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ESR study of radical intermediates formed upon photooxidation of 4,4´-diazidodiphenyl

S. V. Zelentsov,*★ *M. V. Kuznetsov, and N. V. Zelentsova

N. I. Lobachevsky Nizhnii Novgorod State University,
23 prosp. Gagarina, 603950 Nizhnii Novgorod, Russian Federation.
Fax: +7 (831 2) 65 8592. E-mail: zelen@ichem.unn.runnet.ru

Radical intermediates (phenyl and phenylcarbonyl radicals) formed in photooxidation of 4,4´-diazidodiphenyl in benzene and toluene have been studied by ESR spectroscopy. These radicals are formed as a result of abstraction of a hydrogen atom from a solvent molecule by the triplet nitrene—dioxygen complex.

Key words: photooxidation. azide, nitrene—dioxygen complex, radical products, ESR spectra, spin trap.

Photooxidation (PO) of organic azides involves intermediate formation of nitrene complexes with dioxygen in the triplet ($\mathrm{RNOO^T}$) and singlet ($\mathrm{RNOO^S}$) states.**[1—6]** Due to the small singlet—triplet splitting,**[6]** this reaction can proceed both on the singlet and triplet potential energy surfaces (PES) of RNOO. The qualitative and quantitative compositions of the major products formed in the PO of organic azides have now been studied fairly comprehensively.**[7—9]** It was suggested**[5]** that the PO of organic azides proceeding by the "triplet" mechanism affords nitroso compounds and radicals. However, this hypothesis has not yet been reliably verified.

The aim of this work is to study the chemical nature of the radical products formed in the PO of 4,4´-diazidodiphenyl.

Experimental

4,4´-Diazidodiphenyl (DADP) was synthesized as described previously.**[10]** Organic solvents (benzene, toluene) were purified by standard procedures.**[11]**

Photooxidation of DADP was carried out in a quartz reactor in the presence of dissolved dioxygen using the unfiltered light from a DRK-120 lamp. The intensity of the UV radiation was $0.022\ \mathrm{W\,cm^{-2}}$ and the concentration of DADP was 10^{-3} mol $\mathrm{L^{-1}}$.

ESR spectra were recorded using an AE-4700 radiospectrometer.

The radical products were identified by adding spin traps (ST).**[12]** 2-Methyl-2-nitrosopropane synthesized and purified by a known procedure was used as the ST.**[13]** The concentration of ST was 10^{-2} mol $\mathrm{L^{-1}}$. The ESR spectrum was recorded 1 h after the addition of the ST at the following parameters: attenuation of the microwave radiation in the cavity, 10 dB; modulation amplitude of the microwave field, 100 mG; and microwave radiation frequency, 9.45 GHz. ESR spectra were simulated using the WINSIM program package**[14]** and quantum-chemistry methods. The simulated and experimental spectra were compared using least-squares calculations. The relative amount of the radicals was estimated from the ratio of the areas under the absorption curves.

Quantum-chemical calculations of the HFC constants for the hypothetical ST adducts were carried out by the density functional theory (DFT) approach with the UB3LYP functional in the 6-311G(d,p) basis set using the GAUSSIAN-94 program package**[15]** at the Supercomputer Center of the Russian Foundation for Basic Research (Institute of Organic Chemistry, Russian Academy of Sciences). Currently, this is the method of choice for this type of calculation.**[16—18]** The isotropic HFC constants were derived from the calculated values of spin density by a previously described method.**[16,17]**

Results and Discussion

The ESR spectra of the adducts formed by the ST with the radicals arising upon UV irradiation of DADP in benzene and toluene are shown in Figs. 1 and 2, respectively. The magnetic resonance parameters (MRP) of the adducts are listed in Table 1.

Comparison of the experimental ESR spectrum (see Fig. 1, spectrum *1*) recorded on UV irradiation of DADP for 3 min with the simulated spectrum (*1´*) allows one to conclude that the observed spectrum is due to splitting on the ^{14}N nucleus (a_{N} = 1.06 mT) and on two groups of equivalent protons (three protons with a_{H}(*ortho*, *para*) = 0.23 mT and two protons with a_{H}(*meta*) = 0.10 mT) (model 1). These MRP are typical of the adducts formed by the ST with phenyl radicals.**[19—21]** Most likely, the $\mathrm{Ph^{\bullet}}$ radicals result from abstraction of an H atom from the benzene molecule by the triplet nitrene—dioxygen complex**[5]**

$$\mathrm{RNOO^T + PhH \longrightarrow R\dot{N}OOH + Ph^{\bullet}}. \qquad (1)$$

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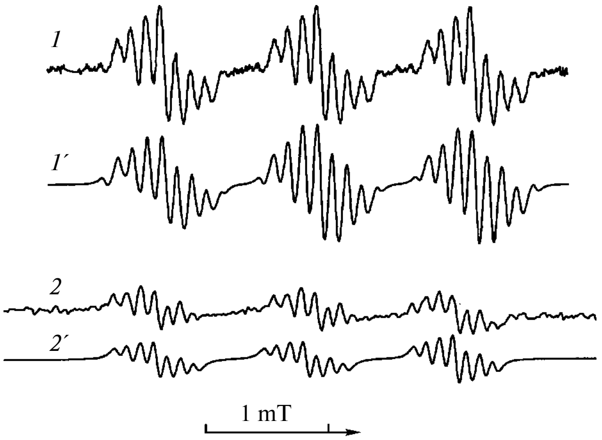

Fig. 1. ESR spectra recorded upon a 3-min UV irradiation of 4,4′-diazidodiphenyl in benzene (*1*), the same with the addition of dichloromethane (*2*), and the corresponding simulated spectra (*1*′, *2*′).

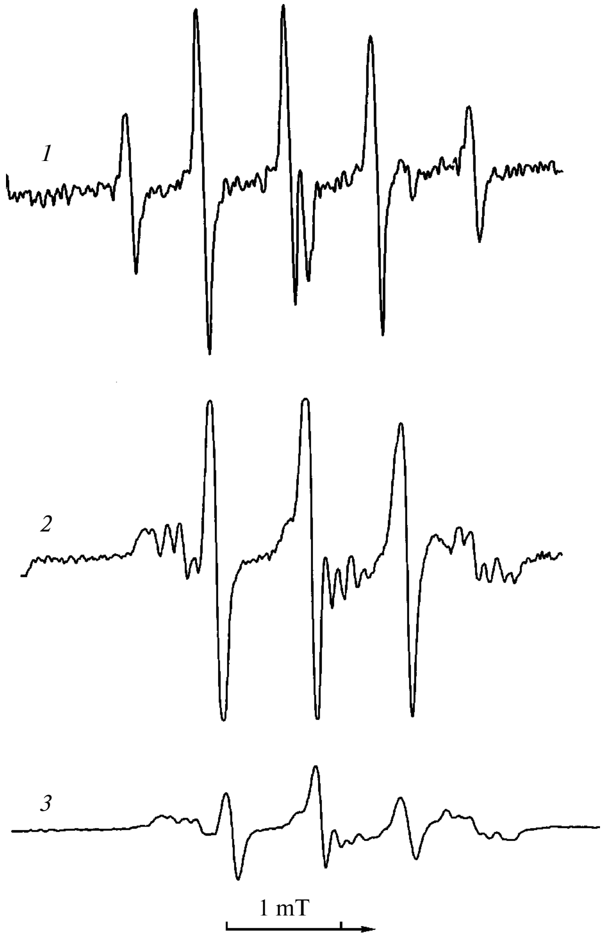

Fig. 2. ESR spectra recorded upon UV irradiation of 4,4′-diazidodiphenyl in toluene for 30 (*1*) and 300 s (*2*) and with the addition of dichloromethane for 300 s (*3*).

Table 1. Magnetic resonance parameters of the ESR spectra of 2-methyl-2-nitrosopropane adducts with radicals formed in the photooxidation of 4,4′-diazidodiphenyl

Radical	Solvent	*g*-Factor	HFC constants*/mT		
			a_N	$a_{\beta\text{-H}}$	$a_{\gamma\text{-H}}$
$\mathrm{Ph}^{\bullet}$	Benzene	2.0059	1.06	0.23	0.10
$\mathrm{Ph}^{\bullet}$	Benzene—CH_2Cl_2 (4 : 1)	2.0059	1.08	0.22	0.10
$\mathrm{PhC(O)}^{\bullet}$	Toluene	2.0065	0.78	—	—
$\mathrm{Bu^{t}}^{\bullet}$	Toluene	2.0058	1.53	—	—
$\mathrm{PhC(O)}^{\bullet}$	Toluene	2.0065	0.82	—	—
$\mathrm{Ph}^{\bullet}$	Toluene	2.0059	1.08	0.24	0.12
$\mathrm{PhC(O)}^{\bullet}$	Toluene—CH_2Cl_2 (4 : 1)	2.0066	0.81	—	—
$\mathrm{Ph}^{\bullet}$	Toluene—CH_2Cl_2 (4 : 1)	2.0059	1.07	0.23	0.11

* The mean error is ±0.05 mT.

The spectral pattern (see Fig. 1) does not rule out the possibility that, in addition to the ST adducts with the $\mathrm{Ph}^{\bullet}$ radicals, the reaction system contains also adducts with *para*-substituted $\mathrm{Ph}^{\bullet}$ radicals. In the presence of dioxygen, the ESR lines are broadened, and unambiguous assignment of the ESR spectra to ST adducts with either $\mathrm{Ph}^{\bullet}$ or *para*-substituted $\mathrm{Ph}^{\bullet}$ radicals seems unlikely. The benzene ring may be *para*-substituted by a hydroxy group, which may result from radical replacement of an H atom in the ring by the hydroxyl radical formed among the decomposition products of the *N*-hydroperoxyaminyl radical[5]

$$\mathrm{R\dot{N}OOH} \longrightarrow \mathrm{RNO} + {}^{\bullet}\mathrm{OH}. \qquad (2)$$

In order to verify this hypothesis, we simulated the experimental ESR spectrum (see Fig. 1, spectrum *1*) assuming that it refers to an adduct formed by the ST with the *para*-substituted $\mathrm{Ph}^{\bullet}$ radical, *i.e.*, results from splitting on two pairs of equivalent protons (model 2). In addition, we represented this spectrum as a superposition of the spectra of the ST adducts with $\mathrm{Ph}^{\bullet}$ and *para*-substituted $\mathrm{Ph}^{\bullet}$ radicals (model 3). The ESR spectra corresponding to the chosen models are shown in Fig. 3. The correlation coefficient is lower for model 2 (0.896) than for model 1 (0.961). Model 2 fails to describe adequately both the wings of the spectrum and the line intensities in the multiplet. Meanwhile, the correlation coefficient for model 3 (0.971) is somewhat higher than for models 1 or 2. The contributions of the spectra corresponding to models 1 and 2 to the experimental spectrum were 90 and 10%, respectively. Thus, even if one assumes that the experimental spectrum is a superposition of the spectra of ST adducts with $\mathrm{Ph}^{\bullet}$ and *para*-substituted $\mathrm{Ph}^{\bullet}$ radicals, the contribution of the latter is rather low.

An additional piece of evidence indicating that the adduct with the $\mathrm{Ph}^{\bullet}$ radical makes a major contribution to the experimental ESR spectrum was gained from quan-

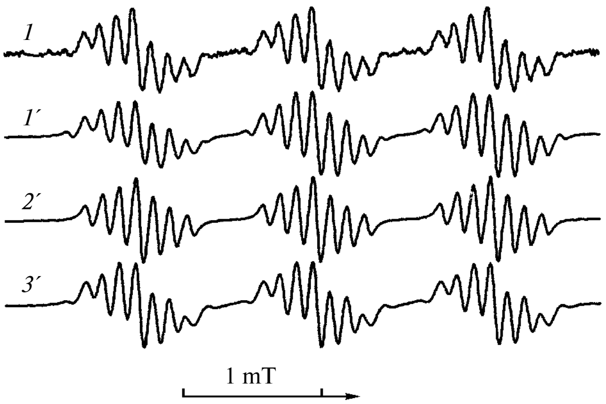

Fig. 3. ESR spectra of the photooxidation products of 4,4′-diazidodiphenyl in benzene: experimental spectrum (*1*); simulated spectra corresponding to models 1, 2, and 3 (*1′*, *2′*, and *3′*, respectively).

tum-chemical calculations. The calculated constants of the HFC on H atoms and the spin densities on the H atoms of the aromatic rings for these adducts are presented in Table 2. It should be noted that the calculated geometric parameters of the radicals are very similar. The differences between the bond lengths do not exceed 0.002 Å. Apparently, the difference in the spin density distribution is dictated by the increase in the angle between the plane of the aromatic ring and the N—O fragment, which is ~0° in the ST adduct with the Ph$^•$ radical and 5.7° in the adduct with the *para*-substituted Ph$^•$ radical.

The data presented above allow one to attribute the ESR spectrum under discussion (see Fig. 1, spectrum *1*) to the adduct with the Ph$^•$ radical. Indeed, in the case of the adduct with the *para*-substituted Ph$^•$ radical, the protons in the *ortho*-position would be nonequivalent both to each other and to the proton in the *para*-position and a splitting (0.07 mT) on the OH-group proton would be observed. The experimental ESR spectra do not exhibit these features.

The assumption that the radicals are formed upon the reaction of the nitrene molecule with the solvent is incorrect, because, due to splitting on a nitrogen nucleus other than the iminoxyl one, these radicals would give rise to a different ESR spectrum rather than that shown in Fig 1.

Table 2. Constants of isotropic hyperfine splitting and spin densities on the H atoms of the aromatic ring (in parentheses) for the spin trap adduct with Ph$^•$ (model 1) and the *para*-substituted Ph$^•$ radical (model 2) determined by quantum-chemical calculations (UB3LYP/6-311G**)

Atom	HFC constants/mT	
	Model 1	Model 2
H_o	0.24 (0.0040; 0.0050)	0.25; 0.22 (0.0050; 0.0070)*
H_p	0.24 (0.0050)	—
H_m	0.12 (0.0025)	0.10; 0.12 (0.0027; 0.0034)*
H_{OH}	—	0.08 (0.0006)

* The protons are nonequivalent.

Adducts formed by the ST with nitrene could also be responsible for the ESR spectra. However, in this case, the ESR spectrum should exhibit splitting not only on the iminoxyl N atom but also on the nitrene N atom, which is not confirmed experimentally. Only in the case where the node of the wave function is localized on the nitrene N atom, can a ESR spectrum similar to that shown in Fig. 1 be observed. However, the results of quantum-chemical calculations[22] demonstrated that this suggestion is faulty. Finally, the hypothesis that carbon-centered radicals are formed upon homolytic decomposition of the C—N bond in the azide molecule is not justified either, because the azide group is destroyed during photochemical decomposition of azides and no dissociation of the C—N bond takes place.[23]

The ESR spectrum recorded upon irradiation of the toluene solution of DADP for 30 s (see Fig. 2, spectrum *1*) is a superposition of two spectra. One of these is a triplet with $g = 2.0065$ and $a_N = 0.78$ mT, which belongs, apparently, to the ST adducts with the $^•$C(O)Ph radical. The MRP indicated above are typical of ST adducts with phenylcarbonyl radicals.[24—29] The second signal with $g = 2.0058$ and $a_N = 1.53$ mT should be attributed to di-*tert*-butyliminoxyl radical. The MRP determined from this ESR spectrum are in line with published values.[29,30]

Curve *2* in Fig. 2 corresponds to the ESR spectrum recorded with irradiation of a solution of DADP in toluene for 3 min and represents a superposition of the spectra of two radicals. One of them, a triplet with $g = 2.0065$ and $a_N = 0.82$ mT refers, as in the previous case, to the ST adduct with the $^•$C(O)Ph radical. The second spectrum, judging by the MRP ($a_N = 1.08$ mT, a_H(*ortho*, *para*) = 0.24 mT, a_H(*meta*) = 0.12 mT), can be assigned to the ST adduct with the Ph$^•$ radicals.

The following mechanism of the formation of phenylcarbonyl and phenyl radicals during photooxidation of DADP in toluene can be proposed:

$$\mathrm{RNOO^T + PhMe \longrightarrow R\dot{N}OOH + Ph\dot{C}H_2,} \qquad (3)$$

$$\mathrm{Ph\dot{C}H_2 + O_2 \longrightarrow PhCH_2O\dot{O} \longrightarrow}$$
$$\mathrm{\longrightarrow Ph\dot{C}{=}O + H_2O,} \qquad (4)$$

$$\mathrm{Ph\dot{C}{=}O \longrightarrow Ph^{\bullet} + CO.} \qquad (5)$$

The triplet complex of the nitrene with dioxygen detaches an H atom from the toluene molecule, giving rise to *N*-hydroperoxyaminyl and benzyl radicals. The benzyl radical reacts with dioxygen being oxidized to the benzylperoxyl radical, which decomposes to give the phenylcarbonyl radical and a water molecule. In turn, the phenylcarbonyl radical decomposes yielding the Ph$^\bullet$ radical and carbon monoxide.

Thus, the radical products of photooxidation of DADP by dioxygen include the phenyl (in benzene) or phenylcarbonyl and phenyl (in toluene) radicals. Most likely, they are formed upon hydrogen abstraction from a solvent molecule by the triplet nitrene—dioxygen complex.

The fact that the formation of radical products during PO is due to reactions of the triplet nitrene complexes with dioxygen is indirectly supported by the results of experiments in which dichloromethane was added to the reaction mixture.

As in the case of irradiation of DADP in benzene, this ESR spectrum (^{14}N (a_N = 1.08 mT), a_H(*ortho*, *para*) = 0.22 mT and a_H(*meta*) = 0.10 mT) corresponds to the ST adduct with the Ph$^\bullet$ radical; however, the amount of this adduct is 3.5 times as low as that observed without dichloromethane (see Fig. 1, spectrum *1*).

The ESR spectrum recorded when a toluene solution of DADP with a dichloromethane additive is exposed to UV light for 3 min is shown in Fig. 2 (spectrum *3*). This spectrum is a superposition of two spectra. The first one (a triplet with g = 2.0066 and a_N = 0.81 mT) is due to the adduct formed by the ST with the $^\bullet$C(O)Ph radical. The second spectrum, whose MRP are given by a_N = 1.07 mT, a_H(*ortho*, *para*) = 0.23 mT, and a_H(*meta*) = 0.11 mT, refers to the ST adduct with the Ph$^\bullet$ radical. As in the case of a benzene solution of DADP with a dichloromethane additive, the intensity of the ESR signal is much lower than that for a solution without the additive. The results of these experiments can be explained by assuming that CH_2Cl_2, which functions as a stabilizer of electron-deficient molecules in the singlet state, increases the probability of PO of organic azides along the "singlet" reaction route.[31]

Previously, similar radical products have been detected upon photoreduction of *p*-nitroaniline.[32,33] It was concluded[6,32,33] that the triplet complex of nitrene with dioxygen is a key intermediate in the photoreduction of *p*-nitroaniline. Thus, it can be stated that the triplet nitrene—dioxygen complex is a general intermediate formed both in the PO of organic azides and in the photoreduction of nitro compounds.

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