviolet light $Pb(AcO)_4$ and thallium(III) ions give rise to the oxidative decarboxylation of carboxylic acids. When TNB and 2-methyl-2-nitroso-3-butanone in CH_2Cl_2 were used at a low temperature (–40°C), adducts with primary alkyl radicals were detected[18,31] and ultraviolet irradiation at 20°C led to the formation of adducts with the secondary radicals R$\dot{C}$HCOOH.

Most attention has been devoted to the mechanisms of the oxidation of alcohols. It has been established with the aid of spin-trapping agents that the mechanisms of the action of various oxidants are not the same. Uranyl nitrate, the radicals t-Bu$\dot{O}$ and $\dot{O}H$, and benzophenone in the triplet state abstract an α-hydrogen atom from the alcohol molecule and the EPR spectra show lines due to the adducts of hydroxyalkyl radicals with TNB, PBN, and DMPO[1,2,33,55,59,103].

In the photochemical oxidation of isopropyl and diphenylmethyl alcohols by benzophenone in the triplet state, the adduct of an H atom was detected together with the TNB adducts of the radical $(CH_3)_2\dot{C}OH$ under the conditions of continuous generation of radicals[30,33]. The appearance of the adduct with atomic hydrogen was explained[1,30,33] by electron transfer from the radical $(CH_3)_2\dot{C}OH$ to the TNB molecule with subsequent protonation of the radical-anion t-$BuNO^{\cdot-}$:

$$(CH_3)_2\dot{C}OH + \text{t-BuNO} \rightarrow (CH_3)_2CO + \text{t-BuNO}^{\cdot-} + H^+$$
$$\text{t-BuNO}^{\cdot-} + (CH_3)_2CHOH \rightarrow \text{t-BuN(}\dot{\text{O}}\text{)H} + (CH_3)_2CHO^-\ .$$

However, one should note that the adducts of TNB with H atoms can be formed not only via electron transfer but also as a result of secondary reactions: (1) the disproportionation of the adducts of TNB with the radicals $(CH_3)_2\dot{C}OH$ involving the formation of the hydroxylamine derivative R–N(OH)–Bu-t; (2) the reaction of t-butylhydroxylamine with a TNB molecule to form an adduct with an H atom. These reversible reactions have been observed[28,29]:

$$\text{t-Bu—N—H} + \text{t-BuNO} \rightleftarrows 2\,\text{t-Bu—N—H}\ .$$

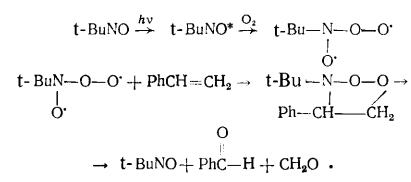
(OH / O·)

The abstraction of an α-hydrogen atom from the alcohol molecule had been suggested earlier also when variable-valence metal ions[104] and persulphate ions[105] are used as oxidants, although such powerful oxidants can convert alcohols into alkoxy-radicals. R$\dot{O}$ radicals could not be detected by EPR in the thermal and photochemical oxidation of alcohols even when a flow technique was used[106–108]. Owing to their high reactivity, R$\dot{O}$ radicals reacted with the alcohol, forming the radicals R$\dot{C}$HOH, which were detected by EPR. Only the use of spin-trapping agents made it possible to show that the oxidation of alcohols (methanol, ethanol, propanols, butanols, 2-phenylethanol, and cyclohexanone) by oxidants such as lead tetraacetate,

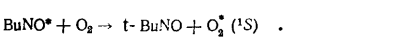
silver nitrate, and potassium persulphate leads to the formation of alkoxy-radicals [18,55,59].

The reactions of ȮH and t-BuȮ radicals have been studied in a number of investigations. The t-BuȮ radicals were generated by the photolysis of alkyl nitrites and also in the thermal decomposition of t-butyl peroxalates and t-butyl hydroperoxide. The oxidation of aldehydes has been investigated with the aid of TNB, nitrosobenzene, and the *N*-oxides of aromatic nitriles [34,39,73]. In the absence of aldehydes the adducts of t-BuȮ radicals are formed and in the presence of aldehydes the spin-trapping agent captures the acyl radicals R–Ċ=O. In addition TNB has been used to study the reactions of t-BuȮ radicals with sulphides, $CHCl_3$, acetate and malonate esters, toluene, ethylbenzene, and isopropylbenzene. The abstraction of the most mobile hydrogen atom was observed in all cases [16,33,34]. The reactions of ȮH radicals with ketones [31] and with sulphoxides and sulphones [32] have been studied with the aid of TNB. The ȮH radicals were generated by the photolysis of H_2O_2 solutions. In the reaction with ketones, mainly the adducts of TNB with the radicals formed by the abstraction of an α-hydrogen atom relative to the carbonyl group were observed. The reactions of ȮH radicals with sulphoxides and sulphones result in the formation of various alkyl and aryl radicals.

Photochemical oxidation by benzophenone in the triplet state was studied with the aid of TNB. Not only alcohols but also amines, phenols, sulphides, thiols, ethers, and hydrocarbons have been investigated under the conditions of the continuous generation of radicals in the resonator [30]. In some cases the spin-trapping agents themselves were involved in photochemical oxidation. The oxidation of alkenes in photolysis by red light in solution in the presence of TNB and oxygen proceeds via the following mechanism according to the authors [10]:



Benzaldehyde and formaldehyde were indeed detected in the reaction products. However, one cannot rule out the possibility of the formation of excited singlet oxygen which behaves as an oxidising agent:



(b) Photolysis of Organic Compounds

It has been shown that the photolysis of aryl iodides in the presence of TNB leads to the formation of aryl radicals which react with TNB to form adducts stable at room temperature. This method is convenient for the synthesis of aromatic nitroxy-radicals [31].

In the photolysis of halogenomethanes of the type CX_4, CHX_3, and CH_2X_2 (where X is a halogen atom) the radicals are formed as a result of the homolytic dissociation of the C–X bond [22,23,25,38,101,109]. The adducts with the $\dot{C}Cl_3$ and $\dot{C}HCl_2$ radicals can be conveniently detected when perfluoro-t-nitroso-butane is used [22,109]. In the presence of TNB, adducts with the X–Ċ=O radicals were detected together with the adducts of $\dot{C}X_3$ radicals [22–25,38,109]. The formation of the former is indicated by secondary reactions of the TNB radical adducts [23,25,38]. The study of the mechanism of the formation of the adducts of TNB with the radicals X–Ċ=O showed that, in the presence of an alcohol or dimethylamine, the nitroxy-radicals X–C(=O)–N(Ȯ)–Bu-t (X = Cl or Br) are transformed into the radicals RO–C(=O)–N(Ȯ)–Bu-t, whose structure has been established with the aid of nitrosoperdeutero-t-butane [23–25] and also by means of independent synthesis.

Photolysis of organometallic compounds of lead, tin, and mercury in the presence of PBN leads to the formation of adducts with radicals of the alkyl, phenyl, or benzyl types, depending on the nature of the substituents. It was found that the capacity for dissociation of the bond with the metal diminishes in the sequence phenyl > alkyl > acetate (or halogen) [1,47]. Adducts with the short-lived radicals $CH_3C(=O)O\dot{O}$ and $PhC(=O)O\dot{O}$ were detected in the photolysis of lead acetate and mercury benzoate, but the same adducts can arise also as a result of the addition of acetate and benzoate ions to PBN (see Section II, subsection 3).

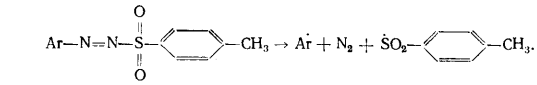
Adducts with phenyl radicals were detected in the photolysis of organometallic compounds of the type Ph_3M (M = N, As, Sb, or Bi) in the presence of PBN, but the adducts of radicals containing a metal atom ($Ph_2\dot{M}$) [100], which should have appeared if the decomposition proceeds via the mechanism



were absent.

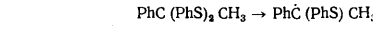
Adducts with radicals of the acyl type RO–Ċ=O were detected in the photolysis of R–Hg–C(O)OR in the presence of BNB. [111] Adducts with ȮH radicals [67] were found in the photolysis of dilute H_2O_2 solutions in the presence of PBN and DMPO [67], while in concentrated H_2O_2 solutions adducts of $H\dot{O}_2$ radicals were detected. One cannot rule out the possibility that the latter appear as a result of the chemical reaction of H_2O_2 with the trapping agent.

The radical products of the photochemical and thermal decomposition of *p*-tolyl arylazosulphones were investigated with the aid of TNB and PBN. [50] It has been suggested that these compounds decompose via the mechanism



The adducts with aryl radicals was identified [50] with the aid of PBN but the adducts with the radicals H_3C–C$_6$H$_4$–$\dot{S}O_2$ were not detected. In the presence of TNB a triplet was observed in the EPR spectra, which the authors attributed to the adduct of TNB with the radicals H_3C–C$_6$H$_4$–$\dot{S}O_2$.

The study of the thermal and photochemical rearrangement of acetophenone diphenylmercaptal with the aid of TNB showed that the process proceeds via a radical stage:



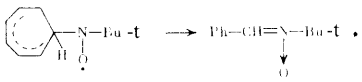
The adducts of TNB with both radicals have been detected. In the presence of O_2, adducts with the $PhC(\dot{O})$–$(PhS)CH_3$ and $PhC(PhS)_2\dot{C}H_2$ radicals were also observed [112].

The photolysis of TNB in the presence of diethyl α-halogenophosphonates leads to the formation of phosphorus-containing nitroxy-radicals [113] of the type t-Bu–N(Ȯ)–CH(R)–P(=O)$(OC_2H_5)_2$. Phosphorus-containing nitroxy-radicals can also be obtained from the nitroso-compound

$(CH_3)_2C(NO)-P(O)(OEt)_2$, whose synthesis has been described [114].

(c) Other Types of Organic Reactions

It has been shown for the first time with the aid of TNB that, when tropylium tetrafluoroborate is reduced with zinc, the product is a tropyl radical, the EPR spectrum of the adduct of which with TNB is a triplet of doublets (a_N = 14.5 G, a_β^H = 2.2 G).[28] This nitroxy-radical is subsequently oxidised to PBN:

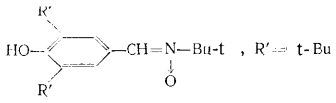


The dark reaction of tetranitromethane with nucleophiles (N_3^-, NO_2^-, OH^-, F^-, Cl^-, I^-, t-BuO^-, etc.) has been investigated with the aid of PBN.[48,115,116] According to the authors, there is electron transfer from the nucleophile to tetranitromethane. The adduct with the NO_2 radical was not detected, the benzoyl-t-butylnitroxy-radical, which is a PBN oxidation product, being formed instead.

The adducts of PBN with radicals derived from nucleophiles [t-BuO^-, $C(NO_2)_3^-$] were detected in the interaction of $FClO_3$ with nucleophiles [116]. In the presence of nucleophiles, the fluorine atom is captured. The formation of nitroxy-radicals was observed also in TNB solutions containing aromatic compounds and nucleophiles (OH^-, CH_3O^-)[48,117,118]. However, the authors' conclusions[48,115,118] are not unambiguous, since nitroso-compounds and nitrones can react with nucleophiles in the absence of oxidants, forming nitroxy-radicals[20,119,120] (Section II, subsection 3). The formation of the t-BuNO$^\cdot$ radical-ion has been noted, for example, in TNB solutions in the presence of t-BuOK [120].

Adducts of PBN with fluorine atoms have been detected in the products of the decomposition of NF_3O in benzene in the presence of PBN.[1] Since NF_3O is used in preparative chemistry as a fluorinating agent, the fluorination reaction may occur with participation of fluorine atoms. Adducts with chlorine atoms have been detected in the thermal decomposition of t-BuOCl in benzene in the presence of PBN [101].

The reaction of *N*-chlorosuccinimide with toluene-*p*-sulphonic acid has been investigated[69,121,122]. In the presence of the bifunctional trapping agent



the phenoxy-radical was detected and in the presence of PBN the product was found to be the radical PhC(O)N(O$^\cdot$)-Bu-t, arising, according to the authors [121], as a result of the oxidation of PBN by chlorine atoms or the succinimyl radical. The adducts of PBN with the succinimyl radical and chlorine atoms were not, however, detected. When t-butylmethylenenitrone and TNB were used as spin-trapping agents, the EPR spectra of the adduct of the succinimyl radical were detected[69,121,122]. The adducts of the succinimyl radical with TNB and MN also appeared in the photolysis of *N*-chloro- and *N*-bromo-succinimides in benzene, but in polar solvents the adducts were not detected [69].

The possibility of the radical rearrangement of $XCH_2\dot{C}HCCl_3$ to $XCH_2CH\dot{C}Cl_2$ (X = t-BuO or CCl_3) has been investigated [123]. In the presence of 2-methyl-2-nitroso-3-butanone the adduct with the radical $XCH_2\dot{C}HCCl_3$ was detected, while in the presence of TNB the product was the adduct with the radical $XCH_2CH\dot{C}Cl_2$. The adducts of both radicals with the same spin-trapping agent were not found, so that secondary reactions of the radical adducts probably take place in the system.

The radical arylation of disulphides has been studied in the presence of TNB. Phenyl radicals attack the disulphide at a sulphur atom and the EPR spectra contain lines due to the adducts of the radicals Ph$\dot{S}$ (triplet with a_N = 16.3 G) [159]:

$$\dot{P}h + (PhS)_2 \rightarrow PhSPh + Ph\dot{S} .$$

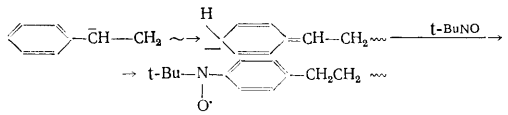
Spin-trapping agents have been used in the study of polymerisation processes[20,124-126]. By varying the concentration of the spin-trapping agent, it is possible to detect adducts with radicals having different degrees of polymerisation. At a high concentration of the spin-trapping agent (0.1 M and above) mainly radicals derived from the initiator are captured, while at low concentrations (0.001 M) polymeric radicals are captured. Radicals arising in the photolysis of TNB have been used to initiate the polymerisation of unsaturated phosphonic acid esters [124].

MN and TNB have been used [125] to investigate the polymerisation of styrene initiated by t-BuO$^\cdot$ radicals:

$$t\text{-}BuO^\cdot + PhCH=CH_2 \rightarrow Ph\dot{C}HCH_2O\text{—}Bu\text{-}t .$$

At a TNB concentration of 0.05 M the adduct with the radical $Ph\dot{C}HCH_2O$-Bu-t (a_N = 14.3 G, a_β^H = 2.3 G) was detected [125]. At low TNB concentrations, (0.001 M) adducts with the longer radicals Ph-$\dot{C}HCH_2(PhCHCH_2)_nO$-Bu-t ($a_N$ = 14.5 G, a_β^H = 3.3 G) were detected.

The spin-trapping agents TNB and PBN terminate the anionic polymerisation of styrene, methyl methacrylate, vinylpyridines, etc. with formation of stable polymeric nitroxy-radicals by the addition of an anion to a nitroso-compound or nitrone [20]:



This process is the simplest pathway to the formation of "spin-labelled" polymers [20]. Spin-trapping agents make it possible to synthesise nitroxy-radicals, the preparation of which in the usual chemical way involves considerable experimental difficulties. The application of nitrones in the synthesis of nitroxy-radicals was first described by Iwamura and Inamoto [5,6].

The electrochemical oxidation of the nitromethanes $C(NO_2)_3^-$, $CH_3C(NO_2)_2^-$, and $(CH_3)_2C(NO_2)^-$ was investigated with the aid of PBN [115,116]. In the reaction with $C(NO_2)_3^-$ the product was found to be an adduct whose spectrum showed splittings with a_N = 14.1 G and a_β^H = 4.2 G. The authors attributed this spectrum to the adduct of PBN with the $\dot{C}(NO_2)_3$ radical. Nitroxy-radicals of the same type are formed also in the photolysis of the anions of nitroso-compounds [115,116]. In the course of the electrochemical reduction of the benzenediazonium cation in the presence of PBN the product is an adduct with the phenyl radical [127]. One must note that nitrones and nitroso-compounds are effective electron acceptors [20,58,92,128,158] and can oxidise anions with formation of the corresponding radicals.

2. THE DETECTION OF RADICALS FORMED IN THE GAS PHASE

Spin-trapping agents can be used for the identification of radicals formed in the gas phase[51,61,129-131]. Both solid trapping agents and their vapours have been used for this purpose. The solid spin-trapping agent (PBN, NTB, or nitrosobenzene) was placed in the stream of gases emerging from the electric discharge and, after switching off the discharge, was transferred (in the absence of oxygen) to a suitable solvent and the EPR spectra of the nitroxy-radicals were observed. The nitroxy-radicals are highly volatile and can be frozen out in a trap cooled with liquid nitrogen[61,129,130].

When a gas discharge was allowed to act on D_2O vapour, H_2, D_2, CH_4, and NH_3, the adducts of PBN with H and D atoms and with the ȮH, ȮD, and $\dot{C}H_3$ radicals were detected[61]. In ammonia only the adducts with H atoms were found and the adducts with $\dot{N}H_2$ radicals were not detected. In a discharge in toluene adducts with radicals of the phenyl and benzyl type were found[60]. A study was also made of the pyrolysis of organosilicon compounds in the presence of PBN[130]. As in the thermal decomposition of t-BuOCl in benzene[101], in the gas-phase photolysis of this substance[129] the adducts of PBN with chlorine atoms and in addition the $PhCCl_2$–N(O)–Bu-t radical were detected. The gas-phase photolysis of alkyl iodides, ketones, and aldehydes has been studied[131]. Adducts with alkyl radicals were detected in the presence of solid PBN and in the presence of TNB in the vapour phase adducts with acyl radicals were found in the reactions with aldehydes and ketones. The radicals arising in cigarette smoke have been studied with the aid PBN[132].

The spin-trapping method has many advantages compared with the direct gas-phase EPR method[133]. In particular, not only adducts with monatomic and diatomic radicals (the usual species for which EPR is used in the gas phase) but also those with radicals such as $\dot{C}H_3$, $\dot{C}_2H_5$, t-BuȮ, Ṗh, $Ph\dot{C}H_2$, and R–Ċ=O have been detected.

3. THE APPLICATIONS OF SPIN TRAPPING AGENTS IN CHEMICAL KINETICS

The high stability of radical adducts makes it possible to use spin-trapping agents in kinetic studies. The reaction of a spin-trapping agent with a radical cannot as yet be observed directly in view of its high rate and the rate constants for these reactions are therefore determined by the method of steady-state concentrations.

The rate constants for the trapping of PhCOȮ radicals by certain PBN derivatives[134] were determined with the aid of the galvinoxy-radical as a competing acceptor. The rate constant for PBN is 4.0×10^5 litre mole^{-1} s^{-1}. The rate constant for the decomposition of di-t-butyl peroxalate into t-BuȮ radicals ($k = 6.8 \times 10^{-5}$ s^{-1} at 35°C) and the activation energy, which is 30 kcal mole^{-1}, were obtained by the same method. The above values agree with the results obtained by other procedures.

The absolute rate constants for the trapping of t-BuȮ radicals by various spin-trapping agents have been obtained taking into account the known rate constants for the abstraction of hydrogen by t-BuȮ radicals from cyclohexane and toluene[68]. Under these conditions, the EPR spectra of the adducts of t-BuȮ radicals and alkyl radicals arising in the competing reaction of t-BuȮ with the hydrocarbon were recorded at the same time. Since the EPR spectra of various PBN radical adducts overlap markedly, DMPO was used as the spin-trapping agent (Section II, subsection 3), since the EPR parameters of the adducts of this trapping agent with RȮ radicals differ markedly from those of the adducts with alkyl radicals. The rate constant for the trapping of t-BuȮ radicals by DMPO molecules proved to be 5×10^8 litre mole^{-1} s^{-1}.[68] The rate constants for the reactions of t-BuȮ radicals with various spin-trapping agents (Table 7) were determined with the aid of the competition of two trapping agents (one of which was DMPO) for the t-BuȮ radical.

The rate constants for the trapping of t-BuO–Ċ=O radicals by TNB and for the decomposition of the adducts of TNB with the t-BuȮ radical ($k_1 = 1.1 \times 10^{-3}$ s^{-1}) have been estimated[59]. The ratio of the rate constants for the reactions of the t-BuȮ radicals with ethylbenzene and toluene[33], determined with the aid of TNB, is 8.6 ± 1.0.

The rate constants for the trapping of Ṗh and PhCOȮ radicals by PBN molecules, which are 1.2×10^7 and 4.0×10^7 litre mole^{-1} s^{-1} respectively at 20°C, have been measured[135,136]. Previously, unduly low values of the order of 10^5–10^6 litre mole^{-1} s^{-1} had been obtained for these constants[134], since an approximate rate constant for the decarboxylation of PhCOȮ radicals, equal to 10^3–10^4 s^{-1}, had been used in the calculations. Using PBN, 5.0×10^5 s^{-1} was obtained for this constant[135].

The rate constants for the attachment of phenyl radicals to benzene with formation of phenylcyclohexadienyl radicals[135] as well as the rate constants for the abstraction of H atoms from alcohol molecules by phenyl radicals[136] have been determined with the aid of PBN (Table 8). The rate constants for the fragmentation of acyl radicals in benzene have been found by the spin trapping method[39].

Table 8. Reaction rate constants determined with the aid of spin-trapping agents.

Reaction	Rate constant	Reaction conditions	Refs.
PhCOȮ → Ṗh + CO_2	5×10^5 s^{-1}	20°C, benzene	135
Ṗh + C_6H_6	7.8×10^4 litre mole^{-1} s^{-1}	20°C, benzene	135
Ṗh + CH_3OH	1.4×10^5 litre mole^{-1} s^{-1}	20°C, alcohol	136
Ṗh + C_6H_5OH	2.3×10^5 litre mole^{-1} s^{-1}	20°C, alcohol	136
Ṗh + 2-propanol	4.1×10^5 litre mole^{-1} s^{-1}	20°C, alcohol	136
R–Ċ=O → Ṙ + CO			
R = CH_3, n-C_3H_7	~1 s^{-1}	40°C, benzene	39
R = iso-C_3H_7	3.9×10^3 s^{-1}	40°C, benzene	39
R = t-Bu	5.2×10^4 s^{-1}	40°C, benzene	39
R = $PhCH_2$	7×10^6 s^{-1}	40°C, benzene	39

The study of the radiolysis of alcohols yielded the rate constants for the trapping of $CH_3\dot{O}$ and $C_2H_5\dot{O}$ radicals by PBN molecules at 20°C: $k(CH_3\dot{O} + PBN) = 1.2 \times 10^8$ litre mole^{-1} s^{-1} and $k(C_2H_5\dot{O} + PBN) = 2.0 \times 10^8$ litre mole^{-1} s^{-1}.[58,139] The absolute rate constants for the reactions of RȮ radicals with alcohols, determined by pulse radiolysis, were used in the calculations[137,138]: $k(CH_3\dot{O} + CH_3OH) = 2.62 \times 10^5$ litre mole^{-1} s^{-1} and $k(C_2H_5\dot{O} + C_2H_5OH) = 1 \times 10^6$ litre mole^{-1} s^{-1}. The rate constant for the trapping of $CH_3\dot{O}$ by TNB molecules proved to be 1.3×10^8 litre mole^{-1} s^{-1} at −45°C in methanol [method based on the use of *N*,*N*,*N'*,*N'*-tetramethyl-*p*-phenylenediamine (TMPD) as a competing acceptor[157]].

Thus the spin-trapping method makes it possible to obtain extensive information about the reactivities of radicals.

4. THE USE OF THE SPIN-TRAPPING METHOD IN RADIATION CHEMISTRY

The earlier procedures for the investigation of radicals in radiation-chemical processes suffer from serious disadvantages. The difficulty of analysing the EPR spectra of radicals in the solid phase has already been noted. The EPR spectra in the liquid phase under the influence of an electron beam also have a low signal-to-noise ratio and the shortest-lived radicals are not detected[56]. Radicals of the type RȮ and ȮH are not detected in the liquid phase owing to their short relaxation times.

The possibility of using the spin-trapping method for the investigation of radicals formed in solid-phase radiolysis was first demonstrated by Lagercrantz and Forschult[37]. The solid substances subjected to preliminary γ-irradiation were dissolved in a weakly alkaline TNB solution. It was observed that the $\dot{C}H_2COO^-$ radical-ions are stabilised in sodium acetate and glycine, while radicals of the type R–ĊHCOOH are stabilised in alanines, potassium malonate, and succinic and glutamic acids. When the solid was dissolved, adducts of these radicals with TNB were formed. After dissolution of γ-irradiated Na_2HPO_3 the adduct of TNB with the $\dot{P}O_3^{2-}$ radical-ion was detected and the adduct with the ṖOH(O) radical was found in γ-irradiated NaH_2PO_2.[140,141]

Spin-trapping agents have been used most frequently in the liquid phase. Adducts with $\dot{C}Cl_3$ radicals and chlorine atoms have been found in CCl_4 irradiated in the presence of PBN,[1] which agrees with the presence of C_2Cl_6 and Cl_2 in the radiolysis products.

In order to identify the radicals arising in aqueous solutions or organic compounds on γ-irradiation, TNB was used[66,94,142]. Adducts of the $\dot{C}H_2OH$ radical (a_N = 15.5 G, a_β^H = 6.1 G), which are stable at 20°C, were detected in 0.5 M aqueous solution of methanol in the presence of TNB.[94] Well resolved EPR spectra of the adducts of TNB with radicals of the type –ĊH–N= were obtained in dipeptides and nucleic bases γ-irradiated in aqueous solutions at 20°C.[94,142]

Thiols RSH (R = Me, Et, n-Br, iso-Pr, or n-Bu), γ-irradiated at low temperatures (–73°, –102°C) in the liquid phase have been investigated[36] with the aid of TNB. The adducts of TNB with thiyl radicals were identified. They have well resolved EPR spectra, which distinguishes them favourably from the EPR spectra of these radicals in the solid phase, where the hyperfine structures are not resolved and the identification is not unambiguous[155]. For example, the spectra of the adducts with $\dot{C}H_3S$ radicals consist of a triplet of quartets (a_N = 18.9 G, a_β^H = 1.2 G).

Water subjected to an electron beam has been investigated[66] at 20°C with the aid of DMPO, TNB, and PBN. The adducts of the above spin-trapping agents with ȮH radicals and H atoms were detected (the spectral parameters are presented in Tables 2, 5 and 6). In the case of DMPO and TNB hydrogen atoms and solvated electrons lead to the same adduct, since the radical-anion formed as a result of the trapping of electrons is protonated in water:

$$DMPO + e^- \rightarrow DMPO^- \xrightarrow{H_2O} DMP\dot{O}{-}H + OH^- .$$

The radiolysis of benzyl alcohol by means of an electron beam has been investigated in the presence of TNB.[143] The formation of benzyl radicals $Ph\dot{C}H_2$ and the radicals PhĊHOH was demonstrated. The addition of electron-accepting agents showed that the benzyl radicals are formed in the reaction of electrons with the alcohol and the t-BuN(Ȯ)–H adduct detected arises, according to the authors, as a result of electron transfer from the PhĊHOH radicals:

$$t\text{-}BuNO + Ph\dot{C}HOH \rightarrow t\text{-}BuN(\dot{O})H + PhCHO .$$

The adducts with $PhCH_2\dot{O}$ radicals were not detected. The TNB concentration employed (0.01 M) is apparently too low for the effective competition of TNB for the $PhCH_2\dot{O}$ radical[143].

Ethylene glycol γ-irradiated in the liquid and solid phases has been studied with the aid of TNB[144–146]. A triplet of doublets (a_N = 15.4 G, a_β^H = 1.5 G) of the adduct with the $HOCH_2\dot{C}HOH$ radical as well as a triplet of triplets (a_N = 14.4 G, a_β^H = 5.1 G),[146] referring to the adduct with the $\dot{C}H_2OH$ radical, and the 3 × 3 × 2 multiplet (a_N = 15.5 G, a_β^H = 9.1 G, and a_γ^H = 0.6 G), identified as the spectrum of the adduct with the $\dot{C}H_2CHO$ radical, were observed in the EPR spectra. The identification of the last adduct is confirmed[146] by the splitting by γ-protons and the magnitude of the splitting by β-protons, which is characteristic of adducts with radicals of the type $\dot{C}H_2R$ (Table 2). The EPR spectrum of ethylene glycol irradiated at –196°C without spin-trapping agents shows only a poorly resolved triplet and singlet due to stabilised electrons.

The radiolysis of alkanes[91] and aromatic hydrocarbons[13,147] has been studied with the aid of spin-trapping agents. Using nitrosodurene and PBN, phenyl radicals were identified in benzene γ-irradiated at 20°C and benzyl radicals and radicals of the phenyl type were identified in toluene[147]. $t\text{-}Bu_2N\dot{O}$ radicals are formed in a yield of 1.5 radicals/100 eV in benzene, toluene, and *o*-xylene irradiated at 20°C in the presence of 0.1 M TNB.[13,147] It has been shown that the radicals $t\text{-}Bu_2N\dot{O}$ are formed as a result of the transfer of excitation from the aromatic hydrocarbon to the TNB molecule and yields of the excited molecules of these hydrocarbons were measured and found to be 2.5 ± 0.5 molecules/100 eV. Thus certain spin-trapping agents can trap not only radicals but also excited species and can be used for the quantitative determination of the yield of excited molecules.

The γ-radiolysis of nitriles has been studied in the liquid phase in the presence of PBN.[160] $\dot{C}H_2CN$ radicals in acetonitrile, H atoms and $CH_3\dot{C}HCN$ radicals in propionitrile, $\dot{C}H(CN)_2$ radicals in malononitrile, and H atoms and ĊN and $\dot{C}H_2CH_2CN$ radicals in succinonitrile have been identified. Splitting by γ-protons has been observed in the EPR spectra of the adducts of PBN with the radicals $\dot{C}H_2CN$ and $\dot{C}H(CN)_2$ (Table 5).

The radiolysis of alcohols in the liquid and solid phases has been studied in greatest detail by the spin-trapping method[11,12,27,35,40,45,57,58,90–92,139,148–150]. TNB, PBN, and BNB served as the spin-trapping agents. The formation of alkoxy-radicals and H atoms in methanol, ethanol, propanols, and t-butyl alcohol, irradiated by γ-rays and electrons in the liquid phase, was demonstrated for the first time in radiation chemistry. For comparison, we may state that neither H atoms nor RȮ radicals were detected in the study of frozen alcohols[155] nor were they observed directly under an electron beam in the liquid phase[108]. After γ-irradiation in the liquid phase in the presence of TNB, hydroxy-alkyl radicals were detected in methanol, ethanol, 1-propanol, and 2-propanol, while adducts of NTB and H atoms, arising as a result of the trapping of both H atoms and electrons with subsequent

protonation of the t-BuNO$^{\cdot-}$ radical anions, were found after exposure to an electron beam:

$$\text{t-BuNO}^{\cdot-} + \text{ROH} \rightarrow \quad \text{t-Bu(O}\dot{)} - \text{H} + \text{RO}^- \ .$$

An analogous electron capture process takes place in the case of BNB. Irradiation of BNB solutions in methanol and ethanol at −196°C leads to the formation of BNB radical-anions which are converted quantitatively into BNB adducts with H atoms on raising the temperature to −155°C.[45]

Analysis of literature data[11,12,35,45,90,94] has shown that TNB and BNB can be used in the radiolysis of alcohols only for the identification of radicals. Complications arise owing to secondary reactions between radical adducts[12] and the low efficiency of the trapping of certain radicals by BNB. As a result of the reaction between TNB adducts with $\dot{C}H_2OH$ radicals and H atoms, the yield of $\dot{C}H_2OH$ and $CH_2\dot{C}HOH$ adducts is low under continuous generation conditions in an electron beam[27,90] and there is a complete absence of $\dot{C}H_2OH$ adducts in methanol γ-irradiated at −80°C[11,35] in the presence of a high TNB concentration. In the case of BNB the adducts of the latter with $CH_3\dot{C}HOH$ radicals were hardly detected[45].

Quantitative yields of primary radicals in the radiolysis of liquid and solid alcohols have been measured successfully with the aid of PBN[58,92,139]. Solvated electrons are fully captured by this trapping agent for [PBN] ≥ 0.1 M and do not contribute to the overall yield of radicals at 20°C, since the adducts of PBN with an electron decompose at temperatures above −150°C without the formation of any radical adducts[92]. The yields of RȮ radicals were determined using irradiation in the presence of O_2. RȮ radicals do not react with O_2, while RĊHOH radicals and H atoms do react with O_2 with high rate constants, forming peroxy-radicals which do not give rise to stable adducts with PBN and are not detected in EPR spectra[92]. The yields of RȮ and RĊHOH radicals and H atoms in methanol, ethanol, 1-propanol, and 2-propanol, γ-irradiated at temperatures from +20° to −196°C, have been measured by the method of competitive kinetics[58,92,130]. For example, in methanol at 20°C $G(CH_3\dot{O}) = 2.5$, $G(H) = 0.6$, and $G(\dot{C}H_2OH) = 3.1$ radicals/100 eV, while in ethanol $G(C_2H_5\dot{O}) = 1.6$ radicals/100 eV. The yields of RȮ radicals obtained with the aid of the spin-trapping method agree with indirect determinations of the corresponding yields by pulse radiolysis[137,138] and with the calculation based on the final products.

Apart from t-BuȮ radicals adducts with the $\dot{C}H_2(CH_3)_2$. COH, $\dot{C}H_3$, and t-Bu̇ radicals were detected in γ-irradiated t-butyl alcohol[11,40]. It was shown[40] that $\dot{C}H_3$ radicals appear only in the decomposition of t-BuȮ radicals and t-Bu̇ radicals do not arise in the radiolysis of alcohol itself, being formed in the decomposition of the spin adducts of TNB and nitrosodurene with t-BuȮ radicals. It has been stated that the use of t-butylmethylenenitrone for the study of the radiolysis of polar systems is promising[70].

Thus the following problems can be solved with the aid of spin-trapping agents: (1) identification of short-lived radicals; (2) determination of the quantity of unstable radicals; (3) determination of the kinetic characteristics of the trapped radicals. In addition, spin-trapping agents can be used for the synthesis of spin-labelled compounds and for the inhibition of chain processes. Spin-trapping agents are used with a high degree of efficiency in various branches of chemistry, primarily in the study of oxidation and reduction reactions, radical rearrangements, catalytic processes, and polymerisation. Another field where they are used involves the chemistry of high energy processes (radiation and laser chemistry, photochemistry, ultrasonic chemistry, plasma chemistry, and mechanochemistry), in the majority of which there are radical stages. The spin-trapping method can prove to be of significant assistance in biological research, particularly in radiobiology.

The spin-trapping method has significant advantages over other versions of the EPR method, primarily because of the possibility of detecting unstable radicals in processes where the radical concentrations are too low for investigation by other methods. The main advantages is the recording of EPR spectra directly in the liquid phase, which makes it possible to increase appreciably the resolving capacity of EPR and to facilitate the identification of radicals compared with the solid phase. Different spin-trapping agents can be used to identify the same radical (Table 1).

The spin-trapping method also suffers from certain disadvantages associated mainly with the fact that a new compound (the spin-trapping agent) is introduced into the test system. In order to eliminate the uncertainty caused by introducing the spin-trapping agent, it is necessary to investigate independently its behaviour in the given system acted upon by the particular procedure. Naturally, one must carry out an additional study of the stability of the radical adducts and the possibility of their participation as free radicals in the test process itself.

The data presented in the review permit certain recommendations for the selection of spin-trapping agents: 1. It is desirable that the spin adducts should have the simplest EPR spectrum with the smallest possible overlapping of lines due to different radicals. 2. The chosen spin-trapping agents should not interact with the test systems. 3. The spin adducts should be fairly stable. 4. The spin-trapping agent should not itself give rise to radical adducts under the influence of light.

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Department of Electrochemistry,
Faculty of Chemistry,
Moscow State University