# THE FORMATION OF PHOSPHORUS-CONTAINING NITROXYL RADICALS IN THE PHOTOLYSIS OF 2-METHYL-2-NITROSOPROPANE IN ESTERS OF UNSATURATED PHOSPHONIC ACID

Ya. A. Levin, A. V. Il'yasov,
I. D. Morozova, A. Sh. Mukhtarov,
and M. S. Skorobogatova

One of the new methods of detection and identification by the ESR method of short-lived intermediate free radicals arising in homolytic conversions of organic compounds is the trapping of their nitroso compounds [1, 2].

$$R^\cdot + R^1NO \longrightarrow \begin{matrix} R \\ \diagdown \\ \diagup \\ R^1 \end{matrix} NO^\cdot$$
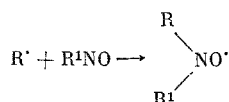
The nitroxyls formed in many cases are stable and are accumulated in solution to the concentrations necessary for their registering by the ESR method. If $R^1 = C(CH_3)_3$, then the observed spectrum is due chiefly to the interaction of the unpaired electron with the nucleus of the nitrogen atom and the magnetic nuclei of the fragment R. Therefore an analysis of the hyperfine structure (HFS) frequently permits a sufficiently unambiguous identification of R even in the presence of several types of unstable free radicals in the system, all the more in that the factors influencing the parameters of the ESR spectra of nitroxyl radicals are known [3].
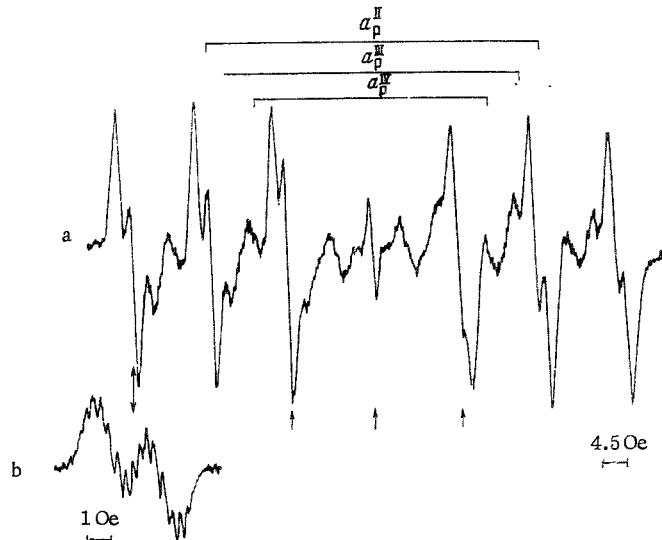

Fig. 1. ESR spectra: a) of free radicals formed in the photolysis of $(CH_3)_3NO$ in $CH_2 = CHP(O)(OCH_3)_2$; b) supplementary splittings of the lines of the radical (II).

TABLE 1. Parameters of the ESR Spectra* Observed in the Photolysis of MNP in α-Alkenyl-phosphonates $CH_2 = C - PX_2$ with Y and O

Y	X	Radical†	$a^P \pm 0,8$ Oe	$a^H \pm 0,1$ Oe
H	OCH_3	(II)	60,0	2,7
		(III)	53,4	2,7
		(IV)	42,3	1,5
H	OC_2H_5	(II)	60,0	2,7
		(III)	53,0	2,7
		(IV)	42,0	
CH_3	OCH_3	(III)	54,8	

*In all cases the triplet of the radical (I) is registered.
†The g-factor of all the phosphorus-containing radicals 2,0061 ± 0,0001, a^N = 14.3 ± 0.1 Oe.

There is information that the ESR method has been used to identify as nitroxyls the radicals that carry the chain in the radical isomerization of vinyl monomers $CH_2 = C \underset{X^1}{\overset{X^2}{<}}$ (M), inhibited by 2-methyl-2-nitrosopropane $(CH_3)_3CNO$ (MNP) [4, 5]. For the generation of such radicals there is no need to use the thermal decomposition of special initiators of the type of ferroxides or azobisisobutyronitrile (AIBN), as was done in the studies mentioned. The process can be initiated at low temperatures by the radicals that are formed in the photolysis of MNP [6].

$$(CH_3)_3 CNO \xrightarrow{h\nu} (CH_3)_3C^. + NO^.$$

Thus, after irradiation even for several seconds of a solution of MNP (10^{-3} M) in methyl acrylate with weak diffuse daylight or with an incandescent lamp at ~20°, an intense ESR signal of the same radical as in the case of initiation of thermal decomposition by AIBN is recorded [5]. Such a method proved to be most suitable for the generation of nitroxyl radicals with an α-phosphonalkyl group at the nitrogen atom from derivatives of vinylphosphonic acid. The thermal decomposition of AIBN at 60° gives a complex spectrum, evidently belonging to the decomposition products of the originally formed nitroxyl; the same spectra are recorded after heating at 60° of samples irradiated at ~20° and heating to 60° of nonirradiated samples that do not contain AIBN.

On the ESR spectra observed in the photolysis of MNP in dimethylvinylphosphonate (Fig. 1) it is evident that in addition to di-tert-butylnitroxyl (I), formed in the case of addition of a tert-butyl radical to the initial nitroso compound (triplet with a^N = 15.6 Oe and g = 2.0060), a series of nitroxyls are recorded, the scheme of formation of which is given for the example of dimethylvinylphosphonate.
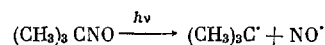

$R = C(CH_3)_3$

An analysis of the observed ESR spectrum shows that at least three types of phosphorus-containing free radicals are formed. The HFS of the ESR spectra of each of these radicals consists of six basic lines of equal intensity, due to the interaction of the unpaired electron with the nucleus of the phosphorus atom ^{31}P (I = 1/2) with constant a^P which, depending on the type of radical, lies within the range 40–60 Oe,* and

*Such a large doublet splitting is absent in the structurally analogous radicals formed in the same way from methylacrylate [5]; the values of a^N and a^H in them and in phosphorus-containing radicals, on the other hand, are close.

TABLE 2. Dependence of the Relative Content (% of Total) of Phosphorus-Containing Radicals from $CH_2=CH-P(O)^-(OCH_3)_2$ on the Concentration of MNP
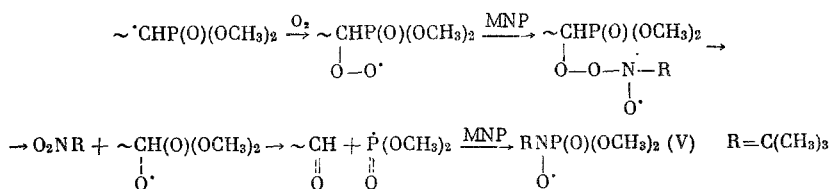
$[MNP] \cdot 10^3$, M	Radical with a^P, Oe		
	60,0	53,4	42,3
10	~100	~0	0
10	90	8	2
5	80	13	7
2,5	75	17	8
1,0	72	14	14

with the nucleus of the nitrogen atom ^{14}N (I = 1) with a^N = 14.3 Oe, coinciding with the value of a^N for nitroxyls of the type t-C_4H_9NC—

[1, 2] (Table 1). The further splitting of each of the six lines into a doublet is evidently due to the proton bonded to carbon in the α-position to the nitrogen atom.

The values of a^H cited in Table 1 are characteristic of a proton in the fragment t-C_4H_9NC—H [1-5]. In the case of a radical with a^P = 60.0 Oe (X = OCH_3, Y = H), further splitting of the indicated doublet into at least 10 lines with constant a ~ 0.37 Oe also appears; supplementary splittings with a low constant of the HFS are also noted for the radical with a^P = 53.4 Oe. Although the assignment of this small splitting cannot yet be considered rigorous, it seems probable to us that it is associated with the interaction of the unpaired electron with the magnetically nonequivalent protons of the tert-butyl group at the nitrogen atom on account, for example, of the direct overlapping in definite conformations of the s-orbitals of these protons with the orbitals of the phosphoryl group, which is more voluminous than the carbonyl and nitroxyl radicals, recorded in the polymerization of methylacrylate [5].

The ratios of the concentrations of all the recordable nitroxyls, estimated according to the intensity of the lines in the ESR spectra, do not change either during the process of irradiation or after it has ceased (for several hours) and depend only on the concentration of MNP, and moreover, in such a way that when it decreases (within the investigated range of concentrations) the fraction of the radical with the smallest a^P increases. The fraction of the radical with an intermediate value of a^P passes through a maximum, while that with a high value of a^P decreases (Table 2). Since the polymer chains generated when the inhibitor concentration is lowered have a longer time to grow, this result means that the difference in a^P is related to the number of monomer units added to the initiating radical and is an inverse function of this number, which also gives a basis for the assignment of phosphorus-containing radicals according to degrees of polymerization (II)-(IV), cited in Table 1. A similar phenomenon was observed in [4] in the polymerization of styrene inhibited by MNP; however, in this case only two types of radicals were recorded. Evidently in the case of phosphorus-containing radicals, the limitation of the spectral characteristics occurs at longer chain lengths.

In the series of radicals (I)-(IV), a certain increase in the width of the basic lines is also observed. The latter finding may be associated both with the difference in the contributions of the unresolved HFS from the peripheral magnetic nuclei to the width of these lines and (which seems more probable) with the change in the time of correlation of the Brownian motion.

The radicals formed in the photolysis of MNP in various α-alkenyl-phosphonates have very close constants of the HFS, which permits them to be assigned to the types (II)-(IV), just as was done in Table 1. The photolysis of MNP in dimethylvinylphosphonate in the presence of air is accompanied by the appearance of a supplementary spectrum of six lines of equal intensity. The parameters of this spectrum (g = 2.0061, a^P = 10.0 Oe, a^N = 13.0 Oe), correspond to the parameters of the nitroxyl radical with a phosphorus-nitrogen bond in (V) described in the literature [7]. The appearance of this radical may be explained by a scheme including the successive formation of a peroxide radical, its addition to MNP, γ-splitting of the peroxide aminoxyl formed, and, finally, β-splitting of the hydroxy radical, leading to the apperance of a phosphone radical in the system, the addition of which to MNP gives the observed stable nitroxyl with N—P bond:
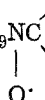
$$\sim \cdot CHP(O)(OCH_3)_2 \xrightarrow{O_2} \sim CHP(O)(OCH_3)_2 \xrightarrow{MNP} \sim CHP(O)(OCH_3)_2 \rightarrow$$

$$\rightarrow O_2NR + \sim CH(O)(OCH_3)_2 \rightarrow \sim CH + \dot{P}(OCH_3)_2 \xrightarrow{MNP} RNP(O)(OCH_3)_2 \text{ (V)} \quad R=C(CH_3)_3$$

TABLE 3. Parameters of the ESR Spectra of Liquid (298°K) and Frozen (77°K) Solutions of Radicals

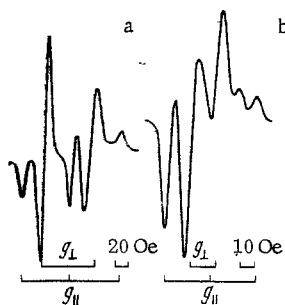| Radical	g-Tensor			Tensor of hyperfine interaction with the nitrogen nucleus				λ^N
	$g_{\parallel} \pm 0.0006$	$g_{\perp} \pm 0.0006$	$g_{iso} \pm 0.0001$	$B_{\parallel}^N$	$B_{\perp}^N$	A_{iso}^N	A^P	
(I)	2,0040	2,0076	2,0060	9,5	—4,8	15,6	—	4
(V)	2,0037	2,0089	2,0061	9,5	—4,8	10,0	13,0	5
(II)	2,0029	2,0076	2,0061	11,5	—5,8	14,3	60	5

Fig. 2. ESR spectra of frozen solutions of radicals: a) (II); b) (V) at 77°K.

Any of these stages is one of the alternative pathways of conversion of the corresponding radicals. At the natural content of oxygen in the solution, the accumulation of the radical with a N—P bond occurs more rapidly than that of the radicals observed in the absence of oxygen. However, after reaching a maximum the content of the phosphonenitroxyl (V) drops and becomes less than the concentration of the basic radicals (I)-(IV).

To determine the mechanism of the distribution of spin density, we were interested in studying the temperature dependence of the HFS constants and investigating the ESR spectra of frozen solutions. Measurements within the interval from −45 to +45° show that the constant of the HFS from the phosphorus nucleus in liquid solutions (the monomer served as the solvent) is practically unchanged. In frozen solutions (77°K) anisotropic spectra are observed (Fig. 2 and Table 3), like those observed previously for nitroxyl radicals that do not contain phosphorus [8]. The hyperfine interaction with the ^{31}P nucleus is practically isotropic. This may be evidence that the spin density on the phosphorus atom is basically of an s-character. The parameter of the hybridization of $\lambda^N = C_p/C_s$ (see Table 3) reflects the ratio of the spin densities on the p- and s-orbitals of the nitrogen atom and is calculated from the data of the anisotropic and isotropic spectra by the well-known method of [9]. The increase in its value in the series of radicals (I), (V), and (II) may be evidence of a change in the valence angles at the nitrogen atom.

Thus, the HFS from the ^{31}P nucleus in the radical (II) is practically isotropic; the mechanism of the transfer of spin density to this nucleus evidently cannot include any significant contribution of the effect of p—d conjugation. Likewise, the delocalization of the unpaired electron from the nitroxyl center to the vacant s-orbitals of the phosphorus atom also cannot make any appreciable contribution, since $_aP$ in the radical (V) with a direct bond of the phosphorus atom to the center is significantly less than a^P in the radicals (II)-(IV), where phosphorus is a β-substituent. The contribution of the spin polarization also probably is not great, since the values of $_a^H$ and $_a^P$ for both magnetic nuclei, connected to the same carbon atom, in the radicals (II)-(IV) do not exhibit any clear correlation (see Table 1). This is indicated by the closeness of the constants a^H in the radicals (II) and (III) and in the analogous radicals with a carbonyl group instead of the phosphoryl group [5].

It might be thought that interaction of the unpaired electron with the σ-bond of C—P is accomplished by means of hyperconjugation, and a definite role may also be played by spin polarization of the σ-electrons of the C—P bond, as occurs in the radical $\dot{C}H_2CH_2PEt_2$ [10]. This hypothesis is supported primarily by the large isotropic constant $_aP$.

Although usually the mechanism of hyperconjugation leads to a predominant orientation of the C—P bond in a position in which maximum overlapping between it and the radical center is realized [11], and the temperature change affects the value of $_a^P$ [12], in our case no temperature dependence of the HFS constants is observed. Possibly the voluminous substituents at the phosphorus create steric hindrances preventing any appreciable change in the conformational state of the radicals (II)-(IV) within the investigated temperature interval. If the basic contribution to the appearance of spin density on the phosphorus is made by hyperconjugation, then the change in $_a^P$ in the series of radicals (II)-(IV) means an influence of the number of monomer units added on the conformation of the nitroxyl.

CONCLUSIONS

1. In the photolysis of 2-methyl-2-nitrosopropane in esters of α-alkenylphosphonic acids, nitroxyl

radicals are formed with a phosphonealkyl group at the nitrogen atom on account of the addition of radical chain carriers to the nitroso compound during the radical polymerization of the phosphonates.

2. The constants of hyperfine interaction with the ^{31}P nucleus in the ESR spectra of the nitroxyls studied depend on the degree of polymerization of the radical to be trapped. The mechanism of this interaction is not associated to any appreciable degree with p–d overlapping and may include as the principal element the hyperconjugation of the orbital of the unpaired electron with the P–C bond.

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