thermodynamic characteristics of the phase transformations of the various complexes of aluminium hydride, etc.

We therefore consider that future work in the field of the complexes of aluminium hydride will be successful only if physical and physicochemical methods are widely employed.

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PARAMAGNETIC DERIVATIVES OF NITROGEN MONOXIDE

E. G. Rozantsev

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1. INTRODUCTION

Just as half a century ago, stable radicals continue to play an important part in the development of the theoretical concepts of contemporary chemical science.

The discovery and the wide use of the electron paramagnetic resonance (EPR) method was a powerful tool in the development of this field of chemistry[1-3].

Stable radicals are quite useful in solving many specific problems arising during the course of chemical, physical, and biological experiments.

This class of substances is successfully used in studying the rates of initiation of chain reactions, in catalysis, and in photochemical and quantum-chemical investigations.

After the discovery and study of the phenomenon of dynamic nuclear polarisation, stable radicals with a simple hyperfine spectral structure became used in the construction of high-sensitivity magnetometers and "Maser" type devices.

In recent years several reviews and monographs devoted to free radicals have appeared[4-12], in which little mention has been made of an important class, the paramagnetic derivatives of nitrogen monoxide.

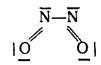
The main focus of the present review is the structure, reactivity, and methods of preparation of the compounds of this class; radiospectroscopic investigations receive less detailed consideration and problems relating to the quantum chemistry of free radicals are not discussed in this review,

2. PARAMAGNETIC NITROGEN OXIDES

The simplest free radical of this series is nitrogen monoxide:

$$\dot{N}=\bar{O}.$$

Despite the presence of a free valency, nitrogen monoxide is considerably less reactive than atomic hydrogen or chlorine and under ordinary conditions it does not dimerise, unless it is present in the liquid (b.p. -151.7°C) or solid (m.p. -163.6°C) states [13-17]. On the basis of spectroscopic investigations of solid nitrogen monoxide it can apparently be ascribed the structure [18-20]:

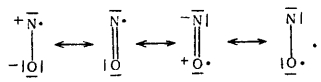


The valence state of nitrogen monoxide can be written as:

$$NO\,[KK\,(N:2s)^2\,(O:2s)^2\,(\sigma 2p)^2\,(\pi 2p)^4\,(\pi^* 2p)^1],$$

where the completely filled orbitals $(\sigma 2p)^2(\pi 2p)^4$ correspond to a triple bond, and $(\pi^* 2p)$ contains an unpaired electron. On transfer of the unpaired electron to the corresponding non-bonding orbital the NO excited species behaves as if it possessed a triple bond [21].

The thermal stability of nitrogen monoxide is so high that it does not decompose appreciably even at 500°. Pauling [22] explains the unusually low level of the ground state of the radical by quantum-mechanical resonance of four structures:



As the two partly ionic structures have approximately equal "weight", the resulting dipole moment of the species should be close to zero. The dipole moment [23] obtained experimentally was in fact very low (μ = 0.16 D).

Nitrogen monoxide can be described by a single formula using Pauling's ideas about a three-electron bond:

$$|N\overset{\cdot}{=}O|\cdot$$

The gain in energy in the formation of such a bond stabilises the species so much that the heat of dimerisation becomes negative [22]. Such a structure for the radical agrees well with the dipole moment and the measured interatomic distance, which is intermediate between the values calculated for double and triple covalent bonds [24]:

N=O	N$\overset{\cdot}{=}$O	N≡O
(1.18 Å)	(1.15 Å)	(1.06 Å)

The cation [25] and anion [26] of nitrogen monoxide have the following structures respectively:

$$[|N\equiv O|]^+\ [|\bar{N}=\bar{O}|]^-.$$

Nitrogen monoxide is a chemically active compound; it is readily reduced in solution to hydroxylamine and ammonia [27]. The gaseous reactions of nitrogen monoxide with chlorine [28,29], bromine [30], and oxygen [31] take place by three-body collisions, through a diamagnetic activated complex, for example:

$$2NO+O_2 \rightarrow [ONOONO] \rightarrow 2NO_2+27\ \text{kcal}.$$

It is interesting that when there is a very large excess of oxygen under these conditions dinitrogen trioxide is formed as the bimolecular reaction:

$$NO+NO_2 \rightarrow N_2O_3+10\ \text{kcal},$$

proceeds much faster than the termolecular reaction [32].

The high-temperature gas reaction of nitrogen monoxide with hydrogen is mainly termolecular [33], but transient states with very short lifetime produced in two-body collisions may occur [34].

Nitrogen monoxide reacts readily with other free radicals [35-38], and hence is not only an indicator [39] but also an effective inhibitor of chain reactions [40,41].

Nitrogen monoxide forms coordination compounds, the nitrosyls, with salts of iron, cobalt, and other transition metals having unpaired *d*-electrons [42-45].

Significantly, in almost all the compounds of nitrogen monoxide the additional covalent bond is formed preferentially with the nitrogen atom [46-48], which is evidence in support of the structure with a free valency at the nitrogen.

In the hyperfine structure (h.f.s.) of the EPR spectrum of nitrogen monoxide there are three transitions between four sublevels. Each line of the rotational-magnetic structure is split into triplets with a separation of ~14.2 Oe between them. Analysis of the h.f.s. parameters of the spectrum also leads to the conclusion that the greater part of the spin density (~60%) is centred on the nitrogen atom [49-52].

Nitrogen dioxide is another stable free radical of this series. The gain in energy on the delocalisation of the unpaired electron does not stabilise it enough to prevent dimerisation into dinitrogen tetroxide [53-57]:

$$2NO_2 \rightleftarrows N_2O_4+13\ \text{kcal}.$$

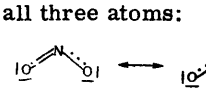
Even in the vapour (b.p. 21°C) nitrogen dioxide is partly dimerised, and in the liquid and solid (m.p. -11°C) states it is a dimer. Only at 150°C is the gas completely dissociated into nitrogen dioxide, which on further heating (~600°C) breaks down into nitrogen monoxide and oxygen [58-60]:

$$N_2O_4 \rightleftarrows NO_2 \rightleftarrows NO+O.$$
$$\uparrow\downarrow$$
$$N_2O_3$$

Sutherland and Penney [61,62] established the structure of nitrogen dioxide [61,62]. They concluded, from an analysis of the absorption bands, that the nitrogen dioxide species is not linear [63]. The molecular parameters of NO_2:

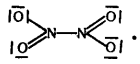
r(N—O)	∠ONO,
1.20 Å	132°

were determined by electron diffraction [64,65]. As the angle ONO is nearer 120° than 90°, it can be approximately assumed that the nitrogen atom is sp^2-hybridised and the σ-bond is formed by the use of the electrons of the molecular orbitals localised between the nitrogen and oxygen atoms. In addition to the ten electron pairs there are another three $2p\pi$-electrons which can form a three-electron bond uniting all three atoms:

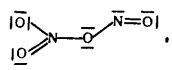


The total bond order should therefore be > 1, but < 1.5, which corresponds to a bond length of 1.20 Å. This lies between the values for the normal N–O (1.43 Å) and double N=O (1.16 Å) bonds[66-70].

X-Ray diffraction studies and data from entropy determinations support a symmetrical structure for dinitrogen tetroxide:



Since in such a structure the neighbouring nitrogen atoms have formal charges of the same sign it could be assumed that the unsymmetrical structure

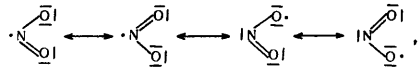


would be more stable.

The chemical properties of dinitrogen tetroxide agree better with the latter structure, as this compound can be used both for diazotisation[71] and for nitration[72].

Nitrogen dioxide is one of the most chemically active of compounds: carbon, sulphur, and phosphorus burn in it. Its free-radical nature is clearly apparent in its reactions of recombination, addition, and initiation[73-76].

Exhibiting a free valency, delocalised at the oxygen and nitrogen atoms:



nitrogen dioxide almost always displays a marked duality of reactivity in its reactions[77,78].

The EPR spectrum of nitrogen dioxide (Fig. 1) is a triplet with a separation of 47.1 Oe between the components. Such an appreciable value for the hyperfine splitting constant is apparently explained by an appreciable contribution of the s-state in the ψ-function of the unpaired electron[79]:

$$\psi = a_1\psi_N(2s) + a_2\psi_N(2p_Z) + b\psi_0(2p_Z).$$



Fig. 1. The EPR spectrum of nitrogen dioxide at 77°K.

In the best resolution of the spectrum into its hyperfine structure there is a large number of components of a rotational-magnetic structure due to independent quanta in the magnetic field of the electron-spin, nuclear-spin, and magnetic moments of the species[50,80]†

3. FREMY'S SALT‡

Over a century ago Fremy obtained a yellow salt of composition $K_2S_2O_7N$, which dissolved in water to give a purple-violet solution[81]. This salt is readily obtained by the action of lead dioxide on an alkaline solution of the corresponding hydroxylimidodisulphate[82]:

$$(KO_3S)_2NOH \xrightarrow[PbO_2]{-H} (KO_3S)_2NO.$$

The initial dipotassium hydroxylimidodisulphate can be obtained by the reaction of sodium nitrite and potassium hydrogen sulphite in aqueous solution[83]. The sodium[84], tetraphenylarsonium[85], and tetraphenylstibonium[86] Fremy salts are also known.

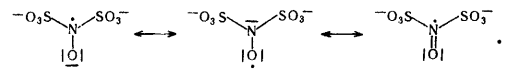
By analogy with dinitrogen tetroxide Fremy ascribed a dimeric structure to the solid salt which breaks down in solution into monomeric anions[87]:

$$(KO_3S)_4N_2O_2 \rightleftarrows 4K^+ + 2ON(SO_3)_2^-.$$

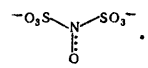
The analogy with nitrogen dioxide is well evident in the reaction of the salt with nitrogen monoxide and the reaction of the resulting addition product with water[88]:

$$(KO_3S)_2NO + NO \rightarrow (KO_3S)_2NONO,$$
$$(KO_3S)_2NONO + H_2O \rightarrow (KO_3S)_2NOH + HNO_2.$$

The bond between the oxygen and nitrogen in the Fremy ion is donor or semipolar, so that the unpaired electron is delocalised between the nitrogen and oxygen atoms of the NO group; the free ion-radical can therefore be described with the aid of several electronic structures:



In a more general form the structure of this radical can be represented with the aid of a formula including a three-electron bond:



The stability§ of Fremy's salt[90-96] in solutions is due to the low level of the ground state of the species which has a three-electron bond[97,98].

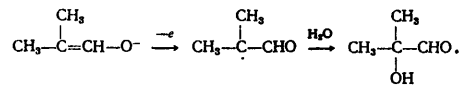
The unusual chemical properties of Fremy's salt permits its use as a selective one-electron oxidant of aromatic amines and phenols[99]. Many *ortho*- and *para*-quinone imines and quinones have been thus obtained in high yields[100-107].

† Ref. 50 is to the EPR spectrum of nitrogen monoxide. Probably Ref. 51 is intended here (Ed. of Translation).]

‡ The anion of Fremy's salt is encountered in the literature under various names: peroxylaminodisulphonate, nitrosyldisulphonate, nitrosodisulphonate, disulphonatonitroxyl, etc.

§ An aqueous solution of Fremy's salt can be kept under ordinary conditions for a few days[89].

Isobutyraldehyde is also smoothly oxidised by Fremy's salt into α-hydroxyisobutyraldehyde, the reaction passing through the stage of single-electron oxidation of the anion of the enol[108]:

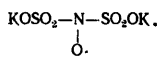


The reaction of Fremy's salt with hydrazine and hydroxylamine allows it to be used for the analytical determination of these reagents[109,110]:

$$4(KO_3S)_2NO+N_2H_4 \rightarrow 4(KO_3S)_2NOH+N_2,$$
$$4(KO_3S)_2NO+2NH_2OH \rightarrow 4(KO_3S)_2NOH+N_2O+H_2O.$$

It has been used successfully in weakly alkaline solutions as a photographic developer[111].

A mechanistic analysis of the chemical reactions suggests that almost all the radical reactions of Fremy's salt take place at the oxygen atom of the NO group, in accordance with the imidoxyl electronic structure of this radical:



The EPR spectrum (Fig. 2) of the Fremy anion (in chloroform) is a triplet with components which are equidistant and of the same intensity, the distance between them being ~13 Oe, and the breadth of each < 0.5 Oe.[112-114]. The hyperfine structure of the EPR spectrum agrees well with the theoretical expectation of interaction of the unpaired electron with the nuclear spin of the nitrogen[115]. A detailed study of the fine structure of the EPR spectrum of Fremy's salt[116-118] enabled it to be used for calibrating radiospectrometers[86].

With the discovery of the dynamic polarisation of nuclei[119-121] (the Overhauser–Abragam effect) Fremy's salt unexpectedly acquired exceptionally important practical value[122-129]. The Overhauser effect, which forms the basis of the double nuclear–electron resonance method, allows the hyperfine structure of EPR spectra of extremely dilute solutions of free radicals to be investigated in weak magnetic fields, where the usual EPR method is insufficiently sensitive.

Aqueous solutions of Fremy's salt are now being used both in the USSR and abroad for the construction of highly sensitive nuclear precession magnetometers[125-128].

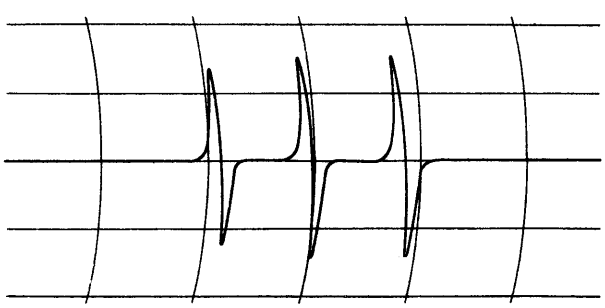
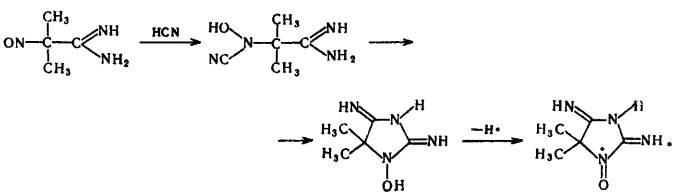


Fig. 2. The EPR spectrum of a chloroform solution of Fremy's salt.

Fremy's salt has found an important application as the working material in "Maser" type devices[129] and also for studying the nature of molecular motion and the microstructure of liquids[130] by the spin-echo method[131,132].

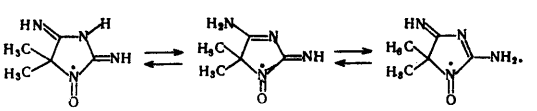
4. NITROXIDES

The paramagnetic compounds of this class are often called in the literature free radicals of quadrivalent nitrogen. The first organic radical of quadrivalent nitrogen was obtained in 1901 by Piloty and Schwerin[133] by the scheme:



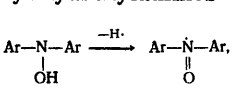
It is a brick-red substance, known as porphyrexide¶, which is reminiscent of nitrogen dioxide and Fremy's salts in its chemical properties. Moreover, porphyrexide readily displaces chlorine from hydrochloric acid, reacts with nitric acid, with alkalis, and also with chlorine to give mono- and di-chloroporphyrexides[134]. The possibility that some of these reactions take place without use of the free valency is not ruled out. Unfortunately neither the structure nor the paramagnetism of the porphyrexide derivatives was established.

Later magnetic susceptibility[135] and EPR spectroscopic studies[136,137] confirmed the free-radical nature of porphyrexide as a nitrogen(IV) compound. The EPR spectrum of porphyrexide is a triplet with a separation of 10 Oe between components, but the hyperfine structure of the components of the triplet has not been interpreted unambiguously. Hausser assumes[138] that the complexity of the hyperfine structure can be explained by the existence of an equilibrium between a few valence-tautomeric† forms in porphyrexide solutions:



In all the tautomeric structures of porphyrexide the bond between the nitrogen and the oxygen is semipolar or donor, which undoubtedly corresponds to a lower (stable) energy level due to possible formation of a conjugated diene or triene system of bonds by which the unpaired electron may be delocalised.

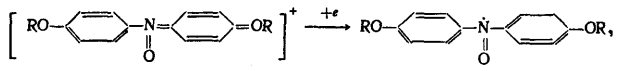
The individual diaryl nitroxides can be sufficiently reliably obtained by one of three methods — by careful oxidation of the diaryl hydroxylamines[139]:



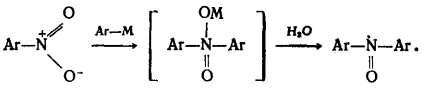
¶ Because its colour is similar to that of murexide (ammonium purpurate).

† [sic]. The author means tautomerism, not valency-tautomerism (Ed. of Translation).

by single-electron reduction of corresponding alkoxyl derivatives of the oxides of diarylammonium salts with perchloric acid [140]:



and by the action of organometallic compounds on nitro--compounds [141]:



The radicals of this class are red, crystalline compounds, stable in air. An important property of these substances is their ability to retain paramagnetism even at very low temperatures (-60°C).

The high stability of aromatic nitroxides permits their detection in a different type of oxidising system which includes aromatic amines,

Hoskins [142] observed the EPR spectrum of diphenyl nitroxide on passing oxygen through a hot mixture of toluene, alcoholic alkali, and diphenylamine. The catalytic oxidation of solutions of aromatic derivatives of naphthylamine, methylaniline, aniline, and phenothiazine also led to the appearance of corresponding EPR signals [143]. Apparently, stable nitroxides can be obtained from a large number of aromatic amines and are widely used as antioxidants and polymerisation inhibitors. EPR has been used to study the oxidation of many aromatic amines in the liquid phase [144,145]. However, it must be borne in mind that the EPR spectrum does not always give unambiguous information about the chemical structure of the oxidation product.

The preparation of the pure free radicals of this class is known to be difficult, which explains why only a few diaryl nitroxides have been isolated in the free state during the last fifty years (Table 1).

The stability of the diaryl nitroxides depends on various factors, including the electronic and steric effects of the substituents, the overall symmetry of the chemical species, the nature of the crystal lattice of the material, etc.

Of the three possible structures for diphenyl nitroxide, the first and last correspond to the maximal gain in energy due to conjugation of the nitrogen–oxygen bond with the aromatic system:

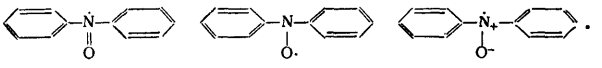
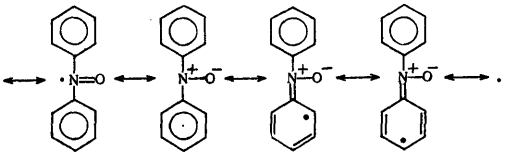


TABLE 1. Individual diarylnitroxides 

R						M.p., °C	Stability	References
1	2	3	4	5	6			
						64	days	139, 146, 147–155
CH_3	CH_3					59–60	hours	146, 147
NO_2	NO_2					109	months	146, 156
CH_3O	CH_3O					161	years	140, 146, 147, 156–171
CH_3O	CH_3O	CH_3O		CH_3O		121.5–122	unstable	140, 157, 158
CH_3O	CH_3O	CH_3	CH_3	CH_3	CH_3	163		140, 158
CH_3O	CH_3O	CH_3O	CH_3	CH_3O	CH_3	175		158
		CH_3O	CH_3O	CH_3O	CH_3O	199–200		141
CH_3O				CH_3O	CH_3O	114.5–115		141

The hyperfine structure of the EPR spectrum of diphenyl nitroxide [172] showed that it can be described with the aid of several electronic structures of covalent and ionic type, the relative contribution of which depends on the polar properties of the medium.



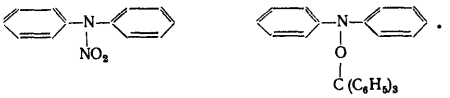
The hyperfine structure of the EPR spectrum of diphenyl nitroxide (Fig. 3) consists of three groups of lines due to the splitting of the level of the unpaired electron at the nitrogen nucleus. Each group is divided into a large number of components owing to delocalisation of the unpaired electron by the π-orbital system of the aromatic nuclei and its interaction with the protons [173].

An analysis of the spectroscopic parameters shows that ~40% of the spin density is at the nitrogen atom, 30% at the oxygen, and 30% at the *ortho*- and *para*-positions of the aromatic nuclei [153].

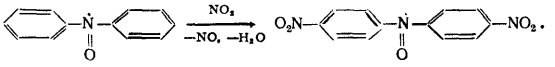
The dipole moments [155,174], the intensity of the colour, and the reactivity of the homologues and derivatives of diphenylnitroxide are consistent with these conclusions.

Wieland and his many students [175] have made the outstanding contributions to the study of the reactivity of diaryl nitroxides.

Aromatic nitroxides rapidly combine at the nitrogen and oxygen with nitrogen(II) oxide and triphenylmethane to form the corresponding derivatives [139]:



The principal interest lies in the reaction of diphenyl nitroxide with nitrogen dioxide, which leads to the formation of a new free radical, 4,4′-dinitrodiphenylnitroxide [147,176]:



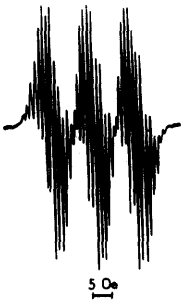
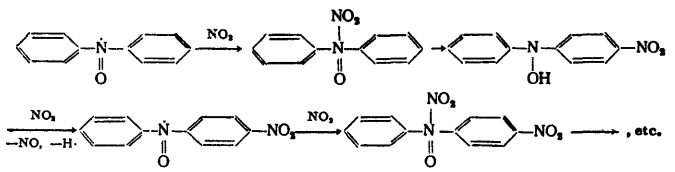
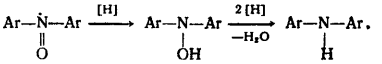


Fig. 3. The EPR spectrum of a benzene solution of diphenyl nitroxide.

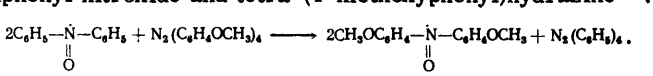
Wieland and Roth[146] demonstrated the complexity of this reaction, which takes place through a series of successive stages‡:



Nitroxides are readily reduced by hydrogen iodide, zinc dust, hydrazine, tin(II) chloride, sulphurous acid, hydrogen sulphide, and hydrogen in the presence of hydrogenation catalysts:



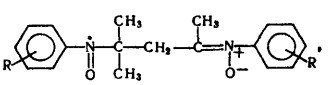
An unusual exchange reaction takes place between diphenyl nitroxide and tetra-(4-methoxyphenyl)hydrazine[147]:



A similar exchange reaction was observed by Möbius and Schneider[177] between 2,2-diphenyl-1-picrylhydrazyl and the peroxide radical[177].

In recent years much attention has been paid to the study of isotropic hyperfine structure parameters of the EPR spectra of diaryl nitroxides. Usually the liquid solutions of these radicals at concentrations $< 10^{-3}$ M show, in addition to the nitrogen triplet, a rich hyperfine structure due to the delocalisation of the unpaired electron at the aromatic nuclei and its reaction with the various *ortho*- and *para*-substituents[157]. For example, the EPR spectrum of bis-(4-methoxy-2,6-dimethylphenyl) nitroxide (Fig. 4) consits of three groups of lines reflecting the interaction of the unpaired electron with the nitrogen nucleus (a_N = = 10 ± 0.3 Oe). Each group has hyperfine structure components with a binomial distribution of intensities due to the splitting of the electronic levels at the 12 protons of the methyl groups and 4 *meta*-protons of the aromatic ring (a_H = 0.8 ± 0.1 Oe). Hence the splitting of the level of the unpaired electron at the methyl groups of the aromatic nuclei serves as a direct experimental proof of the phenomenon of hyperconjugation. Fig. 5 shows the scheme of the interaction of the π-orbital system containing an unpaired electron with the protons of the methyl group.

A special class of aromatic nitroxides is formed by the radicals in which the nitrogen–oxygen group is conjugated with only one aromatic nucleus. A long-known representative of this group is the so-called Banfield and Kenyon's radical, which can be obtained by oxidation of the condensation product of acetone and phenylhydroxylamine[178,179]. Several individual compounds of this class have been described[180,181]:



where R = H, *o*-CH_3, *m*-CH_3, *p*-CH_3, *m*-F, *p*-F, *m*-Cl, *p*-Cl, *m*-Br, *p*-Br, *m*-NO_2.

‡ Analogous reactions can apparently also occur with porphyrexide, mentioned earlier.

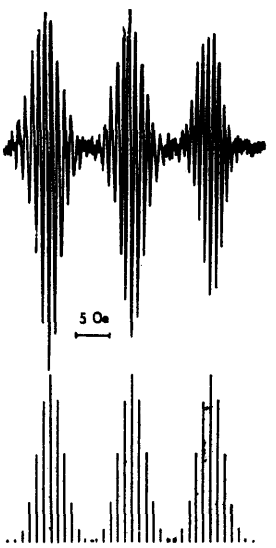


Fig. 4. The EPR spectrum of a benzene solution of bis-(4-methoxy-2,6-dimethylphenyl) nitroxide, with the theoretically calculated spectrum (below).

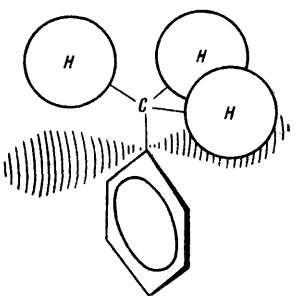
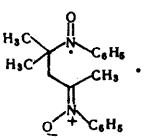


Fig. 5. Scheme of the overlap of the electron clouds of the hydrogen atoms of the methyl group with the π-orbital of the aromatic ring.

The well-resolved EPR spectrum of the Banfield and Kenyon radical was obtained with an oxygen-free tetrahydrofuran solution of the substance. Each of the three quadruplets of the hyperfine spectrum is split into seven lines with a non-binomial distribution of the intensities (Fig. 6).

Detailed analysis of the spectrum showed hyperfine interaction of the unpaired electron with the most removed methyl group, which conformationally can approach closely to the aromatic nucleus containing the unpaired electron[182]:



The other radicals in the series which are known as individual compounds include *trans*-decalyl phenyl nitroxide (I),[183-186] t-butyl 2,6-dimethoxyphenyl nitroxide (II),[141] and 2,6-dimethoxyphenyl 1,1-dimethylbenzyl nitroxide (III).[141] All these substances are obtained by the action

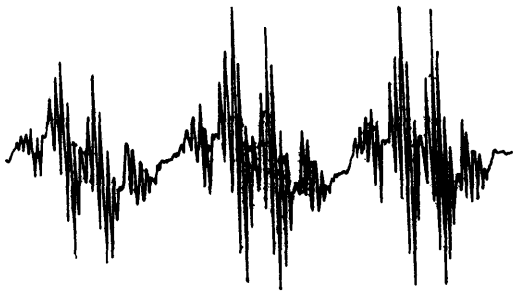
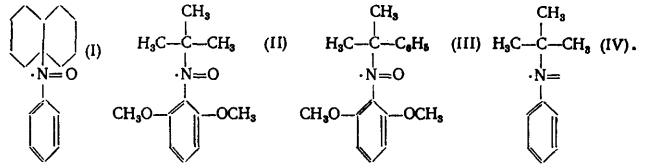


Fig. 6. Hyperfine structure of the EPR spectrum of the tetrahydrofuran solution of the Banfield and Kenyon radical.

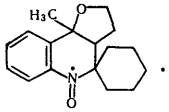
of organometallic compounds on the corresponding nitroso- or nitro-compounds:



(I) m.p. 83°C; (II) m.p. 101–102.5°C; (III) m.p. 77–78°C; (IV).

Attempts to isolate from solution the individual compound t-butyl phenyl nitroxide (IV) were unsuccessful [141,187,188], despite its obvious structural similarity with (I)–(III).

A large number of aliphatic–aromatic nitroxides is known in solution, but there is not always sufficient basis for ascribing to them a definite structure [189,190]. Many stable nitroxides of the hydrogenated quinoline series were first studied in solution by Razuvaev and coworkers [191,192], but only one individual radical of this class has been obtained pure [193].

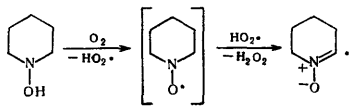


m.p. 101–101.5°C

The hyperfine structure of the EPR spectrum of this radical is a noniplet with ratio of intensities 1 : 2 : 1 : 1 : 2 : : 1 : 1 : 2 : 1, due to the splitting of each component of the nitrogen triplet (a_N = 11.8 Oe) into three lines by the interaction of the unpaired electron with the two protons at positions 6 and 8 of the aromatic ring (a_H = 2.9 Oe).

5. IMINOXYLS

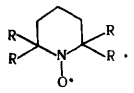
Free iminoxyl radicals§ is the name given to compounds of oxygen(I), which are formed as intermediates in the oxidation of secondary saturated amines [194] and hydroxylamines, for example,



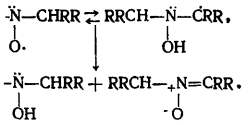
§ This term emphasises the genetic connection of iminoxyls with other radicals of oxygen(I), for example, with hydroxyl (H—O·), alkoxyl (R—O·), and aroxyl (Ar—O·). The terms "amine oxide", "nitroxide", and "aminoxy-radical" are less convenient, as they do not reflect the free-radical nature of these species and contradict the rules for the official nomenclature of organic compounds.

In contrast with the nitroxides it is essential that the NO group of the iminoxyls does not participate in the formation of a conjugated system of multiple bonds, and therefore that the unpaired electron apparently remains localised on the oxygen to a considerable extent.

The existence of free iminoxyls in solutions was first postulated by Rogers and coworkers [195,196]. Rogers assumed that free iminoxyls not possessing α-hydrogen atoms should be stable free radicals. For example, the iminoxyl of piperidine is unstable, but those completely alkylated in positions 2 and 6 of the heterocycle should be stable:

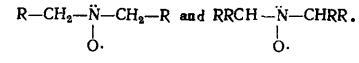


Apparently the substituents R can be not only organic residues, as it is important that the iminoxyls should not be capable of tautomeric conversions of the type:



Lebedev and Kazarnovskii obtained the simplest free radicals of this class by the oxidation of 2,2,6,6-tetramethylpiperidine [197]. The EPR spectrum of this radical in benzene is a triplet with a hyperfine splitting constant of ~ 15.6 Oe [198,199]. Samitov and Lebedev [200] ascribe the anisotropy of the spectrum to contributions from different quantum states in the sublevels of the hyperfine structure and the influence of the quadrupole moment of the nitrogen nucleus [200].

By analysing the parameters $\psi^2(0)$, a_N, and a_H of the EPR spectra of solutions of free iminoxyls in benzene, obtained by oxidising a series of secondary amines and hydroxylamines [201,202], Coppinger and Swalen concluded that the most plausible electronic structure of these radicals corresponds to the formulae:



Hence the valence state of the nitrogen atom, similar to the analogous state of nitrogen in substituted hydroxylamines [66], corresponds to the formula:

$$N[(1s)^2\ (2s+\delta 2p)^2\ (2p+\delta' 2s)^2\ (2p+\delta'' 2s)].$$

The $(2p+\delta' 2s)$ atomic orbitals, being equivalent, should form localised bonding orbitals with the hybrid sp^3-orbitals of the carbon atoms. The $N(2p+\delta'' 2s)$ atomic orbital will overlap with the corresponding orbital of the oxygen atom, forming a third localised orbital.

The EPR spectrum of dialkyliminoxyls in solutions exhibit hyperfine structure due to the interaction of the spin of the unpaired electron with the nuclear spins of the nitrogen atom and the hydrogen atoms adjacent to it (Fig. 7). Table 2 gives the main parameters of the hyperfine structure in the EPR spectra of the free iminoxyls in dilute benzene solutions.

The hyperfine splitting from the nitrogen and hydrogen nuclei is explained by the principal state of the radical's

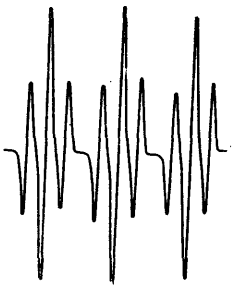
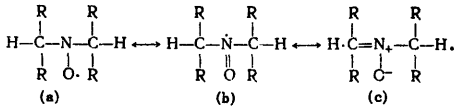


Fig. 7. Hyperfine structure of the EPR spectrum of a benzene solution of di-s--butyl iminoxyl.

TABLE 2. Fundamental parameters of the EPR spectra of free iminoxyls [201].

Formula	a_N	a_H	Number of components	Formula	a_N	a_H	Number of components
$(CH_3CH_2)_2NO$	15.5	10.6	15	$(CH_3CH_2CH)_2NO$	15.4	4.1	9
$(CH_3CH_2CH_2)_2NO$	15.5	10.6	15	CH_3			
$(CH_3CH_2CH_2CH_2)_2NO$	15.7	10.5	15	$(C_6H_5CH_2)_2NO$	15.6	9.5	15
CH_3				$(CH_2{=}CH{-}CH_2)_2NO$	15.5	9.3	15
$(CH_3CH)_2NO$	16.0	4.7	9	$CH_3CH_2CH_2CH_2CH_2NO$	15.4	11.7	15

being capable of representation with the participation of a few valence-isomeric structures [203,204]:



Closely related to the dialkyliminoxyls is a class of labile alkylidene iminoxides of the general formula:

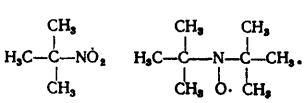


The first radical of this type was observed on subjecting single-crystal dimethyl glyoxime to γ-radiation [205-207].

Many alkylidene iminoxyls were studied in liquid solutions by a flow method [208], using cerium ammonium nitrate [209] and lead tetra-acetate [210] as oxidants.

Most alkylidene iminoxyls are extremely unstable and in the liquid phase many of them have a lifetime measured in fractions of a second, therefore none of the compounds of this class can be obtained in the pure state.

In 1961 Hoffmann and coworkers, using Maki's method [211], observed two EPR spectra (Fig. 8) during the polarographic reduction of 1,1-dimethyl-1-nitroethane, one of these spectra showing the appearance of an unstable anion-radical, and the other belonging to the stable di-t-butyl iminoxyl [212,213]:



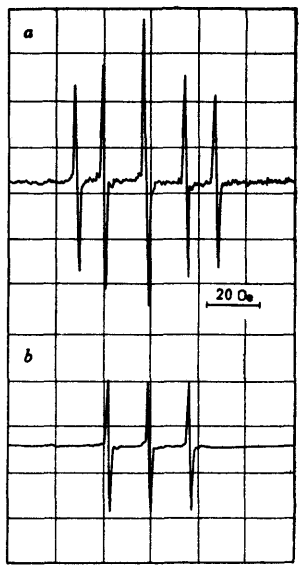


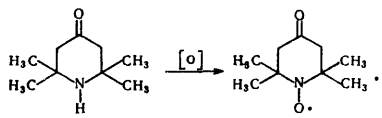
Fig. 8. EPR spectra:
a) mixture of the anion radical of 1,1-dimethyl--1-nitroethane and di-t-butyl iminoxyl; *b*) di-t--butyl iminoxyl (in 1,2-dimethoxyethane).

Di-t-butyl iminoxyl, obtained pure in the reaction of 1,1-dimethyl-1-nitroethane with sodium, is a red liquid, stable in air up to 120°C. [214,215] It is interesting that in the well-resolved hyperfine structure of the EPR spectrum of this radical in addition to three fundamental lines a system doublets — satellites of low intensity — can be observed owing to the interaction of the unpaired electron with the nuclei of the ^{13}C carbon isotope of the methyl groups [216].

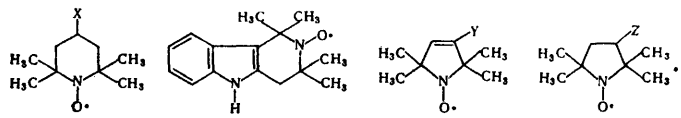
On heating a solution of phorone with a mixture of ammonium nitrate, sodium hydroxide, Trilon B, hydrogen peroxide, and sodium tungstate [217] Razuvaev and coworkers observed that for a few weeks this solution gave a triplet signal which they assumed to belong to a stable radical of triacetonamine formed in the solution [218].

Using preparative thin-layer chromatography on aluminium oxide to separate the paramagnetic mixture, Neiman and coworkers actually separated pure crystalline 2,2,6,6--tetramethyl-4-oxo-piperidine 1-oxide [219].

A new iminoxyl was obtained in high yield by the direct catalytic oxidation of triacetonamine [220]:



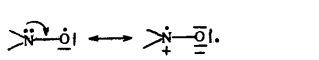
Within a short time many individual iminoxyls of the most diverse structure were synthesised, including [221-225]:



All the free radicals of this series exhibit a singlet when pure, but in solutions they have triplet EPR spectra with a hyperfine splitting constant of ~ 15.5 Oe.

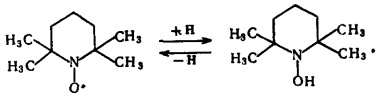
In addition to the ultraviolet, infrared, and EPR spectra, the volatility [226], heat of combustion, and dipole moments of the simplest free iminoxyls have been studied [227].

It is significant that the increase in dipole moment in a free radical, compared with the corresponding hydroxylamine, can in the first approximation be explained by the interaction of the unshared electron pair of the nitrogen atom with the partly free p-orbital atom of the oxygen. Displacement of one of the electrons of the unshared pair of the nitrogen atom to the oxygen atom brings both an increase in the dipole moment of the nitrogen–oxygen bond, and the appearance of spin density at the nitrogen atom:



Comparison of the dipole moments of the radicals and of the corresponding hydroxylamines allowed the distribution of the spin density of the unpaired electron at the N–O bond to be evaluated approximately. The spin density was 27% at the nitrogen atom and 73% at the oxygen atom. Hence the most probable structure of the free iminoxyls is evidently the Coppinger structure [201].

The reduction of free radicals at a mercury dropping electrode [228], hydrogenation [229], and reaction with an alcoholic solution of phenylhydrazine [230] or with an acid solution of a substituted p-phenylenediamine [231] – all these processes lead to the formation of the corresponding substituted hydroxyalamines:

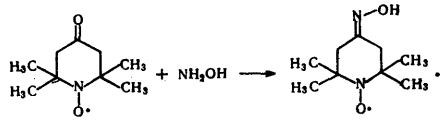


Free iminoxyls readily react with alkyl radicals, which can be used for inhibiting chain radical processes [232-236].

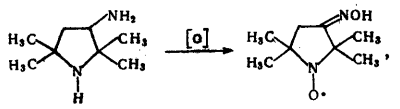
Hence all the free radical reactions of iminoxyls which have been studied proceed exclusively with formation of oxygen derivatives of substituted hydroxylamines, which is also some proof of the predominant localisation of the unpaired electron at the oxygen atom in accordance with the Coppinger structure [201]. However, no proof yet exists that such reactions cannot be accompanied by redistribution of the electron density on the approach of the attacking reagent.

The most notable property of free radicals of this series is their reactions without use of the free valency. This type of reaction can undoubtedly be assumed in various types of chemical and biological systems, especially with high-molecular weight compounds. Nevertheless an unambiguous demonstration that radicals react without participation of the unpaired electron is not available.

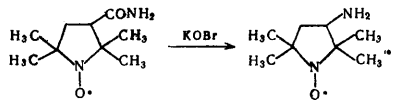
In 1962, Neiman and coworkers first gave an unambiguous proof of the reaction of stable iminoxyls without use of the free valency [237,238], for example¶:



The discovery and organised study of all the possible reactions of iminoxyl radicals without use of the free valency [239-242] defined the limits of its usefulness and this reaction was made a reliable instrument for the synthesis of previously inaccessible free radicals. As an example, it was impossible to obtain an amine radical by oxidising aminopyrrolidine,

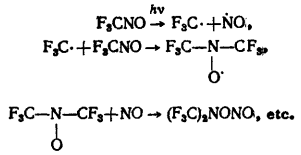


whereas a reaction which did not involve the free valency readily led to the desired product [243]:



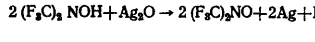
Free iminoxyl radicals very soon acquired great popularity and became the object of steady attention from chemists, physicists, and biologists [244-249].

A study appeared in 1957 which showed that the photochemical decomposition of trifluoronitrosomethane leads to the intermediate formation of bis(trifluoromethyl)-iminoxyl radicals, the existence of which can be judged from their conversion products [250].



Perfluorinated iminoxyl radicals were observed by the EPR method during the polymerisation† of perfluoroethylene in the presence of trifluoronitrosomethane [251] (Fig. 9).

Free bis(trifluoromethyl)nitroxyl was obtained in 1964 by the action of silver oxide on bis(trifluoromethyl)hydroxylamine [253]:



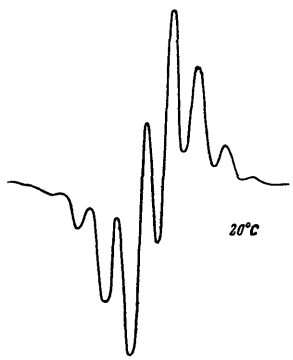


Fig. 9. EPR spectrum of the perfluoroiminoxyl radical.

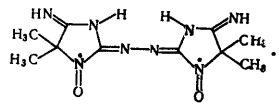
¶ We must remember that Fremy's salt reacts with hydroxylamine by use of the free valency [110].

† Almost simultaneously the hypothesis was propounded that the initiation of the copolymerisation of trifluoronitrosomethane and fluoroalkenes takes place by an anionic mechanism [252].

The same radical was recently obtained pure by a group of Soviet scientists [254,255] who made a detailed study of its properties. It is a violet-pink gas, which readily condenses to a diamagnetic dimer containing ~ 1.5% of the free radical. From the electronic structure of this radical it apparently occupies a position intermediate between the iminoxyls and Fremy's salt.

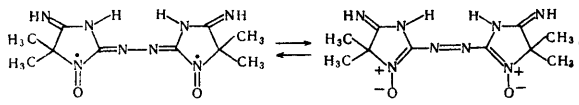
6. INDIVIDUAL POLYRADICALS

As long ago as 1903, Piloty and Vogel, by the reaction of porphyrexide with hydrazine and then with potassium cyanoferrate(III), first obtained a dark blue crystalline compound, which they called porphyrindine [256]:

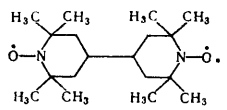


The free-radical nature of this substance was subsequently reliably established by measurement of its magnetic susceptibility [257].

The diamagnetic principal state of porphyrindine is in thermodynamic equilibrium with the excited paramagnetic state which lies only a little higher. This equilibrium shifts in favour of the paramagnetic state on raising the temperature [258]:

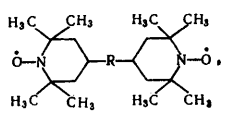


The first representative of the kinetically stable biradicals of the iminoxyl class was obtained during the oxidation of 2,2,2′,2′,6,6,6′,6′,-octamethyl-4,4′-bipiperidyl [259]:



During the study of this substance the discovery was made of the extremely interesting phenomenon of conformational electronic exchange, which is shown in the quintuplet nature of the EPR spectrum (Fig. 10).

To show the mechanism of the interaction of the unpaired electron with the nuclear spins of both nitrogen atoms a series of individual biradicals of diverse chemical structure was synthesised [260]:



where R = OCOO, NHCONH, $OCOC_6H_4COO$, $OCONH[CH_2]_6$. .NHCOO, or $OCO[CH_2]_nCOO$ (n = 0–8). The main method of preparation of the biradicals was by reaction of radicals without use of the free valency. It was found that the effectiveness of the conformational spin–spin interaction is determined not only by the length but also by the flexibility

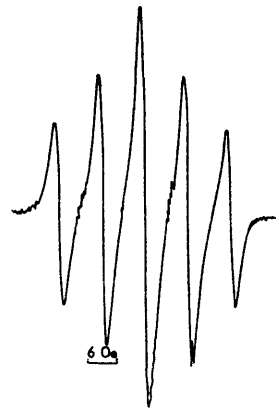
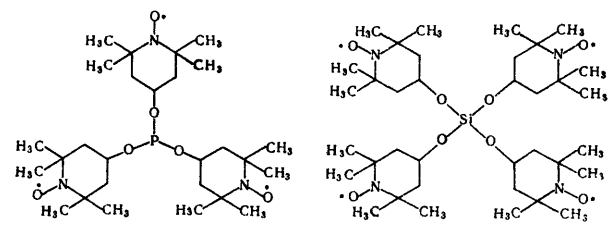


Fig. 10. Hyperfine structure of the EPR spectrum of the first kinetically stable bis--iminoxyl (chloroform solution).

of the bonding chain R, for example, on replacing a polymethylene bridge by p-phenylene, the effect disappeared and the EPR spectrum again became a triplet‡.

A study of free biradicals of the iminoxyl class by the EPR method at different temperatures and in various solvents showed that spin–spin exchange interaction takes place during conformational collisions of two paramagnetic fragments of bis-iminoxyl [266].

A reaction without use of the free valency was successfully used in the syntheses of the first individual free tri- and tetra-radicals of the iminoxyl type [267,268], for example:



The EPR spectra of the triradicals are septets of lines due to the interaction of unpaired electrons with the magnetic moments of three nitrogen nuclei, and for the quadriradicals there are nine components with a separation of ~ 4 Oe between them.

The study of the exchange interaction in polyradicals at different temperatures showed that there is only paired interaction with the neighbouring paramagnetic fragments and during this all the spins of the polyradicals participate in the electronic exchange. In this way instances were first discovered in which the number of unpaired electrons participating in the exchange exceeds two. This brings about the successive transfer of the excitation from one spin to another through the paired collisions. Here we encounter the unusual "memory" of the electron, which is capable of giving information about excitation with a definite rate along the chain of paramagnetic fragments [269].

‡ The EPR spectra of triarymethyl biradicals [261–265] are not significantly different from the analogous spectra of free triarylmethyls.

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REACTIONS OF EPOXYALKANES TAKING PLACE WITH EXPANSION OF THE OXIRAN RING

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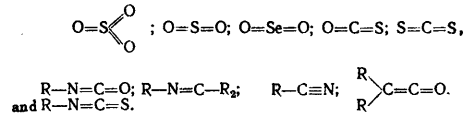
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1. INTRODUCTION

Epoxyalkanes are known to be very reactive; their many reactions have been adequately studied and described in the literature [1-4]. Most of the reactions of epoxyalkanes are accompanied by opening of the epoxide ring. Reactions accompanied by enlargement of the ring have been much less studied. The best known among these reactions are the dimerisation of the oxides and the reaction of the oxides with aldehydes and ketones, leading to the production of dioxolans.

The reactions of the oxides with carbon dioxide, leading to cyclic esters of carbonic acid, have also been studied. This process has been carried out on an industrial scale. The alkylene carbonates obtained find application in organic synthesis, as a solvent and for the production of polymers. The methods of making alkylene carbonates, their properties, and applications have been reviewed [5,6].

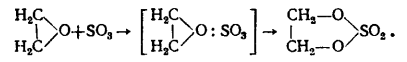
Cyclic products have now been obtained by the reaction of oxides with certain other compounds containing multiple bonds. Such compounds are:



2. REACTIONS WITH SO_3, SO_2, AND SeO_2

The epoxyalkanes react with the anhydrides of some inorganic acids to form cyclic esters.

Thus ethylene sulphate was obtained by the reaction of sulphur trioxide with ethylene oxide in dioxan. It is suggested that initially a coordination compound of sulphur trioxide with ethylene oxide is formed, which then rearranges into the ester [7]:



1,4-Oxathian can be used instead of dioxan [8]. Cyclic alkylene sulphates with 2–6 carbon atoms are obtained by the reaction of corresponding epoxyalkanes with sulphur trioxide in the gas phase at 140°. Sometimes the reagents are diluted with inert gas. 0.1–7.5 moles sulphur trioxide per mole oxide are taken. The cyclic alkylene sulphates formed are removed from the reaction mixture by sublimation [9].

The addition of sulphur dioxide to epoxyalkanes has been studied in greater detail. When sulphur dioxide is passed into ethylene oxide at below 0°, a molecular compound of composition $C_2H_4OSO_2$ is formed [10]. It is used for sterilising soil, as its boiling point is about 20 deg above that of its components.

To obtain ethylene sulphite the reaction is carried out at a higher temperature, either without a catalyst or in the presence of various catalysts. When a catalyst is not used, the ethylene oxide and sulphur dioxide are mixed in the liquid phase and heated under pressure to 140°. The patent states that the reaction is almost complete [11].

Pyridine, amines, amides, phosphines [12], and also quaternary ammonium bases [13,14] have been proposed for use as catalysts in this process.