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Study of Short-lived Chlorine- and Sulphur-containing Radicals by the Spin-trapping Method

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The general aspects of the method for the identification and study of short-lived radicals in the liquid phase by EPR using spin-trapping agents are discussed and the available literature data for the application of the spin-trapping method to the study of short-lived chlorine- and sulphur-containing radicals and reactions involving them are surveyed. Certain methodological solutions, which make it possible to use the method in the study of complex radical reactions, are examined.
The bibliography includes 91 references.

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I. INTRODUCTION

Many free radicals are extremely unstable paramagnetic species and their identification by EPR is possible only when their steady-state concentration is sufficiently high. The existing methods for the direct investigation of short-lived radicals in the liquid phase by EPR therefore consist either in a constant maintenance of a fairly high concentration of the radicals in the spectrometer resonator (flow method[1,2]) or in an increase of the lifetime of the radicals by reducing the temperature[3,4]. These methods suffer from the following disadvantages. In the first case considerable amounts of starting materials are required, and in the second account must be taken of the fact that radical processes can take place in different ways depending on the temperature, so that the results obtained, for example, at −100°C, do not always agree with the reaction mechanism at room or higher temperatures[5,6]. Furthermore, the above methods are very complex experimentally.

Towards the end of the 1960s, a new method was developed for the investigation of the EPR of short-lived radicals in the liquid phase called the "nitroxide method"[7] or the "spin-trapping method"[8]. The essential feature of this method is that the short-lived radicals R$^{\cdot}$ formed during the homolytic reaction add to a "spin-trapping agent" (a nitroso-compound, a nitrone, or another suitable radical acceptor) specially introduced into the reaction mixture, which leads to the formation of nitroxy-radicals ("spin-adducts"[8]), for example:

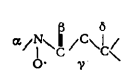
$$\begin{aligned} &a)\ \ R^{\cdot} + R'-N=O \rightarrow R-\underset{\displaystyle O^{\cdot}}{N}-R' \ ; \\ &b)\ \ R^{\cdot} + R'-\underset{\displaystyle O}{CH}=N-R'' \rightarrow R'-\underset{\displaystyle R}{\underset{|}{CH}}-\underset{\displaystyle O^{\cdot}}{\underset{|}{N}}-R'' \ . \end{aligned} \qquad (1)$$

The nitroxy-radicals formed are in many cases sufficiently stable for investigation by EPR. The EPR spectrum of the spin-adduct makes it possible to arrive at a conclusion concerning the structure of the radical R$^{\cdot}$ detected†.

This method naturally suffers from the usual disadvantages of an indirect procedure compared with direct procedures. Nevertheless it has many advantages which have ensured its extensive development and application‡. The largest of spin labels available makes it virtually universal for the detection of a wide variety of radicals. The method is extremely simple experimentally and does not require large amounts of starting materials.

Several reviews devoted to studies on a wide range of different radicals by this method were published in 1970–71.[7,8,14]. However, during this initial period of the development of the method, studies were performed mainly on model reactions, i.e. those where known radicals were generated, and the possibility of their detection by particular trapping agents and the relation between the EPR parameters and the structure of the "trapped" radical were investigated, new trapping agents were proposed, etc. The results served as the basis for the

†The following nomenclature is used to designate the positions in nitroxy-radicals[9]:



(the RR'NO$^{\cdot}$ radicals are referred to in the literature as "nitroxide" and "nitroxy-radicals"[10]. Rozantsev[11,12] argues convincingly that the term "nitroxy-radical" is more justified and this is the term which we shall use in the present review).

‡The method became rapidly popular and, as early as 1971, a paper was published[13] warning investigators against being unduly attracted by this procedure and indicating the limits of its applicability.

employment of the spin-trapping method for the investigation of certain fairly complex radical processes.

Many new investigations devoted to both the development of the method and to its employment in the study of radicals and mechanisms of radical reactions, have now accumulated in the literature. In this review we shall deal mainly with the application of the spin-trapping method to the study of chlorine- and sulphur-containing radicals and the reactions involving them.

II. GENERAL PROBLEMS OF THE SPIN-TRAPPING METHOD

The nitroxy-radicals formed as a result of the addition of short-lived radicals to the trapping agent are characterised primarily by a triplet signal in the EPR spectrum due to the interaction of the unpaired electron with the ^{14}N nucleus. The g-factors for different nitroxy-radicals are very similar [7], but, depending on the substituents at the nitrogen atom, the hyperfine interaction constant a_N for different nitroxy-radicals varies within fairly broad limits—from 4–5 G for diacylnitroxy-radicals [15] to 25 to 28 G for alkoxyalkylnitroxy-radicals [16]. Even the values of a_N for different spin-adducts can therefore yield, to a first approximation, information about the nature of the short-lived radical detected by the trapping-agent. Furthermore, if nuclei with non-zero spins are present in the α- and β-positions relative to the nitroxy-group, then the EPR spectrum shows an additional splitting of the lines of the main triplet. Thus the hyperfine structure (HFS) of the spectrum and the hyperfine interaction (HFI) constants provide in this case additional and very important information for the identification of the "trapped" radical. Lines for hyperfine interaction with more remote nuclei are resolved only in exceptional individual instances; as a rule, hyperfine interactions are manifested only by a smaller or greater broadening of the lines of the main triplet.

It is noteworthy that the spin-trapping method is very convenient and effective for demonstrating the radical mechanism of a particular reaction and for the qualitative identification of the radicals formed. The method has been used recently also to investigate reactions proceeding via a one-electron transfer mechanism (see, for example, Refs. 17–19). As regards the determination of quantitative data, for example, the relative concentration of the radicals formed, then in the general case this cannot be done on the basis of a comparison of the integrated intensities of the spectra of their spin–adducts. This is because not all the radicals are trapped to an equal extent and not all the spin-adducts are equally stable. Quantitative estimates therefore require the knowledge of the relative rates of reaction with the given trapping agent of the radicals being compared and of the rates of the subsequent transformations of the nitroxy-radicals formed. It is therefore of interest to note the studies published recently on the quantitative determination by the spin-trapping method of the yields of radicals formed in the radiolysis of methanol under various conditions [20,21].

1. Spin-Trapping Agents

The range of compounds used as spin-trapping agents is now fairly wide. As already mentioned, nitroso-compounds and nitrones are mainly used for this purpose.

a) Nitroso-compounds. Tertiary or aromatic nitroso-compounds are as a rule used as trapping agents, so that the EPR spectrum of the spin-adduct formed is not complicated by the hyperfine interaction with the β-hydrogen atoms of the nitroso-compound. Among non-aromatic nitroso-compounds, 2-methyl-2-nitrosopropane (nitroso-t-butane, MNP) and its deuterated analogue [14], as well as 2-methyl-2-nitroso-3-butanone (MNB) [7] are most frequently used. 2-Nitroso-2-trifluoromethylhexafluoropropane [22] and trisethoxycarbonylnitrosomethane [23] have been proposed recently. A number of workers put forward a very interesting combination in a single compound of sources of the spin-trapping agent and of the radicals [24-29]. They showed that, when aryl-N-hydroxytriazenes are oxidised by lead dioxide, aryl radicals and a nitroso-compound, capable of behaving as a spin-trapping agent, are formed simultaneously:

$$\mathrm{Ar{-}N{=}N{-}\underset{\displaystyle OH}{\underset{|}{N}}{-}R \xrightarrow{PbO_2} Ar^{\cdot} + N_2 + R{-}N{=}O} \quad . \qquad (2)$$

The advantages and disadvantages of the above trapping agents are widely discussed in the literature; MNP is the most universal agent. It will be clear from subsequent exposition (see Sections III–V) that the majority of radicals react with MNP to form fairly stable and readily identifiable spin-adducts. However, this compound suffers also from many disadvantages. Firstly, it is dimeric in the solid state, and is converted into the active monomeric form in solution to only a slight extent; complete transformation into the monomeric form is achieved under the influence of radiation [30]. Secondly, when acted upon by lead dioxide or ultraviolet light, or on heating [8], MNP may decompose·

$$\begin{gathered}(CH_3)_3C{-}N{=}O \rightarrow (CH_3)_3\dot{C} + NO,\\ (CH_3)_3\dot{C} + (CH_3)_3C{-}N{=}O \rightarrow [(CH_3)_3C]_2N{-}\dot{O},\end{gathered} \qquad (3)$$

and the resulting t-butyl radicals may add to the initial molecule to form a nitroxy-radical, the spectrum of which consists of a triplet with a_N = 15–17 G (depending on the solvent used) [16]. This triplet is frequently so intense that it may overlap the lines corresponding to the other spin-adducts formed§. In addition, when MNP is used, the reaction mixture often has to be freed from oxygen to avoid the formation of certain secondary radicals [32].

MNB is also present as an inactive dimer, which partly dissociates in solution to the monomer [7]. Ultraviolet irradiation promotes such dissociation, causing at the same time the fragmentation of the nitroso-compound into radicals:

$$\mathrm{(CH_3)_2C{-}CO{-}CH_3}\begin{cases}\rightarrow (CH_3)_2\dot{C}{-}CO{-}CH_3 + NO\\ \rightarrow (CH_3)_2\dot{C}{-}NO + CH_3{-}\dot{C}O\end{cases} \quad , \qquad (4)$$

These add to the initial molecule to form the spin-adducts

$$[(CH_3)_2(COCH_3)C]_2N{-}\dot{O} \text{ and } (CH_3)_2(COCH_3)C{-}\underset{\displaystyle \dot{O}}{\underset{|}{N}}{-}CO{-}CH_3$$

characterised in the ESR spectrum by triplets with a_N = 14 to 15 G [16] and 7–8 G [7] respectively.

A distinctive feature of this trapping agent is that radicals containing chlorine atoms at the radical centre cannot be detected with its aid [33]. This limits its applicability, on

§Since the main absorption band of MNP is in the region of 680 nm, its fragmentation may be avoided by using shorter-wavelength radiation [31].

the one hand, and constitutes a significant advantage in the selective detection of various radicals in complex homolytic reactions, on the other (see Section V).

2-Nitroso-2-trifluoromethylhexafluoropropane (nitroso-perfluoro-t-butane, NFB) is an extremely convenient trapping agent for chlorine-containing radicals. For example, its spin-adduct with $Cl_3C^{\cdot}$ has an EPR spectrum which can be more readily interpreted than that of the corresponding MNP adduct (see Section III). A disadvantage of NFB is, as for the other nitroso-compounds mentioned above, its decomposition under the influence of radiation. The nitroxy-radical formed as a result of a secondary reaction,

$$(CF_3)_3C{-}N{=}O \rightarrow [(CF_3)_3\dot{C} + NO \quad ,$$

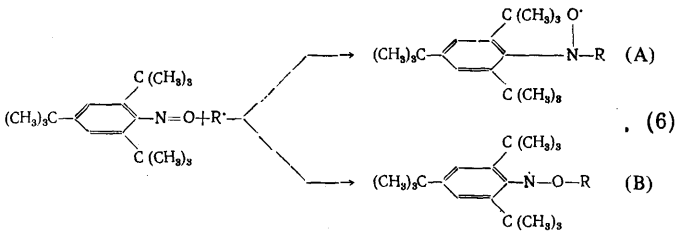
$$(CF_3)_3\dot{C} + (CF_3)_3C{-}NO \rightarrow [(CF_3)_3C]_2N{-}\dot{O} \quad , \qquad (5)$$

gives rise to a triplet with a_N = 11.9 G in the spectrum, with very appreciably broadened (~6 G) lines owing to hyperfine interaction with γ-fluorine atoms [34].

The application of trisethoxycarbonylnitrosomethane is so far restricted to isolated examples only [23]. It is apparently convenient for the detection of alkyl radicals. There are as yet no literature data for investigations of chlorine- and sulphur-containing radicals with its aid.

Among aromatic nitroso-compounds, only nitrosobenzene was used in the early stages [8]. However, although this trapping is fairly universal, it suffers from a significant disadvantage: the EPR spectrum of the corresponding spin-adducts consists of many components owing to hyperfine interaction with the *o*- and *p*-hydrogen atoms in the benzene ring (the splitting by the *m*-hydrogen atoms is as a rule insignificant—less than 1 G). This hinders to a large extent the identification of the "trapped" radical.

Nitrosodurene [35] and 2,4,6-tri-(t-butyl)nitrosobenzene, proposed subsequently [36,37], are much more convenient in this respect. The latter trapping agent is of interest also because, depending on the nature of the radical combining with it, different spin-adducts are formed:



. (6)

Primary alkyl radicals as well as phenyl and phenylthio-radicals give rise to the nitroxy-radical A, while tertiary radicals form the anilino-radical B; secondary radicals form a mixture of the two products. The spin adducts A and B can be readily distinguished on the basis of their ESR spectra (the *g*-factors for A and B are respectively 2.006–2.007 and 2.0035–2.0040). [36]

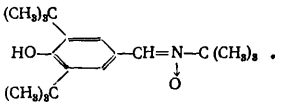
An advantage of this trapping agent is that it is monomeric also in the solid state and, furthermore, even if it does decompose under the influence of ultraviolet radiation [38], it never gives any additional EPR signals under these conditions. It is apparently unsuitable for the identification of radicals of the type $\dot{C}Cl_3$ and $\dot{C}HCl_2$. [36]

(b) Nitrones. Among nitrones, *N*-t-butyl α-phenyl nitrone (BPN) is most frequently used as a spin-trapping agent [8].

$$C_6H_5{-}CH{=}N{-}C(CH_3)_3 \quad .$$
$$\qquad\qquad\qquad\quad \downarrow$$
$$\qquad\qquad\qquad\quad \dot{O}$$

In addition, the use of *N*-t-butyl nitrone [39], α-*N*-diphenyl nitrone [40] and cyclic nitrones [8,41] has been described. The advantages and disadvantages of nitrones have been analysed in detail in a review [8]. We shall mention only that, in contrast to nitroso-compounds, nitrones make it possible to detect chlorine (see Section III) and hydrogen atoms [8,20]. However, they suffer from the important disadvantage that the spectrum of the spin-adducts formed as a result of the addition of short-lived radicals (see Scheme 1, b) has a hyperfine structure due solely to the splitting of the lines by the interaction with the nitrogen and β-hydrogen atom (a triplet of doublets). For the majority of spin-adducts, a_N and $a_{H\text{-}\beta}$ depend little on the structure of the trapped radical. An unambiguous identification of the radicals is therefore often possible only on the basis of the comparison of the resulting EPR spectrum with that of the corresponding spin-adduct, obtained by a standard procedure [8]¶.

A very interesting "bifunctional" trapping agent has been proposed [42]:



Alkyl and aryl radicals add to it with formation of nitroxy-radicals, while alkoxy-radicals abstract the hydroxyl-hydrogen, giving rise to a stable phenoxy-radical.

(c) Other trapping agents. Aromatic nitrile oxides, forming very stable spin-adducts (iminoxy-radicals) with short-lived radicals

$$Ar{-}C{\equiv}N{\rightarrow}O + R^{\cdot} \rightarrow \begin{matrix} Ar \\ \diagdown \\ \quad C{=}N{-}\dot{O} \\ \diagup \\ R \end{matrix} \quad , \qquad (7)$$

are extremely convenient trapping agents for hydrocarbon radicals [43]. However, they are relatively unsuitable for chlorine-containing radicals, because of an unduly low value of a_{Cl} (for example, a_{Cl} = 0.5 G for $Ar{-}\underset{\displaystyle CCl_3}{\underset{|}{C}}{=}N{-}\dot{O}$).

The above data permit the conclusion that complex radical reactions should evidently be investigated with the aid of various trapping agents, taking into account their advantages and disadvantages, selectivity, etc, and not just a single trapping agent.

2. Experimental Conditions

Most of the reactions described in the literature were investigated directly in the resonator of the EPR spectrometer. A small amount of the trapping compound is usually added to the experimental reaction mixture and the sealed tubes containing the solution are placed in the resonator where they are irradiated, heated, or cooled (depending on the conditions required for the reaction). As a rule, the reaction mixture is not freed from oxygen. However, it has been shown (see, for example, Zubarev et al. [20]), that the presence of oxygen reduces the intensity of the spectral

¶ The use of N-t-butyl α-(2,4,6-trimethoxyphenyl) nitrone, the spin-adducts of which are characterised by a much greater sensitivity of $a_{H\text{-}\beta}$ to the nature of the trapped radical than for the spin-adducts of other nitrones, has been described recently [89].

signals and broadens individual lines. When necessary, oxygen is removed by evacuation or by passing a stream of an inert gas through the reaction mixture in the course of 10–15 min. Depending on the polarity of the reaction mixture, cylindrical or planar tubes are used[36].

The concentration of the trapping compound is as a rule 0.001–0.05 M for nitroso-compounds and 0.05–0.06 M for nirtones. Evidently the above concentrations are extremely approximate, since the choice of the concentration of the trapping agent for each given chemical reaction depends on a number of factors. Indeed, in the general case, apart from interaction with the molecules of the trapping agent, the test radicals are involved in other competing reactions with the molecules of the medium M:

$$\text{Initiator} \rightarrow R_1^{\cdot} \quad , \tag{8}$$

$$R_1^{\cdot} + M \xrightarrow{k_1} R_2^{\cdot} \quad , \tag{9}$$

$$R_1^{\cdot} + RNO \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} R_1RN{-}\dot{O} \quad , \tag{10}$$

$$R_2^{\cdot} + RNO \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} R_2RN{-}\dot{O} \quad . \tag{11}$$

The formation of spin-adducts at an adequate concentration requires that the conditions $k_2 \gg k_{-2}$ and $k_2 \gg k_{-3}$ be fulfilled. It follows even from this simple scheme that the ratio of the concentrations of the nitroxy-radicals $R_1RN\dot{O}$ and $R_2RN\dot{O}$ in solution in the steady state depends on the concentration of the trapping agent, the substance M, and the rate constants k_1 and k_2. Thus, without knowing the constants (the constants k_2 are known only in a few instances[44-46]), it is impossible to determine beforehand the required concentration of the trapping compound.

(a) Solvents. The choice of solvent has been discussed in detail[7]. The most convenient solvent above 5°C is apparently benzene, since, in contrast to many other solvents employed, it does not form radicals under the experimental conditions†. Methylene chloride is frequently used at low temperatures[7], but one should note that, following ultraviolet irradiation in the presence of MNP, signals due to the nitroxy-radical $H{-}CO{-}\underset{\dot{O}}{N}{-}C(CH_3)_3$ formed via a side reaction, consisting of a triplet of doublets with $a_N = 7.0$ and $a_H = 1.41$ G are usually observed in this case[47].

(b) Temperature. The reactions are as a rule carried out at room temperature, but the stability of many nitroxy-radicals depends significantly on temperature. Furthermore, as already mentioned, the reaction may lead to different radicals, depending on temperature. Therefore, in the study of radical processes by the spin-trapping method, the temperature plays an extremely important role (see Section V). It is noteworthy that the parameters of the EPR spectra of nitroxy-radicals are almost independent of temperature.

(c) Methods of generating radicals. This problem has been discussed in fair detail in a number of studies[7,8,14,48]. Here it is of interest to note certain differences between the photochemical methods for the generation of radicals which are investigated directly and radicals identified in the form of their spin-adducts. Owing to the very short lifetime of the radicals, ultrahigh-pressure 1–2 kW mercury lamps are used to obtain them in sufficient concentrations when a flow method[2] is used and in low-temperature experiments[4]. In the study of radicals by the spin-trapping method it is sufficient to employ 100–150 W mercury lamps. It is desirable that the arrangement for ultraviolet irradiation should include appropriate filters, gratings, and diaphragms for regulating the wavelength and intensity of the incident light. Since certain nitroxy-radicals are fairly stable above room temperature, many of them can be obtained by thermal as well as photochemical methods[47].

Numerous chlorine-containing radicals have been obtained by abstracting hydrogen from the correspoding chloroalkanes by the phenyl radicals formed in the oxidation of hydroxytriazenes (Scheme 2).[28] Thiyl radicals are as a rule generated by ultraviolet and γ-irradiation of the corresponding disulphides and thiols. In addition, they can be generated by abstracting hydrogen from thiols by various radicals obtained thermally or photochemically. Sulphonyl radicals are obtained from the corresponding sulphonyl halide as a result of the abstraction of the halogen by triethylsilyl radicals or photochemically (see Section IV).

III. EPR SPECTRA OF NITROXY-RADICALS—SPIN-ADDUCTS OF CHLORINE-CONTAINING RADICALS

Chlorine-containing nitroxy-radicals with one, two, and three chlorine atoms in the β-position, i.e. $R_nCCl_{3-n}N(\dot{O})-R'$, are in many cases sufficiently stable to be investigated by EPR under steady-state conditions. This applies particularly to spin-adducts of chlorine-containing radicals with MNP and its perdeutero- and perfluoro-derivatives as well as nitrosodurene.

The hyperfine structure of the spectra of chlorine-containing nitroxy-radicals is extremely complex. This is caused, firstly, by the fact that the chlorine nucleus has a spin of 3/2, which leads to $2n \times 3/2 + 1$ (n is the number of equivalent β-chlorine atoms) lines in the spectrum and, secondly, it arises because the two chlorine isotopes present in natural chlorine in fairly large amounts (75.53% of ^{35}Cl and 24.47% of ^{37}Cl) have different magnetic moments, (0.821 and 0.683 μ_B respectively) which leads to an increase of the multiplicity of the spectral lines as a result of the interaction of the unpaired electron with these nuclei.

This Section describes studies carried out on model examples of known chlorine-containing radicals in order to develop further the spin trapping method as well as studies in which the method has been used to investigate complex chemical processes involving the intermediate formation of short-lived chlorine-containing radicals.

Chlorine-containing radicals can be arbitrarily divided into three groups: (1) chlorine atoms; (2) mono- and poly-chloromethyl radicals; (3) higher chlorine-containing radicals.

1. Chlorine

The spin-adducts of chlorine of the type $Cl{-}N(\dot{O}){-}R$ are unknown. The attempt to add chlorine to MNP [8] has been unsuccessful, which indicated, according to the

†Certain aryl radicals can add to benzene with formation of the corresponding substituted cyclohexadienyl radicals, which are then detected by the trapping agent[90,91].

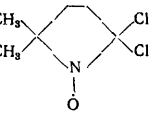
author [8], the instability of the expected spin-adduct. The preparation of the nitroxy-radicals $R^1R^2CCl-N(\dot{O})R$, formed both by the interaction of chlorine donors with nitrones [8,49-52] and by the addition of the radical $R^1R^2\dot{C}Cl$ to nitroso-compounds, has been described. The first method of obtaining β-chloronitroxy-radicals is discussed below.

The interaction of chlorine with α-phenyl-t-butyl-nitrone (PBN) in benzene at room temperature leads to the benzoyl-t-butylnitroxy-radical and not to the spin-adduct—t-butyl-α-chlorobenzylnitroxy-radical [53]:

$$C_6H_5-CH=N-C(CH_3)_3 + Cl_2 \rightarrow \begin{cases} C_6H_5-CHCl-N(\dot{O})-C(CH_3)_3 \\ C_6H_5-\overset{\overset{O}{\|}}{C}-N(\dot{O})-C(CH_3)_3 \end{cases} \quad (12)$$

The same nitroxy-radical is formed in the reaction of PN with nitrosyl chloride [53], *N*-chlorosuccinimide [39], and poly-nitro-compounds [54].

Table 1. Parameters of the EPR spectra of R-N(Ȯ)-R′ nitroxy-radicals (chlorine spin-adduct).

No.	Trapping agent	R	R′	a_N, G	a_{Cl}, G	a_H, G	Method of synthesis of nitroxy-radicals	Temp. °C	Solvent	References
1	BPN	C_6H_5CHCl	$C(CH_3)_3$	12.1	6.05; 4.88*	0.75	BPN + $(CH_3)_3COCl$	35	C_6H_6	8,49
2	BPN	C_6H_5CHCl	$C(CH_3)_3$	12.1	6.0; 4.9*	0.8	BPN + SO_2Cl_2 + $h\nu$	20	C_6H_6	51
3	BPN	$C_6H_5CCl_2$	$C(CH_3)_3$	13.2	3.3	—	BPN + $(CH_3)_3COCl$	35	CCl_4	49
4	DMPO			10.67	3.57	—	DMPO + Cl_2 or DMPO + $(CH_3)_3COCl$	—	C_6H_6	50

*The values of a_{Cl} for ^{35}Cl and ^{37}Cl respectively.



Figure 1. The EPR spectrum of the t-butyl-α-chlorobenzylnitroxy-radical in benzene [49].

Subsequently it was possible to obtain t-butyl-α-chlorobenzylnitroxy-radicals by the interaction of PBN with t-butyl hypochlorite in the absence of oxygen [49] (Table 1, No. 1). The resulting EPR spectrum is illustrated in Fig. 1. The doublet with a small splitting (a_H = 0.75 G) refers to the β-hydrogen atom. The overlapping quartets result from the hyperfine interaction with the ^{35}Cl and ^{37}Cl nuclei. It is clear from the spectrum that the larger splitting constant corresponds to $a_{^{35}Cl}$ = 6.05 G and the smaller constant corresponds to $a_{^{37}Cl}$ = 4.88 G.

The same spectrum has been obtained following the interaction of PBN with trichlorosilane and chlorotrimethylsilane [49]. The authors suggest that in this case the reaction proceeds with the intermediate formation of t-butyl hypochlorite. The mechanism of the formation of monochloronitroxy-radicals has not been investigated by this procedure [49]. t-Butyl-monochlorobenzylnitroxy-radicals have been obtained also in the photolysis of sulphuryl chloride in the presence of PBN [51,52] (Table 1, No. 2). The authors believe that in this case a chlorine atom adds to PBN.

On the basis of the EPR spectrum in CCl_4 of the product obtained by treating PBN with t-butyl hypochlorite in a gaseous phase [49] (Table 1, No. 3), the authors attributed the structure $C_6H_5CCl_2-N(\dot{O})C(CH_3)_3$ to the nitroxy-radical obtained.

The EPR spectra of the spin-adducts of various radicals with the cyclic nitrone 5,5-dimethyl-1-pyrrolin-1-oxyl (DMPO) have been obtained [50]. According to the results, chlorine as well as t-butyl hypochlorite react with DMPO to form a dichloro-derivative (Table 1, No. 4).

It is seen from the foregoing that at least some of the nitroxy-radicals investigated are products of more complex processes than the direct addition of chlorine to the trapping agent. This is particularly clear from the last two examples, since substitution of β-hydrogen by chlorine also occurs in these reactions.

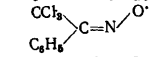
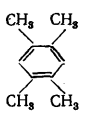
2. Mono- and Poly-Chloromethyl Radicals

(a) The trichloromethyl radical. The trichloromethyl radical has been widely investigated because of its considerable role in synthetic organic chemistry [55-57] and because it is readily obtained when CCl_4, $CHCl_3$, and CCl_3Br are acted upon by radical-forming agents as well as in the photolysis of CCl_3Br.

The study of the spin-adducts of the radicals $\dot{C}Cl_3$ with nitroso-compounds initially involved many difficulties. When $\dot{C}Cl_3$ radicals are generated by the irradiation of $CHCl_3$ or CCl_4 with ultraviolet light in the presence of benzoyl peroxide and various nitroso-compounds, the more stable chlorocarbonyl nitroxy-radicals Cl-CO-N(O)-R are formed together with the trichloromethylnitroxy-radicals $\dot{C}Cl_3-N(O)-R$, which led to confusion in the determination of the parameters of the spectra of trichloromethylnitroxy-radicals (for a more detailed discussion, see below). On the other hand, the first correctly identified nitroxy-radical of this type, namely $(CCl_3)_2N\dot{O}$, was detected [58] in the synthesis of trichloronitrosomethane and not in a mixture known to contain $\dot{C}Cl_3$ radicals [58]. The constants a_N = 11.8 G and a_{Cl} = 1.25 G were determined in this investigation [58] which constituted the first example of the determination of the hyperfine coupling constants for β-chlorine atoms in nitroxy-radicals (Table 2, No. 1). These data were subsequently confirmed [48].

The spectrum of the nitroxy-radical $CCl_3-N(\dot{O})-C(CH_3)_3$ was described for the first time by Leaver et al. [31] It was characterised by the following parameters: a_N = 12.73; a_{Cl} = 2.41 G; g = 2.0065 (Table 2, No. 5). This spectrum was obtained on irradiation ($\lambda \simeq 300$ nm) of a solution of indole or its methyl derivatives in solution in CCl_4 containing MNP. The same workers stated [59] that this spectrum can be obtained by abstracting hydrogen from $CHCl_3$ in the presence of MNP. When a spectrum with a resolved hyperfine structure, due to the interaction with the four

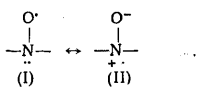
Table 2. Parameters of the EPR spectra of R–N(O·)–R′ nitroxy-radicals (spin-adducts of mono- and poly-chloromethyl radicals).

No.	Trapping agent	R	R′	a_N, G	a_{Cl}, G	Method of generation of radicals	Temp., °C	Solvent	Refs.
1	CCl_3NO	CCl_3	CCl_3	11.8	1.25	decomposition of CCl_3NO	room	—	48, 58
2	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.5	2.2	$CHCl_3$ + TBP ***** + $h\nu$	—	—	61
3	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.4	2.3	CCl_3Br + $h\nu$	35	—	49
4*	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.73	2.41	CCl_4 + indole + $h\nu$	—	CCl_4	31, 62
5	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.2	2.2	CCl_4 + $(C_2H_5)_3SiH$ + TBP	—	CCl_4	66
		CCl_3	$C(CH_3)_3$	12.2	2.2	$CHCl_3$ + TBP + $h\nu$	—	$CHCl_3$	66
6	$(CH_3)_3CNO$	CCl_3	$C(CH_3)_3$	12.9	2.2	$CHCl_3$ + C_6H_5—N=N—N(OH)—$C(CH_3)_3$ + + PbO_2	room	$CHCl_3$	28
7	$(CD_3)_3CNO$	CCl_3	$C(CD_3)_3$	12.5	2.2	$CHCl_3$ + TBP + $h\nu$	30	$CHCl_3$	47
8	$(CF_3)_3CNO$	CCl_3	$C(CF_3)_3$	13.1	1.5	CCl_4 + $(C_2H_5)_3SiH$ + TBP or $CHCl_3$ + $h\nu$	—	CCl_4, $CHCl_3$	22
9**	C_6H_5–C≡N→O			32.7	0.5	$CHCl_3$ + TBP + $h\nu$	room	$CHCl_3$	43
10	Nitroso-durene	CCl_3		10.73	1.31	CCl_4 + $[(C_6H_5)_3Sn]_2$ + $h\nu$	room	CCl_4	35
						$CHCl_3$ + TBP + $h\nu$	room	$CHCl_3$	35
11	$(CH_3)_3CNO$	$CHCl_2$	$C(CH_3)_3$	12.2	3.27; 2.7******	CH_2Cl_2 + C_6H_5N=N—N(OH)—$C(CH_3)$ + + PbO_2	room	CH_2Cl_2	28
12	$(CD_3)_3CNO$	$CHCl_2$	$C(CD_3)_3$	11.7	4.8; 4.05******	CH_2Cl_2 + di-t-butyl peroxydioxalate	30	CH_2Cl_2	47
13***	$(CF_3)_3CNO$	$CHCl_2$	$(CF_3)_3C$	14.0	1.6	CH_2Cl_2 + TBP + $h\nu$	25	CH_2Cl_2	22, 66
14****	$(CH_3)_3CNO$	CH_2Cl	$C(CH_3)_3$	11.9	8.35; 6.90******	CH_2ClI + C_6H_5N=N—N(OH)—$C(CH_3)_3$ + + PbO_2	room	CH_2ClI	28

*g = 2.0065.
**g = 2.0048.
***a_H < 0.1 G.
****a_H = 3.55 G.
*****t-butyl peroxide.
******the values of a_{Cl} for ^{35}Cl and ^{37}Cl respectively.

possible combinations of the nuclei of chlorine isotopes in the CCl_3 group, is obtained, each line of the main triplet of the ^{14}N signal should be split into 72 lines, of which only 10 were observed. The authors calculated the spectrum by an iterative procedure using the method of least squares; they took into account only the two most important isotope combinations: $^{35}Cl_3$ and $^{35}Cl_2{}^{37}Cl$. The best agreement with the experimental spectrum was obtained for $a_{^{35}Cl}$ = 2.46 G and $a_{^{37}Cl}$ = 2.05 G. Subsequently, the formation of the spin-adducts of the trichloromethyl radical with MNP was noted repeatedly (Table 2, Nos. 2–6).

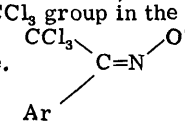
It has been noted[49] that a_{Cl} for the bistrichloromethyl-nitroxy-radical is appreciably less than for the t-butyl-trichloromethylnitroxy-radical (1.25 and 2.3 G respectively). The authors point out that this may be associated with the lower spin density at the nitrogen atom in the bis-trichloromethylnitroxy-radical. The more pronounced electron-accepting properties of the CCl_3 group compared with the $(CH_3)_3C$ group favour structure (I) rather than structure (II):



(see also Refs. 14 and 60). The constants a_N differ less than the constant a_{Cl}. The authors[49] also do not rule out the possibility that the small difference between the planarities of the nitroxy-group, caused by the differences between the steric interactions in the above radicals, may likewise give rise to differences between the hyperfine coupling constants a_N and a_{Cl}.

The splitting of the ^{14}N signal due to the commonest combinations of chlorine isotopes (present in the mixture) in the CCl_3 group, i.e. $^{35}Cl_3$ and $^{35}Cl_2{}^{37}Cl$, was achieved for the first time by Perkins et al.[61] The EPR spectrum obtained when $CHCl_3$ was acted upon by TBP in the presence of MNP (Table 2, No. 2) consisted of three ten-component groups of lines, which partly overlapped (Fig. 2). It is seen from the insert in the figure that the extreme line is split into two components, which can be accounted for by the presence of different chlorine isotope combinations.

It has been shown[28] that the oxidation of 3-t-butoxy-1-phenyltriazene by lead dioxide (Scheme 2) in chloroalkanes leads to the formation of chlorine-containing radicals, which interact with the MNP formed simultaneously. The EPR spectrum then shows signals due to the corresponding spin-adducts. In particular, when the reaction was carried out in $CHCl_3$ or CCl_4, the product was the nitroxy-radical CCl_3–N(O·)–$C(CH_3)_3$, whose spectrum was identical with that described by Perkins et al.[61] (Table 2, No. 6).

When a solution of TBP in chloroform containing benzonitrile *N*-oxide or *p*-chlorobenzonitrile *N*-oxide as the spin-trapping agent was irradiated with ultraviolet light (see Scheme 7), a spectrum with a_N = 32.7 G, a_{Cl} = 0.5 G, and g = 2.0048, corresponding to an iminoxy-radical with the CCl_3 group in the *syn*-position relative to the N–O bond, i.e. , was obtained (Table 2,

No. 9).[43] The formation of an iminoxy-radical by the oxidation of chloroaldoxime has also been described[62].

The values of a_N for the spectrum obtained in the detection of the trichloromethyl radical with the aid of 2-nitroso-2-trifluoromethylhexafluoropropane are greater and those of a_{Cl} are smaller (Table 2, No. 8) than for the corresponding spin-adduct obtained when the $CCl_3^{\cdot}$ radical adds to MNP; the spectrum of the spin-adduct with the fluorinated trapping agent is therefore better resolved (Fig. 3)[22].

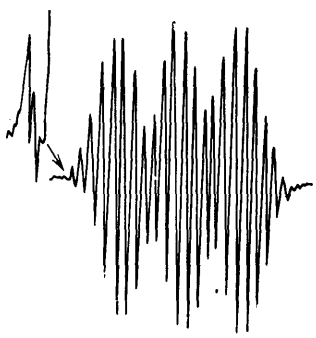


Figure 2. The EPR spectrum of the $CCl_3-N(\dot{O})-C(CH_3)_3$ radical. The insert on the left represents the splitting of the extreme line due to the presence of $^{35}Cl_3$ and $^{35}Cl_2{}^{37}Cl$.[61]

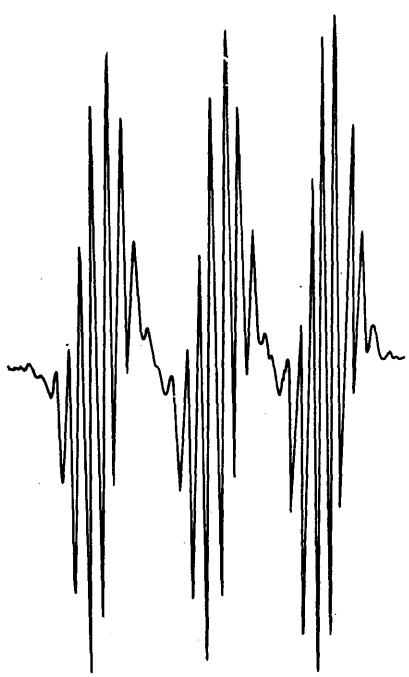


Figure 3. The EPR spectrum of $(CF_3)_3C-N(\dot{O})-CCl_3$.[66]

The trichloromethyl radical has also been detected with the aid of nitrosodurene when a solution of TBP in chloroform was irradiated and also when chlorine was abstracted from CCl_4 by triethylsilyl radicals[35] (Table 2, No. 10).

(b) The $Hal-CO-N(\dot{O})-R$ nitroxy-radicals. Nitroxy-radicals of the type

$$\begin{array}{l} Hal-C-N(\dot{O})R \\ \quad\quad\| \\ \quad\quad O \end{array}$$
(III)

are some of the most important radicals of this kind, obtained by a side reaction during the formation of the spin-adducts of the trichloromethyl radical with nitroso-compounds. Ultraviolet irradiation of solutions of benzoyl peroxide (BP) in CCl_4 or $CHCl_3$ as well as the photolysis of CCl_3Br in benzene in the presence of nitroso-compounds lead to the formation, together with other nitroxy-radicals, of radicals whose EPR spectrum is a triplet with $a_N = 6.5$ G and $g = 2.0070$.[63] These spectra were initially assigned to the spin-adducts of the $CCl_3^{\cdot}$ radical with nitroso-compounds[63]. The assignment was found to be erroneous when spectra of the nitroxy-radicals

$$CCl_3-N(\dot{O})-R$$
(IV)

were obtained in a number of studies with quite different hyperfine structures and hyperfine coupling constants (Table 2).

In one of the early investigations Chalfont[64] observed the formation of two long-lived radicals in the photolysis of CCl_3Br in the presence of MNP. One of these radicals was identified as the nitroxy-radical (IV), where $R = C(CH_3)_3$. It was erroneously assumed that the other radical, having $a_N = 6.65$ G, may be the bromine-containing nitroxy-radical $Br-N(\dot{O})-C(CH_3)_3$. This hypothesis was disproved when irradiation of CBr_4 in benzene in the presence of MNP led to a nitroxy-radical whose EPR spectrum had a similar constant $a_N = 6.5$ G, but contained a well resolved quartet with $a_{Br} = 2.1$ G.[47] On the basis of the results of Mackor et al.[30], Torssell[48] was the first to point out that the nitroxy-radicals with such a low constant a_N (6.5–6.7 G) probably have the structure of acylalkylnitroxy-radicals.

Subsequently Hartgerink et al.[63] reinvestigated the photolysis of CCl_4 and concluded[65] that the spectra under consideration (with $a_N = 6.5$ G and $g = 2.0070$) are due to the chlorocarbonylnitroxy-radicals (III). A well resolved splitting of the signal due to the β-chlorine in species of type (III) could never be detected.

The photolysis of CBr_4 in the presence of MNP leads to the formation of the bromocarbonylnitroxy-radical $Br-CO-N(\dot{O})-C(CH_3)_3$ with $a_N = 6.7$ G, $a_{Br} = 2.0$ G, and $g = 2.0071$.[65] These data were subsequently confirmed in yet another study[47]. The results quoted[47] for the photolysis of CCl_3Br show that the corresponding nitroxy-radicals (III) are undoubtedly formed in the presence of MNP or its perdeutero-derivative. Although the authors[47] assign the EPR spectrum (with $a_N = 6.65$ G and $a_{Hal} = 0.5$ G), obtained in the photolysis of CCl_3Br in the presence of a deuterated trapping agent, to the chlorine-containing radical nitroxy-radical (III) with Hal = Cl and $R = C(CD_3)_3$, adequate data for this assignment are not available and one cannot rule out the possibility of forming the bromocarbonylnitroxy-radical (III), with Hal = Br, or a mixture of two halogenocarbonylnitroxy-radicals. In particular, the above assignment conflicts with the observation[47] that the lines of the main ^{14}N triplet in the EPR spectrum of the nitroxy-radical obtained by the photolysis of CCl_3Br in the presence of MNP (Fig. 4) show a quartet splitting, which, although poorly resolved, is nevertheless sufficient to

calculate a_{Hal}. On the basis of the spectrum obtained following the irradiation of bromotrichloromethane in the presence of MNP, Gasanov et al.[66] also determined the constants a_N = 6.7 G and a_{Br} = 2.2 G.



Figure 4. The EPR spectrum of the nitroxy-radical obtained on ultraviolet irradiation of CCl_3Br in the presence of MNP.[47]

This difference between the parameters of the spectra obtained on irradiation of CCl_4 and CCl_3Br may be attributed to the fact that in the latter case the Cl–CO–N(Ȯ)–$C(CH_3)_3$ spectrum is overlapped by another spectrum with similar parameters, but with a better resolution of the splitting in the quartet. It apparently corresponds to the nitroxy-radical Br–CO–N(Ȯ)–$C(CH_3)_3$.

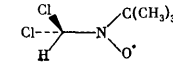
All the halogenocarbonylnitroxy-radicals obtained in the photolysis of bromotrichloromethane in the presence of trapping agents are therefore designated in Table 3 as Hal–CO–N(Ȯ)–R. The photolysis of CCl_4 or CCl_3Br in the presence of secondary nitroso-compounds (Table 3, Nos. 7–10) leads to the formation of the nitroxy-radicals Cl–CO–N(Ȯ)–CHR_2 whose spectrum shows splitting due to the β-hydrogen (a_H = 2.7–2.8 G).[63]

It has been suggested[47,65] that the nitroxy-radicals (III) are products of secondary reactions of the spin-adduct (IV) formed initially. The following evidence is quoted in support of this hypothesis: the gradual appearance of signals due to species (III) as the signals due to the adduct (IV) disappear, the high intensity of the signals in the spectra of (III), and the failure of the attempt to obtain (III) by the addition of the ClĊO radical (generated by the photolysis of phosgene or dibromocarbonyl in the presence of benzoyl peroxide) to MNP. Several possible versions of the mechanism of the above reaction are discussed in the studies indicated, but there has been no experimental confirmation of any of the suggested mechanisms.

(c) The $\dot{C}HCl_2$ and $\dot{C}H_2Cl$ radicals. The preparation of the spin-adducts of MNP with the $\dot{C}HCl_2$ and $\dot{C}H_2Cl$ radicals in the oxidation of 3-t-butyl-3-hydroxy-1-phenyltriazene by lead dioxide in CH_2Cl_2 and CH_2ClI respectively has been described[28] (Table 2, Nos. 11 and 14). In the first instance a multicomponent spectrum was obtained, whose analysis showed that the unpaired electron in the above spin-adduct interacts with the ^{14}N nucleus and the two equivalent chlorine nuclei. The spectrum contains lines which the authors assigned to the isotopic forms (V) and (VI):

$$\underset{\text{(V)}}{H^{35}Cl_2C{-}N(\dot{O}){-}C(CH_3)_3};\quad \underset{\text{(VI)}}{H^{35}Cl^{37}ClC{-}N(\dot{O}){-}C(CH_3)_3}\ .$$

The relative content of form (V) is 56.8% and that of (VI) 37.2%. The ratio of the hyperfine coupling constants $a_{^{37}Cl}/a_{^{35}Cl}$ = 0.83 is equal to the ratio of the magnetic moments $\mu_{^{37}Cl}/\mu_{^{35}Cl}$ = 0.832; hyperfine coupling with β-hydrogen was not observed. Similar observations were also made in a study[47] of the EPR spectrum of the nitroxy-radical $HCCl_2$–N(Ȯ)–$C(CD_3)_3$ (Table 2, No. 12). The absence of splitting by β-hydrogen was explained[28] by the fact that the preferred conformation



in which the proton is located in the plane of the molecule, is apparently formed in the given instance.

Table 3. Parameters of the EPR spectra of halogenocarbonylnitroxy-radicals (III).

№	R	Hal	a_N, G	Other HCC, G	Method of synthesis	Solvent	Refs.
1*	$(CH_3)_3C$	Cl	6.5	—	CCl_4 + MNP + BP + hν	CCl_4	63, 65
2*	$(CH_3)_3C$	Cl	6.65	—	CCl_4 + MNP + BP + hν	CCl_4	47
3	$(CH_3)_3C$	Cl or Br	6.65	—	CCl_3Br + MNP + hν	CCl_3Br	47
4	$(CH_3)_3C$	Cl	6.5	—	CCl_4 + (cyclo-$C_6H_{11}OCO)_2$ + MNP	CCl_4	33, 66
5	$(CH_3)_3C$	Cl or Br	6.7	a_{Hal}=2.2	CCl_3Br + hν	CCl_3Br	66
6	$(CD_3)_3C$	Cl or Br	6.65	a_{Hal}=0.5	CCl_3Br + hν	CCl_3Br	47
7**	1-Adamentyl	Cl or Br	6.5	$a_{H\text{-}\gamma}$=0.47	A***, B****, C*****	C_6H_6	63
8**	$(CH_3)_2CH$	Cl or Br	6.3	a_H=2.8	A, B, C	C_6H_6	63
9**		Cl or Br	6.4	a_H=2.8	A, B, C	C_6H_6	63
10**		Cl or Br	6.2	a_H=2.7	A, B, C	C_6H_6	63
11**	$(CH_3)_2CHC{-}(CH_3)_2$	Cl or Br	6.5	—	A, B, C	C_6H_6	63

*g = 2.0070.

**It has been erroneously described[63] as CCl_3–N(Ȯ)–R (see Refs. 65 and 47).

***CCl_4 + RNO + $h\nu$.

****$CHCl_3$ + $(C_6H_5COO)_2$ + RNO + $h\nu$.

***** CCl_3Br + RNO + $h\nu$.

The EPR spectrum of the nitroxy-radical $H_2CCl-N(\dot{O})-C(CH_3)_3$ consists of a superposition of the spectra of the two isotopic forms containing ^{35}Cl and ^{37}Cl. The spectrum includes lines corresponding to the interaction of the unpaired electron with the ^{14}N nucleus, the ^{35}Cl and ^{37}Cl nuclei, and the two equivalent protons[28] (Table 2, No. 14).

The $\dot{C}HCl_2$ radical, generated by the ultraviolet irradiation of methylene chloride in the presence of TBP, was also identified as the spin-adduct with 2-nitroso-2-trifluoromethylhexafluoropropane[22] (Table 2, No. 13). As for the spin-adduct of the same trapping agent with $\dot{C}Cl_3$, the value of a_N for the above compound is greater and that of a_{Cl} smaller than for the spin-adduct of the $\dot{C}HCl_2$ radical with MNP.

When hydrogen is abstracted from CH_2Cl_2 by the radicals formed in the decomposition of di-t-butyl peroxydioxalate at 30°C in the presence of perdeutero-2-methyl-2-nitrosopropane, the spectrum of the formyl derivative $HCO-N(\dot{O})-C(CD_3)_3$, for which $a_N = 7.0$ G and $a_H = 1.41$ G, was obtained togehter with that of the spin-adduct of the $\dot{C}HCl_2$ radical (Table 2, No. 12).[47]

3. Higher Chlorine-Containing Radicals

The study of higher radicals, containing one or two chlorine atoms at the radical centre, by the spin-trapping method in most cases involved the solution of chemical problems (see Section V), so that the examples compiled here do not constitute a systematic series. In all the cases investigated, MNP or its deutero-analogues were used to bind the $RCCl_3$ radicals.

The spectra of the spin-adducts of the $CHCl_2\dot{C}Cl_2$ radical with the above two trapping agents show a hyperfine structure due to the interaction of the unpaired electron with the ^{14}N nucleus and the nuclei of the two non-equivalent chlorine atoms (Table 4, Nos. 1 and 2). It has been suggested[47] that the non-equivalence of the chlorine atoms is associated with the high energy barrier to the rotation of two such atoms about the C–C bond in the tetrachloroethyl group. Theoretical analysis showed that the ratio of the constants $a_{^{35}Cl}$ and $a_{^{37}Cl}$ is in this case such that only components corresponding to the predominance of the form with two ^{35}Cl atoms should be detected in the EPR spectrum; the presence of other isotopic forms is revealed only by the "blurring" of the hyperfine structure of the spectrum[28].

The oxidation of 3-t-butyl-3-hydroxy-1-phenyltriazene in tetrachloroethylene takes place in an interesting manner[28]. It apparently entails the formation of the telomeric radicals $C_6H_5(CCl_2CCl_2)_n^{\cdot}$, which bind the MNP formed simultaneously; in this case it was also possible to detect the splitting by the ^{35}Cl and ^{37}Cl nuclei (Table 4, No. 5).

It has been shown[33,66] that, in the system of radicals formed via a rearrangement according to the scheme

$$\underset{\text{(VII)}}{XCH_2\dot{C}HCCl_3} \rightleftharpoons \underset{\text{(VIII)}}{XCH_2CHCl\dot{C}Cl_2}\ ,$$

$$X = CCl_3 \text{ or } (CH_3)_3CO \qquad (13)$$

the radicals (VIII) combined selectively with MNP and did not give rise to a stable spin-adduct with MNB, while the radicals (VII) gave rise to an EPR spectrum in the presence of MNB but not in the presence of MNP. These two trapping agents behave similarly also in relation to the radicals (IX) and (X), which are present simultaneously in solution[51]:

$$\underset{\text{(IX)}}{XCH_2\dot{C}HCCl_2F} \rightleftharpoons \underset{\text{(X)}}{XCH_2CHCl\dot{C}ClF}\ ,$$

$$X = CCl_3 \text{ or } CHCl_2\ . \qquad (14)$$

Table 4. Parameters of the EPR spectra of $R-N(\dot{O})-C(CH_3)_3$ nitroxy-radicals (spin-adducts of MNP with higher radicals containing chlorine at the radical centre).

№	R	a_N, G	a_{Cl}, G	Other HCC, G	Method of generation of radicals	Temp., °C	Refs.
1	$HCCl_2CCl_2$	12.8	Cl_1 : 4.50; Cl_2 : 0.80	—	$CHCl_2CHCl_2 + C_6H_5N{=}N{-}N(OH){-}C(CH_3)_3 + PbO_2$	room	28
2*	$HCCl_2CCl_2$	12.75	Cl_1 : 4.5; Cl_2 : 1.1	—	$CHCl_2CHCl_2$ + di-t-butyl peroxydioxalate	30	47
3**	$CCl_3CH_2CHClCCl_2$	12.4	2.2	—	$CCl_3Br + CH_2{=}CHCCl_3 + h\nu$	25	33, 66
4**	$(CH_3)_2COCH_2CHClCCl_2$	12.4	2.2	—	TBP $+ CH_2{=}CHCCl_3 + h\nu$	25	33
5	$C_6H_5(CCl_2CCl_2)n$	12.0	4.2; 3.5****	—	$CCl_2{=}CCl_2 + C_6H_5N{=}N{-}N(OH){-}C(CH_3)_3 + PbO_2$	room	28
6	$CCl_3CH_2CHClCFCl$	14.1	4.1	$a_F = 1.6$	$CHCl_3 + CH_2{=}CHCCl_2F$ + TBP $+ h\nu$	55—60	87
7	$CCl_3CH_2CHClCFCl$	14.0	4.1	$a_F = 1.5$	$CCl_4 + CH_2{=}CHCCl_2F + (C_2H_5)_3SiH$ + TBP $+ h\nu$	55—60	87
8	$CHCl_2CH_2CHClCFCl$	14.4	4.3	$a_F = 1.6$	$CH_2Cl_2 + CH_2{=}CHCCl_2F$ + TBP $+ h\nu$	55—60	87
9	$CH_2ClCHCl$	12.1	7.0; 5.8****	—	$CH_2ClCH_2Cl + C_6H_5N{=}N{-}N(OH){-}C(CH_3)_3 + PbO_2$	room	28
10	$(CH_3)_2CCl$	12.1	7.0; 5.8****	—	$(CH_3)_2CHCl + C_6H_5N{=}N{-}N(OH){-}C(CH_3)_3 + PbO_2$	room	28
11**	$CCl_3CH_2CHClCHCl$	14.3	3.6	$a_H = 1.7$	$CCl_4 + CH_2{=}CHCHCl_2 + (C_2H_5)_3SiH$ + TBP $+ h\nu$	55—60	87
12	HOOCCHCl	12.5	5.5	$a_H = 1.1$	$CHClBrCOOH + (C_6H_5)_3SiH$ + TBP $+ h\nu$	25	88
13***	$C_6H_{12}CH_2CCl$ (COOH)	14.2	0.8	—	$C_8H_{16} + CHClBrCOOH$ + TBP $+ h\nu$	room	88

*Trapping agent—$(CD)_3CNO$.
**Formed as a result of rearrangement with 1,2-migration of chlorine atoms.
***Formed as a result of rearrangement with 1,3-migration of hydrogen atoms.
****The values of a_{Cl} for ^{35}Cl and ^{37}Cl respectively.

According to the results of Camaggi et al.[47], the interaction of t-butoxy-radicals with 1,1-dichloroethane and $\alpha\alpha$-dichlorotoluene in the presence of MNP yielded EPR spectra characteristic of acetyl- and benzoyl-t-butylnitroxy-radicals respectively, and not of chlorine-containing nitroxy-radicals.

The nitroxy-radicals $CH_2ClCHCl-N(\dot{O})-C(CH_3)_3$ (Table 4, No. 9), in the EPR spectrum of which there is no splitting by β-hydrogen, was obtained by the oxidation of aryloxytriazene with lead dioxide in dichloroethane[28]. The authors suggest that the hydrogen atom in this nitroxy-radical is close to the nodal plane of the p-orbital of the nitrogen atom occupied by the unpaired electron. In this arrangement the extent of the interaction of the unpaired electron with β-hydrogen is a minimum.

IV. EPR SPECTRA OF NITROXY-RADICALS—SPIN-ADDUCTS OF SULPHUR-CONTAINING RADICALS

The study of the free radicals formed as intermediates in various reactions of organosulphur compounds under the influence of ultraviolet and γ-radiation or of thermal initiation is of great importance both for the elucidation of the mechanisms of such processes and for the solution of problems which are extremely important from a practical point of view[55,67].

However, direct detection of thiyl radicals by EPR in the liquid phase is evidently impossible owing to their π-orbital degeneracy[68,69]. Furthermore, recent studies have shown that RS$^\cdot$ radicals cannot be investigated by EPR in the solid phase: many of the earlier reports apparently refer to the dimeric species $RS^{\cdot}SR_2$ and not to RS$^\cdot$ radicals[68].

The spin-trapping method makes it possible to obviate these difficulties and its use for the identification of sulphur containing radicals is apparently of particular interest. Fairly numerous examples of the study of a wide variety of sulphur-containing radicals by this method are now known. The radicals investigated can be arbitrarily divided into three groups: (1) thiyl radicals RS$^\cdot$, (2) sulphonyl radicals $RSO_2^\cdot$, and (3) other radicals in which the unpaired electron is at a carbon or oxygen atom (Ċ and Ȯ radicals), while the sulphur-containing group is attached to a β- or γ-carbon atom.

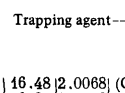
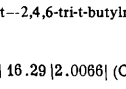
The data discussed below illustrate examples of the investigation of sulphur-containing radicals of each of these three types with the aid of spin-trapping agents. Comparison of these results shows that the EPR spectra of thiyl- and sulphonyl-nitroxy-radicals, $RS-N(\dot{O})-R'$ and $RSO_2-N(\dot{O})-R'$, are characterised in the general case only by a ^{14}N triplet, but the values of a_N and of the g-factor can frequently serve as adequate criteria for the identification of these nitroxy-radicals.

1. The Thiyl Radicals

The first attempt to identify by EPR free radicals with an unpaired electron at a sulphur atom in the form of spin-adducts with a trapping agent (MNP) was undertaken in 1968.[70] Solid polycrystalline specimens of various aminoacids were γ-irradiated and then dissolved in an aqueous solution of MNP and placed in the resonator of the EPR spectrometer. However, in contrast to all other examples, sulphur-containing aminoacids (cysteine, cystine, and methionine) altogether failed to give rise to any EPR signals under these conditions. This enabled the authors to conclude that the adducts of the RS$^\cdot$ radicals with MNP are evidently much less stable than the adducts of Ċ radicals.

A study was therefore made of the possibility of identifying with the aid of MNP the thiyl radicals formed on photolysis of thiols and disulphides directly in the resonator of the spectrometer[31]. The RS$^\cdot$ radicals were generated by irradiating solutions of butane-1-thiol or di-n-butyl sulphide in oxygen-free heptane with light having $\lambda = 245$ and 300 nm respectively. It was possible to avoid in this way the secondary formation of the di-t-butylnitroxy-radical from MNP, which complicates the EPR spectrum (see Section II). When dibutyl disulphide was irradiated in the presence of MNP, a spectrum consisting of a triplet with $a_N = 18.52$ G and $g = 2.0071$ was obtained. The authors assigned it to the spin-adduct of the $C_4H_9S^\cdot$ radicals with the trapping agent. The adduct (Table 5, No. 10) indeed proved to be very unstable: the EPR signals disappeared almost immediately after irradiation ceased. Apart from the above triplet, the spectrum showed another less intense triplet with $a_N = 14.93$ G and $g = 2.0058$, the origin of which the authors could not establish. After the irradiation of butanethiol, the triplet corresponding to the spin-adduct of the $C_4H_9S^\cdot$ radical was also detected[31,59].

Table 5. Parameters of the EPR spectra of the $RS-N(\dot{O})-R'$ nitroxy-radicals (spin-adducts of thiyl radicals).

№	RS	a_N, G	g-Factor	Method of generation of radicals	Temp., °C	Solvent	Refs.
Trapping agent—MNP, $R'=C(CH_3)_3$							
1*	CH_3S	18.9	2.0064	$CH_3SH+h\nu$	—103	CH_3SH	73
2	C_2H_5S	17.4	2.0063	$C_2H_5SH+h\nu$	—92	C_2H_5SH	73
3	C_3H_7S	17.8	2.0063	$C_3H_7SH+h\nu$	—85	C_3H_7SH	73
4	iso-C_3H_7S	16.7	2.0062	iso-$C_3H_7SH+h\nu$	—97	iso-C_3H_7SH	73
5	iso-C_3H_7S	16.99	2.0068	(iso-$C_3H_7)_2S+$ $+(C_6H_5)_2CO+h\nu$	room	—	71
6	iso-C_3H_7S	16.99	2.0068	(iso-$C_3H_7)_2S_2+h\nu$	room	(iso-$C_3H_7)_2S_2$	71
7	C_4H_9S	17.8	2.0063	$C_4H_9SH+h\nu$	—73	C_4H_9SH	73
8	C_4H_9S	18.5	2.0071	$C_4H_9SH+h\nu$	room	heptane	31
9	C_4H_9S	18.52	2.0071	$C_4H_9SH+h\nu$	room	heptane	59
10	C_4H_9S	18.52	2.0071	$(C_4H_9)_2S_2+h\nu$	room	heptane	31
11	C_4H_9S	18.21	2.0070	$(C_4H_9)_2S_2+$ $+(C_6H_5)_2CO+h\nu$	room	—	71
12	C_6H_5S	16.75	2.0066	C_6H_5SH+ $+(C_6H_5)_2CO+h\nu$	room	benzene	71
13	C_6H_5S	16.5	2.0066	$C_6H_5C(SC_6H_5)_2CH_3+$ $+h\nu$	—65÷—25	CH_2Cl_2	74, 75
Trapping agent—nitrosodurene, $R'=$ 							
14	CH_3S	16.48	2.0068	$(CH_3)_2S_2+h\nu$	room	benzene	35
15	C_3H_7S	16.82	2.0068	$(C_3H_7)_2S_2+h\nu$	room	benzene	35
16	C_6H_5S	16.01	2.0065	$(C_6H_5)_2S_2+h\nu$	room	benzene	35
Trapping agent—nitrosobenzene, $R'=C_6H_5$							
17**	C_6H_5S	11.42	2.0059		25	benzene	76
Trapping agent—2,4,6-tri-t-butylnitrobenzene, $R'=$ 							
18***	C_6H_5S	16.29	2.0066	$(C_6H_5)_2S_2+h\nu$	25	benzene	36

*$a_{H(CH_3)} = 1.2$ G.
**$a_{H\text{-}o} = a_{H\text{-}p} = 2.52$ G; $a_{H\text{-}m} = 0.86$ G.
***$a_{H\text{-}m} = 0.85$ G.

The EPR spectra of the spin-adducts of other thiyl radicals (iso-$C_3H_7S^\cdot$, $C_6H_5S^\cdot$) with MNP were observed by the same workers[71] in the photochemical reduction of

benzophenone by thiols and sulphides. The spectra consisted of triplets having similar g-factors and a_N constants in the range 16.5–18.5 G (Table 5, Nos. 5, 6, 11, and 12).

It is noteworthy that, when thiophenol is used for the photochemical reduction of benzophenone in the presence of MNP, the formation of not only the $C_6H_5S-N(\dot{O})-C(CH_3)_3$ nitroxy-radical, but also of the $H-N(\dot{O})-C(CH_3)_3$ t-butylnitroxy-radical (which may be formally regarded as the spin-adduct of a hydrogen atom and MNP), whose spectrum has $a_N = 13.6$ G, $a_{H(NH)} = 12.36$ G, and $g = 2.0062$, was observed[71]. It is of interest to compare with this result a study[72] where it was shown that thiophenol is reduced to a nitroso-compound on ultraviolet irradiation:

$$2RNO + 2C_6H_5SH \rightarrow 2R-N(\dot{O})-H + (C_6H_5S)_2 \quad . \qquad (15)$$

The EPR spectrum then shows (for $R = t\text{-}C_4H_9$) a triplet of doublets with $a_N = 13.1$ G, $a_H^{NH} = 11.2$ G, and $g = 2.0063$. The authors[72] do not mention the formation under these conditions of the t-butylphenylthionitroxy-radical, but it is seen from the spectrum quoted in their paper that it is formed: the spectrum shows a low-intensity triplet with $a_N = 16.6$ G.

The spectra of the spin-adducts of MNP with different aliphatic RS$^\cdot$ radicals (Table 5, Nos. 1–4 and 7) have been recently described by Wargon and Williams, who investigated the γ-radiolysis of thiols, sulphides and disulphides at temperatures between −50° and −110°C.[73] The constants a_N and the g-factors which they obtained (16.7–18.9 G and 2.0062–2.0064) are close to those quoted above. It is noteworthy that the spectrum of the spin-adduct of the $CH_3S^\cdot$ radical shows clearly the splitting of the lines of the ^{14}N triplet into quartets due to the interaction with the hydrogen atoms of the methyl group ($a_H = 1.2$ G; Table 5, No. 1). For other RS$^\cdot$ radicals, the splitting of the signals by hydrogen atoms is much less intense, and the hyperfine coupling is manifested solely by increased width of the lines of the main triplet.

The characteristic constant $a_N = 16.5–18.5$ G can serve as a criterion of the assignment of such a triplet in the EPR spectrum to the spin-adducts of MNP with thiyl radicals. Another characteristic feature of the spectra of these spin-adduct is the rapid disappearance of the signal after irradiation has been stopped, i.e. the low stability of the radical. For example, these data enabled the authors[74,75] to assign the triplet with $a_N = 16.5$ G, observed in the complex EPR spectrum during the photolysis of acetophenone diphenylmercaptal, to the spin-adduct of the $C_6H_5S^\cdot$ radical with MNP (Table 5, No. 13; see also Section V).

Because of the ease of the generation of thiyl radicals from disulphides and thiols, many systematic studies devoted to the investigation of new spin-trapping agents contain data about the adducts of RS$^\cdot$ radicals with such agents. For example, the detection of thiyl radicals with the aid of nitrosodurene[35], nitrosobenzene[76], and 2,4,6-tri-t-butylnitrosobenzene[36] has been described (Table 5, Nos. 14–18). The nitroxy-radicals formed under these conditions have relatively high values of a_N.

It is seen from the data presented that thiylalkyl- and thiylaryl-nitroxy-radicals are in general characterised by higher values of a_N than dialkyl- and alkylaryl-nitroxy-radicals and by a g-factor which is appreciably displaced downfield compared with that of the free electron. This can be apparently accounted for by the fact that the spin-orbital coupling constant for heteroatomic substituents such as sulphur is fairly considerable (approximately 382 cm^{-1}).[31]

The data at present available also make possible the conclusion that neither temperature nor the solvent have a significant influence on the parameters of the spectra of thiylnitroxy-radicals.

Table 6. Parameters of the EPR spectra of $RSO_2-N(\dot{O})-C(CH_3)_3$ nitroxy-radicals [MNP spin-adducts (in benzene at room temperature)].

№	RSO_2	a_N, G	Method of generation of radicals	Refs.
1*	$C_6H_5SO_2$	12.2	see Schemes (16) and (17) in text	78
2	$p\text{-}CH_3C_6H_4SO_2$	12.5	$CH_3C_6H_4SO_2I$ + see also Schemes (18) and (19) in text	40
3	$C_6H_5SO_2$	12.0	$C_6H_5SO_2Cl + h\nu$	51, 52
4	$C_6H_5SO_2$	12.2	$C_6H_5SO_2F + (C_2H_5)_3SiH$ + TBP + $h\nu$	51, 52
5	$C_6H_5SO_2$	12.1	$C_6H_5SO_2Br + h\nu$	52
6	$C_2H_5SO_2$	12.2	$C_2H_5SO_2Cl + h\nu$	51
7	$C_2H_5SO_2$	12.2	$C_2H_5SO_2Cl + (CH_3COO)_2 + h\nu$	51
8	$ClSO_2$	11.7	$C_6H_5SO_2Cl + h\nu$	51, 52
9	$ClSO_2$	11.6	$SO_2Cl_2 + h\nu$	51, 52
10	FSO_2	12.4	$C_6H_5SO_2F + h\nu$	51, 52
11	FSO_2	12.6	$SO_2FCl + h\nu$	51, 52
12	$BrSO_2$	11 9	$C_6H_5FO_2Br + h\nu$	52

*$g = 2.0061$; the parameters of the EPR spectra of a large number of $RSO_2-N(\dot{O})-R'$ nitroxy-radicals have also been published by Wajer et al.[78], but, since they were obtained by procedures other than the spin-trapping method, they are not considered here.

2. Sulphonyl Radicals

The EPR spectrum of the $RSO_2-N(\dot{O})-R'$ nitroxy-radical ($R = R' = CH_3$) was obtained for the first time by Lagercrantz[77]. The spectrum was recorded in a study of the reaction of dimethyl sulphoxide with nitrogen dioxide. The assignment was based on the hyperfine structure: the lines of the main ^{14}N triplet are split owing to hyperfine coupling with two non-equivalent H atoms of the methyl group ($a_H = 11.0$ G and $a_{H'} = 0.094$ G). The values of a_N and the g-factor for the spectra of radicals of this type (12.2 G and 2.0059 respectively) were obtained for the first time. The validity of this assignment was fully confirmed in a study[78] where the spectra of a number of sulphonyl-nitroxy-radicals of the above type (R = aryl and R′ = alkyl, phenyl, phenylsulphonyl, etc.) were investigated. These nitroxy-radicals were obtained either by the oxidation of N-alkyl- or N-aryl-benzenesulphonylhydroxylamines by lead dioxide:

$$RNO + C_6H_5SO_2H \rightarrow \underset{\underset{OH}{|}}{R-N-SO_2C_6H_5} \xrightarrow{PbO_2} \underset{\underset{O^\cdot}{|}}{R-N-SO_2C_6H_5} \quad , \qquad (16)$$

or by the photolysis of N-methyl-N-nitrosotoluene-p-sulphonamides in solution in methylene chloride or toluene in the presence of MNP:

$$p\text{-}CH_3C_6H_4SO_2-\underset{\underset{NO}{|}}{N}-CH_3 \xrightarrow[h\nu]{MNP} (CH_3)_3C-\underset{\underset{O^\cdot}{|}}{N}-SO_2C_6H_4CH_3\text{-}p \quad . \qquad (17)$$

The spectra of the resulting nitroxy-radicals are characterised by the constants $a_N = 11–12$ G (a_N is somewhat less than 10.1 G only for the bisbenzenesulphonylnitroxy-radical) and $g = 2.0061$ (Table 6, No. 1). Such a high value

of a_N is unusual for nitroxy-radicals with powerful electron-accepting substituents of this kind (for example a_N = 4–5 G for diacylnitroxy-radicals)[15]. The authors[78] explain this by the fact that the nitrogen in sulphonylnitroxy-radicals has a pyramidal structure, and the unpaired electron occupies an orbital with enhanced *s*-character.

Unfortunately the authors of the above investigations say nothing about the stability of the sulphonylnitroxy-radicals investigated, which is an important characteristic of the spin-adducts in the spin-trapping method.

The detection of toluene-*p*-sulphonyl radicals with the aid of MNP was also noted in the photolysis and thermolysis of *p*-tolyl arylazo sulphones[40]:

$$\mathrm{Ar{-}N{=}N{-}SO_2C_6H_4CH_3}\text{-}p \rightarrow \mathrm{Ar^{\cdot}} + \mathrm{N_2} + p\text{-}\mathrm{CH_3C_6H_4SO_2^{\cdot}}$$

$$p\text{-}\mathrm{CH_3C_6H_4SO_2^{\cdot}} + \mathrm{MNP} \rightarrow (\mathrm{CH_3})_3\mathrm{C{-}\underset{\underset{\mathrm{O^{\cdot}}}{|}}{N}{-}SO_2C_6H_4CH_3}\text{-}p \quad . \qquad (18)$$

The spectrum of the nitroxy-radical obtained in this way had a_N = 12.5 G and g = 2.0061. To confirm this assignment, the same nitroxy-radical was obtained by an independent procedure: by the photolysis of toluene-*p*-sulphonyl iodide in the presence of MNP (Table 6, No.2). The authors note a very low stability of this nitroxy-radical—its half-life is only 44 s, so that its spectrum disappears rapidly after irradiation ceases. The formation of the same nitroxy-radical has been noted[79] in the detection with the aid of MNP of toluene-*p*-sulphonyl radicals generated via the mechanism.

$$[(\mathrm{CH_3})_3\mathrm{COOCO}]_2 \rightarrow 2\,(\mathrm{CH_3})_3\mathrm{C\dot{O}} + 2\mathrm{CO_2} \quad ,$$
$$(\mathrm{CH_3})_3\mathrm{C\dot{O}} + (\mathrm{C_4H_9})_3\mathrm{SnH} \rightarrow (\mathrm{CH_3})_3\mathrm{COH} + (\mathrm{C_4H_9})_3\mathrm{Sn^{\cdot}} \quad ,$$
$$(\mathrm{C_4H_9})_3\mathrm{Sn^{\cdot}} + p\text{-}\mathrm{CH_3C_6H_4SO_2Cl} \rightarrow (\mathrm{C_4H_9})_3\mathrm{SnCl} + p\text{-}\mathrm{CH_3C_6H_4SO_2^{\cdot}} \quad . \qquad (19)$$

The photochemical decomposition of benzenesulphonyl halides $C_6H_5SO_2Hal$ (Hal = F, Cl, or Br) was investigated by the spin-trapping method[51,52]. These compounds may decompose both at the C–S and at the S–Hal bonds[80]. This can lead to the formation of either $C_6H_5SO_2^{\cdot}$ or $HalSO_2^{\cdot}$ radicals, or both. The adducts of these radicals with MNP should give rise to triplets with similar values of a_N in the EPR spectra. Nevertheless, the employment of independent methods for the generation of these radicals (for example, $ClSO_2^{\cdot}$ from SO_2Cl_2, $FSO_2^{\cdot}$ from SO_2FCl, etc.) and allowance for the different stabilities of the corresponding spin-adducts enabled the authors[51,52] to make unambiguous assignments of the EPR spectra (Table 6, Nos. 3–12, see also Section V).

Thus one may conclude that $RSO_2^{\cdot}$ radicals may be identified with the aid of the spin-trapping method, and the differences between the stabilities of their spin-adducts can serve as additional information in the assignment of extremely similar signals in the EPR spectra of the latter.

There are no literature data for other trapping agents used in the detection of sulphonyl radicals. One can only note that, in the photolysis of SO_2Cl_2 in the presence of t-butyl phenyl nitrone, it is possible to detect only the adduct of a chlorine atom with the trapping agent[52]; the $ClSO_2^{\cdot}$ radical evidently does not give rise to stable spin-adducts with the nitrone.

In the study of radical reactions of various sulphones (initiated by the $\dot{O}H$ radicals formed in the photolysis of hydrogen peroxide), in the presence of MNP and MNB as trapping agents, it is impossible to detect the spin-adducts of the sulphonyl radicals[81]. Some of the sulphones investigated totally failed to give rise to radical signals visible in the EPR spectrum, while others formed radicals by abstraction of a hydrogen atom from the methylene group adjoining the sulphonyl group (these were in fact detected by the trapping agents)[81]. It is of interest to note that, under these conditions, the sulphoxides R_2SO give rise to alkyl radicals R$^{\cdot}$ (identified from the spectra of their spin-adducts)[81]. On this basis, the authors[82,83] developed a method for the radical alkylation of aromatic and heteroatomic compounds by sulphoxides.

3. Other Sulphur-Containing Radicals

In the study of the radical reactions of organosulphur compounds by the spin-trapping method the formation of the spin-adducts of not only S radicals, but also of sulphur-containing $\dot{C}$ radicals is frequently noted. For example, in a study, already mentioned above[71] the $(CH_3)_2\dot{C}{-}S{-}CH(CH_3)_2$ radicals were detected (as their spin-adducts with MNP) together with iso-$C_3H_7S^{\cdot}$ radicals in the photochemical reduction of benzophenone by isopropyl sulphide. The formation of $\dot{C}$ radicals ($\dot{C}H_2SH$, etc.), identified from the spectra of their spin-adducts, was also noted in the γ-radiolysis of thiols[73] below –70°C. Apart from the $C_6H_5S^{\cdot}$ radicals, other sulphur-containing $\dot{C}$ and $\dot{O}$ radicals were detected in the photochemical reactions of acetophenone diphenylmercaptal[74,75] (Table 7, Nos. 1–6). This reaction is discussed in greater detail in Section V.

The data presented in Table 7 show that the constants a_N for the MNP adducts with $\dot{C}$ radicals containing the thiyl group in the β-position vary in the range 12–15 G, which is in general characteristic of dialkylnitroxy-radicals[16,84]. The adducts of MNP with $\dot{C}$ radicals containing the SO_2Cl group in the β-position have a much lower value of a_N (approximately 7 G; see Table 7, No. 7), i.e. of the same order of magnitude as for acylalkylnitroxy-radicals[85].

With the exception of isolated examples, there have so far been no studies of the possibility of the selective detection of particular organosulphur radicals with the aid of various spin-trapping agents (virtually all the investigations have been carried out solely with MNP), but this approach may prove to be extremely promising in this field also.

V. THE APPLICATION OF THE SPIN-TRAPPING METHOD IN THE STUDY OF THE MECHANISMS OF CERTAIN REACTIONS OF ORGANOCHLORINE AND ORGANOSULPHUR COMPOUNDS

This Section deals with examples, which have already been partly considered, where spin-trapping agents were used to investigate complex radical reactions of organochlorine and organosulphur compounds. The experimental facts accumulated in systematic studies (i.e. in those where radicals of known structure were detected with the aid of spin-trapping agents and the parameters of the EPR spectra of the corresponding spin-adducts were described) made it possible to assign them subsequently on the basis of the parameters of the observed EPR spectra to the spin-adducts of particular radicals formed in the course of a chemical reaction. Radical reactions include, as a rule, the intermediate formation of various radicals (owing to chain propagation and transfer, rearrangements, etc.). If these reactions are carried out in the presence of spin-trapping agents, very complex EPR spectra, corresponding to a mixture of various nitroxy-radicals, are therefore observed. The individual lines are then frequently superimposed, which greatly

Table 7. Parameters of the EPR spectra of R–N(Ȯ)–C(CH$_3$)$_3$ nitroxy-radicals (spin-adducts of MNP with sulphur-containing radicals).

№	R	a_N, G	Method of generation of radicals	Temp., °C	Solvent	Refs.
1*	$(CH_3)_2CSCH(CH_3)_2$	14.21	(iso-$C_3H_7)_2S + (C_6H_5)_2CO + h\nu$	room		71
2**	$C_6H_5SCH_2$	13.83	$C_6H_5SCH_3 + (C_6H_5)_2CO + h\nu$	room		71
3***	$C_6H_5C(SC_6H_5)_2CH_3$	14.3	$C_6H_5C(SC_6H_5)_2CH_3 + h\nu$	10—25	CH_2Cl_2	74,75
4	$C_6H_5C(SC_6H_5)CH_2SC_6H_5$	11.9 12.1	$C_6H_5C(SC_6H_5)_2CH_3 + h\nu$	room	CH_2Cl_2 CCl_4	74,75
5	$C_6H_5C(SC_6H_5)CH_2SC_6H_5$	12.0	$C_6H_5CH(SC_6H_5)CH_2SC_6H_5 + TBP + h\nu$	room	CH_2Cl_2, CCl_4	74,75
6	$C_6H_5C(SC_6H_5)CH_3$	25.7	$C_6H_5C(SC_6H_5)_2CH_3 + h\nu$	—50——65	CH_2Cl_2	74,75
7****	CH_3CHSO_2Cl	6.9	$C_2H_5SO_2Cl + (CH_3COO)_2 + h\nu$	room	Benzene	81

*g = 2.0061.
**g = 2.0064; $a_{H(CH_2)}$ = 5.9 G.
***$a_{H(CH_2)}$ = 7.6 G.
****$a_{H(CH)}$ = 1.5 G.

hinders the interpretation of the spectrum. However, certain procedures which make it possible to simplify this task have been used recently.

1. The Selectivity of Spin-Trapping Agents

It was already noted above (see Section II) that certain spin-trapping agents are capable of detecting particular short-lived radicals to different extents. The selectivity of various spin-trapping agents in relation to radicals of different types has been used by the present authors [33]. As shown previously [86], a study of the rearrangement of polychloroalkyl radicals with 1,2-migration of the chlorine atom in accordance with Eqn.(13) yielded spectroscopic proof of the simultaneous presence in the reaction mixture of both radicals—the rearranged radical (VIII) and the non-rearranged radical (VII). Fig. 5 illustrates the EPR spectra obtained in the photochemically initiated reaction of TBP with 3,3,3-trichloropropene in the presence of MNP and MNB. Fig. 5 shows that MNP detects selectively only the rearranged radical (VIII); for X = $(CH_3)_3CO$, the spectrum with the characteristic splitting by the two β-chlorine atoms corresponds to the $(CH_3)_3COCH_2CHClCCl_2$–N(Ȯ)–C(CH$_3$)$_3$ nitroxy-radical (Table 4, No. 4), while MNB combines only with the non-rearranged radical (VII): the spectrum with doublet splitting by β-hydrogen corresponds to the $(CH_3)_3COCH_2CH(CCl_3)$–N(Ȯ)–$C(CH_3)_2COCH_3$ radical. Analogous results were obtained also in other instances of the rearrangement of radicals with 1,2-migration of chlorine [86,87].

The use of the selectivity of spin-trapping agents also permitted the study of the photochemical decomposition of various sulphonyl halides [51,52]. It was shown, for example, that SO_2Cl_2 decomposes on ultraviolet irradiation into $ClSO_2^{\cdot}$ radicals and Cl$^{\cdot}$ atoms, the former being selectively detected by MNP and the latter by BPN. The decomposition of benzenesulphonyl chloride involves the dissociation of the C–S bond together with that of the S–Cl bond [51,52]:

$$C_6H_5SO_2Cl \rightarrow C_6H_5^{\cdot} + ClSO_2^{\cdot} \quad . \qquad (20)$$

Phenyl radicals were detected with the aid of BPN and chlorosulphonyl radicals were detected with the aid of MNP.

The available data do not as yet show why certain trapping agents are incapable of detecting particular radicals. This can probably be accounted for by two causes: either the trapping agent does not react with the radical owing to unfavourable polar or steric effects or the spin-adduct formed is insufficiently stable for its identification by EPR. Nevertheless, the above purely empirical approach to the study of radical reactions, using the selectivity of various spin-trapping agents, appears to be extremely convenient and promising.

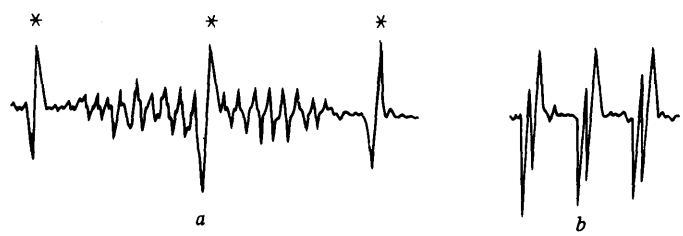


Figure 5. The ESP spectra of the nitroxy-radicals formed in the photochemical reaction of TBP with 3,3,3-trichloropropene [33]: *a*) in the presence of MNP (the triplet corresponding to the spin-adduct of MNP with t-butoxy-radicals is designated by asterisks); *b*) in the presence of 2-methyl-2-nitroso-3-butanone.

2. The Different Stabilities of Spin-Adducts

It was already noted previously that the adducts of spin-trapping agents, particularly of MNP, with various radicals have different stabilities. The time required for the disappearance of their signals from the EPR spectrum varies from several seconds to many hours. The possibility therefore arises of identifying certain radicals present in a mixture with other radicals by recording the

EPR spectrum immediately at the beginning of the reaction and after some time. The initial complex spectrum in some instances becomes greatly simplified owing to the destruction of less stable nitroxy-radicals.

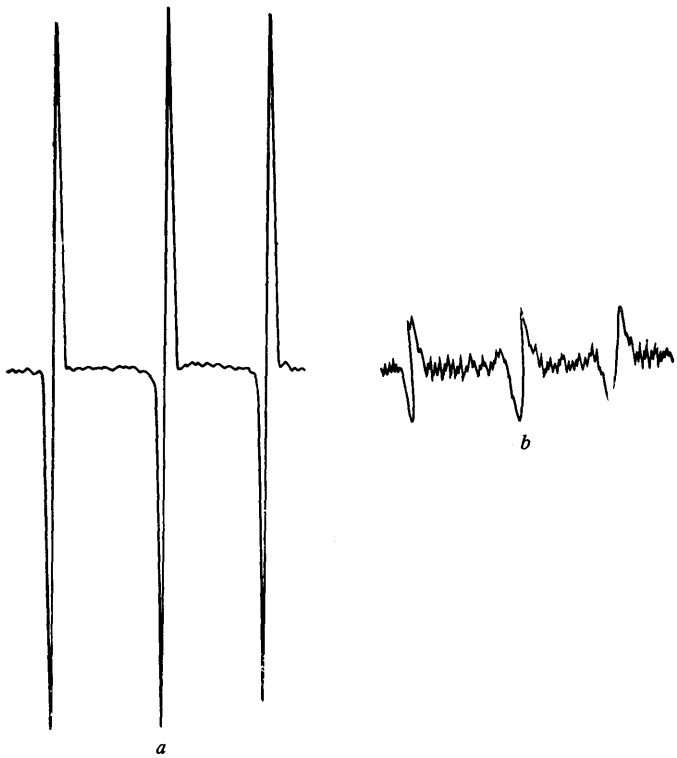


Figure 6. The EPR spectrum of a benzene solution of $C_6H_5SO_2Cl$ [52]: *a*) on ultraviolet irradiation; *b*) 2 min after the cessation of irradiation.

This procedure has been used successfully [51,52]. Ultraviolet irradiation of a benzene solution of benzenesulphonyl chloride in the presence of MNP gave an EPR spectrum consisting of a triplet with a_N = 12.0 G (Fig. 6*a*). When 2 min elapsed from the cessation of irradiation, the spectrum showed a much less intense triplet with a_N = 11.7 G (Fig. 6*b*); subsequently its intensity did not change for at least 30 min. This suggested that the triplet in Fig. 6*a* is a result of the superposition of signals due to two different nitroxy-radicals with similar values of a_N. Such nitroxy-radicals might be the spin-adducts of MNP with the $C_6H_5\dot{S}O_2$ and $Cl\dot{S}_2$ radicals. By generating these radicals using independent methods [Schemes (21) and (22)] in the presence of MNP,

$$SO_2Cl_2 \xrightarrow{u.v.} \dot{S}O_2Cl + Cl^{\cdot} \quad ,$$
$$\dot{S}O_2Cl + \underset{(XI)}{MNP} \rightarrow ClSO_2-N(\dot{O})-C(CH_3)_3 \quad ; \qquad (21)$$

$$C_6H_5SO_2Cl + [(CH_3)_2CO]_2 + (C_2H_5)_3SiH \xrightarrow{2537\,\text{Å}} C_6H_5\dot{S}O_2 + (CH_3)_2COH + (C_2H_5)_3SiCl \quad ,$$

$$C_6H_5\dot{S}O_2 + \underset{(XII)}{MNP} \rightarrow C_6H_5SO_2-N(\dot{O})-C(CH_3)_3 \quad ; \qquad (22)$$

it was shown that the nitroxy-radical (XI) is stable for a long time, while the signals due to the nitroxy-radical (XII) vanish almost immediately after irradiation ceases. The conclusion that the photochemical decomposition of benzenesulphonyl chloride involves the dissociation of both C–S and S–Cl bonds was thus confirmed [51,52].

The different stabilities of the spin-adducts of MNP also permitted the elucidation of the mechanism of another extremely complex reaction—the addition of bromochloroacetic acid to oct-1-ene with photochemical initiation. This process can be represented by the following scheme [88]‡:

$$\text{Initiator} \longrightarrow R^{\cdot} \quad ,$$

$$R^{\cdot} + HOOCCHClBr \longrightarrow RBr + \underset{(XIII)}{HOOC\dot{C}HCl} \quad ,$$

$$(XIII) + CH_2{=}CHC_6H_{13} \longrightarrow \underset{(XIV)}{HOOCCHClCH_2\dot{C}HC_6H_{13}} \quad ,$$

$$(XIV) \xrightarrow{1,3\text{-}H} \underset{(XV)}{HOOC\dot{C}ClCH_2CH_2C_6H_{13}}$$

$$(XIV) \xrightarrow{CH_2=CHC_6H_{13}} \underset{(XVI)}{HOOCCHClCH_2CH(C_6H_{13})CH_2\dot{C}HC_6H_{13}} \quad ,$$

$$(XVI) \xrightarrow{1,5\text{-}H} \underset{(XVII)}{HOOC\dot{C}ClCH_2CH(C_6H_{13})CH_2CH_2C_6H_{13}} \quad .$$

The scheme shows that, when the reaction is carried out in the presence of MNP, the formation of five spin-adducts corresponding to radicals (XIII)–(XVII), may be expected. The spin-adducts of radicals (XIV) and (XVI) as well as (XV) and (XVII) should not have different EPR spectra. Thus the problem reduces to the identification of three nitroxy-radicals:

$$\underset{(XVIII)}{HOOCCHCl-N(\dot{O})-C(CH_3)_3}, \quad \underset{(XIX)}{RCH_2CH(C_6H_{13})-N(\dot{O})-C(CH_3)_3} \quad ,$$

$$\underset{(XX)}{RCH_2CCl(COOH)-N(\dot{O})-C(CH_3)_3} \quad .$$

The spectrum of radical (XVIII) is extremely complex and hinders the identification of other signals, overlapping them. However, special experiments showed that the stability of radical (XVIII) is very low, and its spectrum disappears almost immediately when irradiation ceases. It was therefore possible to identify the nitroxy-radicals (XIX) and (XX) by recording the spectrum several minutes after stopping irradiation.

In certain cases the spin-adducts have a very low stability and their EPR spectra cannot be recorded at all at room temperature. The study, mentioned previously, of the homolytic rearrangement of acetophenone diphenylmercaptal, occurring under the influence of ultraviolet irradiation, is of interest in this connection [74,75]. By carrying out this reaction in the presence of the MNP spin-trapping agent, it was possible to identify all the intermediate radicals in conformity with the scheme

$$C_6H_5C(SC_6H_5)_2CH_3 \longrightarrow \underset{(XXI)}{C_6H_5\dot{C}(SC_6H_5)CH_3} + \underset{(XXII)}{\dot{S}C_6H_5} \quad ,$$

$$(XXI) \xrightarrow{O_2} \underset{\dot{O}^{\cdot}\ (XXIII)}{C_6H_5C(SC_6H_5)CH_3} \quad ,$$

$$(XXIII) + C_6H_5C(SC_6H_5)_2CH_3 \longrightarrow \underset{(XXIV)}{C_6H_5C(SC_6H_5)_2\dot{C}H_2} \quad ,$$

$$(XXIV) \xrightarrow{\varrho} \underset{(XXV)}{C_6H_5\dot{C}(SC_6H_5)CH_2SC_6H_5} \quad ,$$

$$(XXV) + DH^{\S} \longrightarrow C_6H_5CH(SC_6H_5)CH_2SC_6H_5 \quad .$$

‡The symbols 1,3-H and 1,5-H denote rearrangements involving 1,3- and 1,5-migrations of a hydrogen atom respectively.

§DH is a hydrogen donor.

At room temperature the EPR spectrum shows signals corresponding to the spin-adducts of radicals (XXI), (XXII), (XXIV), and (XXV). Only at a low temperature (between −65° and −50°C) was it possible to detect the spectrum of the spin-adduct of radical (XXI) (Table 7, No. 7) and hence elucidate the stage involving the initiation of this reaction.

Thus the method of spin-trapping agents has been used successfully recently to investigate a wide range of radical reactions of organochlorine and organosulphur compounds. The value of this method is particularly evident in those cases where the reactions proceed via several pathways, leading to a complex mixture of products. The identification of the intermediate radicals in these systems yields important information about the reaction mechanism, the role of individual stages, etc.

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