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#### DYNAMIC EFFECTS IN ESR SPECTRA OF 4-TRIPHENYLMETHYL-

## 6-TERT-BUTYL-2-HYDROXYPHENOXYL AND

4-TRIPHENYLMETHYL-6-PHENYL-2-HYDROXYPHENOXYL

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A characteristic feature of 2-hydroxyphenoxyl radicals is intramolecular migration of the hydrogen atom between the oxygen atoms [1, 2],



The rate of migration depends on the number, nature, and arrangement of the substituents. If there is no symmetry in the positioning of the substituents relative to the oxygen atoms, the migration rate is lower, and this is manifested in attemperature-independent form of the ESR spectra of such radicals [3, 4].

Here we are reporting on an investigation of the nature of the dynamic effects in the ESR spectra of 4-triphenylmethyl-6-tert-butyl-2-hydroxyphenoxyl (I)-H, 4-triphenylmethyl-6-phenyl-2-hydroxyphenoxyl (II)-H, and the analogous compounds deuterated at the hydroxyl group (I)-d and (II)-d:

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Fig. 1. ESR spectra of radical (I) in toluene at various temperatures, °C: a) 160; b) 40; c) -20.

Fig. 2. ESR spectra of radical (I)-d in toluene at various temperatures, °C: a) 160; b) 100; c) 40.



Common features in the spectra of the radicals (I) and (II), the same as in unsubstituted 2-hydroxyphenoxyl (QH) [5, 6], 3,6-di-tert-butyl-2-hydroxyphenoxyl (3,6-QH) [1], and 4,6-di-tert-butyl-2-hydroxyphenoxyl (4,6-WH) [3] (Table 1) is the presence of maximum spin density of the unpaired electron in position 4, a weak dependence of the hfi of the hydroxyl-group proton ( $\alpha_{\rm H}^{\rm OH}$ ) on the substituent and on the temperature, and nonequivalence of the hfi of the meta protons (positions 3 and 5).

As there is a large kinetic isotope effect in the migration of the H and D atoms [1, 2], we can use a comparison of the temperature dependences of the ESR spectra of the OH and OD derivatives (Figs. 1 and 2) as a criterion in determining the nature of the dynamic effects in the ESR spectra of these radicals.

At 160°, the ESR spectrum of the radical (I) consists of a doublet that should be assigned to HFI with the hydroxyl-group proton  $(a_{\rm H}^{\rm OH} = 1.5 \text{ Oe})$  (see Table 1). Each component of this doublet is split into a triplet as a result of hfi with the two equivalent protons of the aromatic ring  $(a_{\rm H}^3 = a_{\rm H}^5 = 1.15 \text{ Oe})$ . As the temperature is lowered, the central components of the triplet are broadened; and at 40°, the ring H atoms are nonequivalent  $(a_{\rm H}^3 = 1.6, a_{\rm H}^5 = 0.8 \text{ Oe})$ . With a further lowering of temperature, a triplet is formed  $(a_{\rm H}^3 = a_{\rm H}^{\rm OH} = 1.7 \text{ Oe})$  (see Fig. 1c), and  $a_{\rm H}^5$  is reduced to zero (see Table 1). The assignment of the hfi constants is based on data for other 2-hydroxyphenoxyl radicals and is further supported by analysis of the ESR spectra of the deuterated analog (I)-d. The central component of the triplet of the equivalent ring protons ( $a_{\rm H}^3 = a_{\rm H}^6 = 1.45 \text{ Oe}$ ) is broadened (Figs. 2a and 2b); and at 40°, a doublet is formed ( $a_{\rm H}^3 = 1.8, a_{\rm H}^6 = 0 \text{ Oe}$ ); the hfi with the hydroxyl-group deuterium nucleus is small, and it is manifested in the presence of an inflection point on the outer, unbroadened components of the triplet.

A similar picture is observed in the ESR spectra of the radicals (II) and (II)-d (Figs. 3 and 4). The introduction of the phenyl substituent into position 6 changes the density of spin distribution in the phenoxyl ring to a slight degree (see Table 1).

TABLE 1. hfi Constants in ESR Spectra of Certain 2-Hydroxyphenoxy1s

4 O' 2 OH						
Radical	$a_{ m H}^{ m OH}$	$a_{ m H}^3$	$a_{ m H}^{4}$	${}^{a}{}^{5}_{{ m H}}$	$a_{\mathrm{II}}^{6}$	Lit. ref.
QH	1.5 (20°) 1.7 (-100°)	1,54	-8,2	0,16	3,85	[6,7]
3,6-QH	1.6 (20°) 1.8 (-100°)	-	-7,8	0		[1,2]
4,6-QH	1.7 (100±040°)	1.8	0,4*	0	-	[8]
(I)	1.5 (160°) 1.7 (80°)	1,15 1,8	-	1.15 0	-	
(11)	1.5 (180-to 20°)	1.8 (20°) 1,8 (200°)		3.8 (20°) 3.0 (200°)	-	

\*hfi from protons of tert-butyl group in position 4.



Fig. 3. ESR spectra of radical (II) in toluene at various temperatures, °C: a) 140; b) 80; c) 40.

Fig. 4. ESR spectra of radical (II)-d in toluene at various temperatures, °C: a) 200; b) 140; c) 60; d) 20.

An analysis of the temperature dependences of the ESR spectra of the OH and OD derivatives shows that the observed dynamic effects are not related to intramolecular transfer of the hydrogen or deuterium atom between the oxygen atoms of the radicals (I) and (II), a transfer that is characteristic for the radicals (QH) and (3,6-QH). The assignment of the hfi constants (Table 1) indicates that in the radicals (I) and (II), the unpaired electron is localized on the sterically shielded 0 atom, since if the free valence were localized on the oxygen atom in position 2, we should observe hfi from the ring proton in position 5 on the order of 8.0 Oe, and this is not consistent with the experimental data.

The broadening of the lines in the ESR spectra is likewise unrelated to the dynamics of rotation of the OH or OD group around the CO bond. The weak dependence of  $a_{
m H}{}^{
m OH}$  on the substituents in the phenoxyl ring and on the temperature (Table 1) indicates strong intramolecular H-bonding between the univalent O atom and the proton of the OH group.

The only hypothesis that remains is that the spectral features of the radicals (I) and (II) are due to the retarded character of rotation of the triphenylmethyl (TPM) substituent.



Fig. 5. Arrhenius dependences of rate constants of intramolecular transition between conformations A and B for radicals: 1) (I); 2) (II)-d.

The observed redistribution of spin density in the phenoxyl ring (the changes in the hfi constants  $a_{\rm H}^3$  and  $a_{\rm H}^5$ ) in these radicals can be explained by direct interaction between the orbital of the phenoxyl ring carrying the unpaired electron and the highest occupied orbitals of the phenyl rings of the triphenylmethyl substituent.

As already mentioned, the maximum spin density is found in the para position relative to the univalent 0 atom, i.e., in the position bonded to the TPM substituent. We can assume that the magnitude of the direct interaction will depend on the location of the TPM relative to the p orbital carrying the unpaired electron.

This direct interaction may bring about partial delocalization of the spin of the unpaired electron in the TPM substituent and a redistribution of the spin density in the phenoxyl ring. The proposed mechanism of unpaired electron delocalization in the radicals of (I) and (II) is supported by the absence of dynamic effects in the spectra of 4,6-QH, which contains a tert-butyl group in position 4, incapable of such interaction.

For a description of the experimental data, we can visualize the presence of two conformations A and B differing in the degree of direct interaction. For example, let us say that conformation A corresponds to the maximum of this interaction and conformation B to the minimum. As a result of retarded rotation of the TPM group, there is a transition between conformations A and B, which differ in their thermodynamic stability. If we assume that, for the radical (I) in conformation A,  $\alpha_{\rm H}^3 = 0$ ,  $\alpha_{\rm H}^5 = 1.85$  Oe, and in conformation B that  $\alpha_{\rm H}^{3} = \alpha_{\rm H}^{5} = 1.15$  Oe, then, in accordance with the experimental data (Figs. 1 and 2), conformation A is stabilized at low temperature, and conformation B at high temperature. The changes in the hfi constants ( $\alpha_{\rm H}^3$  and  $\alpha_{\rm H}^5$ ) indicate a shift of the equilibrium between conformations A and B when the temperature is changed, and hence, we can use the mean value of one of these quantities ( $\dot{\alpha}$ ) to estimate the equilibrium constant: K<sub>e</sub> (20°) = 0.58,  $\Delta$ H = 2.7 kcal/mole.

The thermodynamic parameters that have been obtained, together with an analysis of the line widths in the ESR spectrum as a function of temperature, enable us to estimate the rate constants  $(k_1 \text{ and } k_{-1})$  of the reversible transition between the A and B conformations. According to the theory given in [7], general expression relating the rate of the intramolecular processes to the line width has the form

$$(\Delta T_2)^{-1} = \frac{\alpha (1-\alpha) \gamma_e (\Delta a)^2}{k_1 + k_{-1}}$$

where  $\gamma_e$  is the gyromagnetic ratio for the electron;  $\Delta \alpha$  is the distance between the exchanging lines ( $\Delta \alpha \simeq \alpha_H^3$  in the B conformation). Using K<sub>e</sub>, we can express one of the elementary rate constants in explicit form and can obtain the kinetic parameters of the transition between the A and B conformations. We find that the general expressions for the elementary constants  $k_1$  and  $k_{-1}$  are:  $k_1 = 1.8 \cdot 10^{11} \exp \left[-(5800 \pm 1500)\right]/\text{RT} \sec^{-1}$ ,  $k_1$  (20°) =  $9 \cdot 10^5 \sec^{-1}$ ;  $k_{-1} =$  $3.1 \cdot 10^9 \exp \left[-(3100 \pm 1000)\right]/\text{RT} \sec^{-1}$ ,  $k_{-1}(20^\circ) = 1.5 \cdot 10^7 \sec^{-1}$ . Let us emphasize that replacement of the H atom by D in the OH group of the radical (I) has practically no effect on the values of  $k_1$  and  $k_{-1}$  (Fig. 5), which is evidence in favor of the proposed mechanism of the intramolecular dynamic processes. The geometry of the radicals (I) and (II) corresponds to the geometry of tetraphenylmethane; consequently, the character of the rotation of the phenyl groups in tetraphenylmethane relative to their bond with the central carbon atom is apparently similar to that in the radicals we have investigated.

According to the available estimates, the energy barrier to rotation of phenyl groups in tetraphenylmethane is 14.9 kcal/mole, this value pertaining to complete rotation of a phenyl group relative to the bond with the central C atom [8].

It must be noted that the barrier to rotation in free radicals is usually higher than that in neutral molecules. For example, in alkoxy-substituted phenoxyl radicals, the barrier to rotation of the OR group relative to the CO bonds is 8-10 kcal/mole, whereas incanisole, this value is approximately 1.5 kcal/mole [7]. The rather large barriers to rotation in the radicals are usually explained by the "double-bondedness" that arises because of interaction of the unpaired electron with the p orbital of the oxygen atom in the COR fragment. Proceeding on this basis, we can assume that in the radicals (I) and (II), as a result of direct interaction of the unpaired electron with the  $\pi$  orbital of the phenyl groups, the barriers to rotation should be higher than in the case of tetraphenylmethane.

Thus, from the comparison we have made, we can assume that the low values obtained for the energy barriers of the dynamic effects in the ESR spectra of the radicals (I) and (II) pertain to certain torsional vibrations of the free-radical fragment relative to the C-C bond with the central C atom between the forms A and B, and the redistribution of spin density that appears as a result of such vibrations indicates direct interaction of the  $\pi$  orbital of the unpaired electron with the  $\pi$  system of the phenyl substituents.

## EXPER IMENTAL

The radicals (I) and (II) were obtained by interaction of the corresponding quinones and pyrocatechols in accordance with the scheme  $Q + QH_2 = 2\dot{Q}H$ . This equilibrium is shifted in the direction of free radicals as the temperature is increased. When necessary, the shift of this equilibrium was effected by means of UV irradiation in the resonator of the ESR spectrometer. The deuterated analogs of the radicals were obtained by adding  $D_2O$  to the solution. The temperature dependences of the ESR spectra of the ordinary and deuterated radicals were obtained under similar conditions in water-toluene mixtures in order to level out any possible formation of H-bonds.

<u>3-Phenyl-5-triphenylmethylpyrocatechol</u> was synthesized from phenylmagnesium bromide and 4-triphenylmethylquinone, mp 196-198°C. Found: C 86.5, H 5.5%. C<sub>31</sub>H<sub>24</sub>O<sub>2</sub>. Calculated: C 86.9, H 5.6%.

<u>3-Phenyl-5-triphenylmethyl-o-benzoquinone</u> was obtained by the oxidation of an alcoholic solution of the corresponding pyrocatechol by nitric acid, mp 212-214° from toluene. Found: C 87.4, H 5.0%.  $C_{31}H_{22}O_2$ . Calculated: C 87.3, H 5.2%.

The synthesis of the 3-tert-buty1-5-triphenylmethylpyrocatechol and the corresponding o-benzoquinone was described in [9].

#### CONCLUSIONS

In the ESR spectra of 6-triphenylmethyl-4-tert-butyl-2-hydroxyphenoxyl and 6-triphenylmethyl-4-phenyl-2-hydroxyphenoxyl and their deuterated analogs, temperature-dependent dynamic effects have been found; these are explained from the standpoint of a reversible intramolecular transition between different conformations of the radicals, differing in the spin density distribution, owing to direct interaction of the unpaired electron with the  $\pi$  orbitals of the phenyl rings of the triphenylmethyl substituent.

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NATURE OF <sup>13</sup>C NMR PARAMAGNETIC SHIFTS INDUCED BY Cr(acac)<sub>3</sub> IN MOLECULES OF ORGANIC SOLVENTS

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Nuclear magnetic resonance, although it is inferior in sensitivity to certain other physicochemical methods, is irreplaceable in the investigation of weak interactions in paramagnetic metal complexes in solution. Magnetic interactions of electronic and nuclear spins are so great that even if the solution has a large excess of diamagnetic components over the paramagnetic components, the NMR parameters of the components are subject to substantial perturbation that can be registered.

This effect has been used successfully in determining that, in the presence of paramagnetic metal complexes, spin density appears in the molecules of alkyl halide solvents RX, leading to contact shifts of the  $^{13}$ C NMR of the RX (see [1] and literature references therein). It was shown that transfer of spin density takes place, with the formation of weak, shortlived bonds between the C-X fragments of the alkyl halide and the metal complex ("X-coordination"). Analysis of the entire body of experimental data has led to rather well-justified conclusions (although not final conclusions) as to the outer-sphere nature of the X-coordination [1]. Even if it is assumed that the spin density on the RX is transferred directly from the metal ions, not from the ligands of the inner coordination sphere of the metal complexes, the X-coordination can most likely be attributed to outer-sphere processes, since it is not manifested in the electronic spectra of the metal complexes, and it is observed even for complexes with an octahedral environment [1, 2].

Preliminary studies have shown that not only halogen-substituted hydrocarbons, but also other types of organic solvents, are capable of taking on spin density in the outer sphere [3]. We can assume that a broadening of the circle of solvents will provide a better understanding of the nature of the outer-sphere interactions responsible for the transfer of spin density. As the paramagnetic probe for this purpose, we selected chromium(III) tris(acetylacetonate),  $Cr(acac)_3$ . This complex is readily soluble in a broad group of organic solvents. It is stable, and it is coordination-saturated. Therefore, there can be no doubt that even in the case of donor solvents, the spin density induced by  $Cr(acac)_3$  cannot be related to trivial processes of inner-sphere coordination. A relative disadvantage of the  $Cr(acac)_3$  is the smaller contact shifts induced by this complex in comparison with those induced by paramagnetic metal halide complexes [1].

# EXPERIMENTAL

The NMR spectra were registered in a Bruker SXP-4-100 spectrometer with a carbon resonance frequency of 22.63 MHz. The procedures used in measuring the induced paramagnetic shifts  $\Delta\delta$  have been described in detail in [4]. All of the test solutions contained 10% cyclohexane by volume, serving as an internal standard. The error in measuring the carbon shifts ranged from 0.01 to 0.05 ppm. Downfield paramagnetic shifts are considered as positive.

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