EPR SPECTRA OF SOME SUBSTITUTED 2-(a-HYDROXYETHOXY) PHENOXYL RADICALS

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Photoexcited quinones are effective oxidants; in particular, they easily dehydrate alcohols and phenols with the formation of semiguinone and hydroxyalkyl radicals [1]

$$\begin{array}{c} Q \xrightarrow{hv} Q^* \\ Q^* + AH \rightarrow Q'H + A' \end{array}$$

In the case of primary and secondary alcohols, these processes result in the formation of α -hydroxyalkyl radicals [2], which can in turn be accepted by the starting quinone with the formation of hydroxyalkoxy-substituted phenoxyls [3]. In the photolysis of 3,6-di-tert-butyl-o-benzoquinone in ethanol, the EPR spectrum of the 3,6-di-tert-butyl-2-(α -hydroxyethoxy)phenoxyl radical (I) is recorded



X = t-Bu.

No dynamic effects caused by intramolecular migration of the α -hydroxyalkyl fragment between the equivalent 0 atoms of the pyrocatechol ligand are found in the EPR spectrum of (I). The absence of affinity for carbon in 3,6-di-tert-butyl-2-alkoxyphenoxyls up to the temperature of their decomposition (200°C) in solution was demonstrated recently [4], and it was concluded that the absence of intramolecular migration of alkyl groups is due to the impossibility of coordination of the monovalent 0 atom of the corresponding phenoxyl radical to the sp³-hybridized C atom of the alkoxyl substituent.

The spectra of phenoxyl radicals formed in photolysis of some asymmetrically substituted quinones in order to obtain the corresponding 2-hydroxyethoxyphenoxyl radicals and study their EPR spectra were investigated in the present study. The interest in these systems is due to the possibility of revealing slow processes (on the EPR time scale) of intramolecular migration of the α -hydroxyalkyl fragment between the 0 atoms of the pyrocatechol ligand. This possibility is due to the nonequivalence of these 0 atoms, and as a result, different structurally isomeric phenoxyl radicals (forms A and B) can be obtained in photoreduction as a function of which 0 atom in o-benzoquinone the primary α -hydroxyl alkyl radical is added to.

The change in the relative intensity of the EPR spectra corresponding to forms A and B on variation of the temperature could indicate intramolecular migration of the α -hydroxyalkyl group

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	- L	d"	m.	0	р 1 1	d.	w	0
Form A		Ӊ _р	ч	H _p	FOIM B	H _a	Н _р	H _р
x-0R		13,1	2,0	0,4 (tert-Butyl)	x o.	43,1	2,0	0,4 (tert-Butyl)
x or or		0,34 (tert-Buryl)	2,1	I	The second secon	10,4	t .	I
H ₃ 0). 0R	1,1 (Me tho xỳ)	2,2	I	CH _s O CH _s O CH _s O	13,0	i.	. 1

 $a_{\rm H}{}^{\circ}=0,6$ † $a_{\rm H}{}^{m}=0,25$ †

I

12,8

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2,0

0,4 (tert-Butyl)

Ph OR

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(IV)

0.R

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 Pb_sC

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1,4; 2,2 *

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0B

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Spectral Parameters of Substituted $2 + (\alpha - Hydroxyethoxy)$ phenoxyl Radicals, Oe TABLE 1.

*Spectral parameters at 20°C. [†]HFI with protons of phenyl substituent.

ОR ОВ

PllaC

2

1156



Fig. 1. EPR spectra of substituted 2-(α -hydroxyethyl)phenoxyl radicals in ethanol at 20°C (the components of the spectra of form B are indicated by the arrows); a) radical (II); b) radical (III); c) radical (IV); d) radical (V).

Fig. 2. Change in the intensity of the EPR signals of A (1) and B (2) forms of radicals (IV) in time after UV irradiation at 60° C was stopped.



We solved similar problems on the example of nondegenerate silyl affinity in radicals obtained in the reaction of nonsymmetrically substituted o-benzoquinones with triethylsilyl radicals, and demonstrated the possibility of nondegenerate silyl-affinity transitions between forms A and B [5]



In the present study, 3,5-di-tert-butyl-(IIQ), 3,6-di-tert-butyl-4-methoxy-(IIIQ), 3,5di-tert-butyl-6-phenyl-(IVQ), and 3-tert-butyl-5-trityl-(VQ) o-benzoquinones underwent photolysis. The EPR spectra corresponding to the two types of particles, apparently forms A and B, of the corresponding phenoxyl radicals were recorded (Fig.1). The EPR spectra with doublet splitting of 10-13 Oe were assigned to form B. In this case, such large splitting can be attributed to the HFI of the unpaired electron with the ring proton in the para position to the monovalent O atom. The para and ortho positions in phenoxyl radicals are characterized by important values of the spin density [6]. Additional splitting of each component of the doublet in the EPR spectra of radical (IVB) (cf. Fig. 1c, Table 1), caused by the HFI with the protons of the phenyl substituent, confirms this assignment. In the case of form A, the ring proton is in the meta position to the monovalent 0 atom and the HFI constant is ~2 Oe, which is characteristic of meta protons of phenoxyl radicals [6]. Each component of this doublet is split into a multiplet caused by the magnetic nuclei of the para substituent (see Table 1).

This treatment of the spectra corresponds to the spin density distribution in the aromatic nucleus characteristic of phenoxyl radicals [6] and confirms the validity of the assignment of the spectra.

The study of dark processes of quenching of radicals (II)-(V) formed during photolysis showed that at the temperature of 60°C, form B totally disappears after 10 min, while the concentration of form A does not change (Fig. 2). The relative instability of form B is apparently due to dimerization of the corresponding radicals with the formation of quinoline esters. This dimerization is characteristic of phenoxyl radicals [7] and should be less characteristic of form A due to the shielding effect of the para substituent.



The independence of the kinetic behavior of forms A and B of the phenoxyl radicals studied at temperatures under 80°C thus unambiguously indicates the absence of intramolecular processes of migration of the α -hydroxyethyl radical between the 0 atoms of the pyrocatechol ligand. It is possible to state that this process takes place much more slowly than quenching of form B in the dimerization reaction.



With an increase in the temperature (to 180° C) without UV radiation, it is possible to observe the appearance and an increase in the intensity of the EPR spectrum of form B, which indicates dissociation of the dimer formed into radicals. A feature of the high-temperature spectra is that above 100° C, a simultaneous increase in the intensity of the spectra of forms A and B is observed on the example of radical (IV) (Fig. 3). This indicates that form B, formed during dissociation in the $120-180^{\circ}$ C range, is transformed into form A, and consequently migration of the α -hydroxyalkyl radical between the O atoms of the pyrocatechol ligand in the radical. Unfortunately, we were unable to estimate the kinetic and thermodynamic parameters of this process, since it is necessary to precisely know the concentration of the dimer of form B. However, a qualitative conclusion on the presence of migration processes follows from the temperature dependences of the EPR spectra.

It was also found that the shape of the EPR spectra of form A of radical (V) is essentially dependent on the temperature (Fig. 4). A triplet which can be assigned to the HFI with two m-protons of the pyrocatechol ligand $(a_H^m = 1.7 \text{ Oe})$ is recorded at temperatures below -40°C. When the temperature is increased to 0°C, dynamic effects are observed, and this spectrum is transformed into a doublet (1.3 Oe) of doublets (2.3 Oe). With a further increase in the temperature, the two central components of the preceding spectrum broaden and a new doublet (1.0 Oe) of doublets (1.7 Oe) with smaller HFI constants from the ring m-protons appears at 140°C. The temperature evolution of the spectra is totally reversible, which indicates the existence of intramolecular processes accompanied by insignificant redistribution of the spin density in the phenoxyl ring. Similar spectral changes were identified for 6-tert-butyl-4-trityl-2-hydroxyphenoxyl and its deuterated analog [8], which are attributed to hindered rotation of the triphenylmethyl group and the direct interaction of the π orbitals of the unpaired electron with the π system of the phenyl substituents.



Fig. 3

Fig. 4

Fig. 3. Temperature dependence of the relative intensity of the EPR spectra of forms A and B of radical (IV) (the components of the spectrum of form B are indicated by the arrows): a) 180, b) 160, c) 140, d) $120^{\circ}C$.

Fig. 4. Temperature dependence of the EPR spectrum of form A of radical (V): a) 140; b) 100; c) 80; d) 60; e) 20; f) -40°C.

CONCLUSIONS

1. Isomeric forms of 2-hydroxyethylphenoxyl radicals were obtained by the reaction of nonsymmetrically substituted orthobenzoquinones with ethyl alcohol under the effect of UV radiation.

2. At temperatures above 100°C, the spectral changes recorded correspond to migration of the α -hydroxyethyl group between the oxygen atoms of the pyrocatechol ligand.

3. The spectral changes recorded in the case of 4-trityl-6-tert-butyl-2-(α -hydroxyethoxy)phenoxyl indicate the direct interaction of the π orbitals of the unpaired electron with the π system of the phenyl rings of the trityl substituent.

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