

INFLUENCE OF THE ELECTRONIC STRUCTURE  
OF A FREE RADICAL ON COMPLEX-FORMATION  
WITH A DIAMAGNETIC MOLECULE

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It has been established previously [1, 2] that the strength of H complexes of diamagnetic molecules depend to a larger extent on the electronic nature of the molecule of the base than on the molecule of the acid. A similar phenomenon should apparently be observed in paramagnetic H complexes formed in a free radical-diamagnetic polar molecule system in which the free radical acts as a base. Furthermore, in such systems the influence of the electronic structure of the free radical on the thermodynamics of complex-formation and the degree of transfer of the spin density from the radical to the diamagnetic molecule may be shown. It must be observed that at the present time only a few publications are known on investigations of the complex-formation of free radicals of various electronic natures with diamagnetic ligands [3], and it is practically impossible to compare the results of these investigations, since they were obtained under different experimental conditions (medium, ligand, temperature).

In the present work we have investigated the complex-formation of aromatic and aliphatic nitroxyl radicals having various structures (I-VII) (Table 1) with 2,6-di-tert-butyl-4-methylphenol (Ionol). The hyperfine structure (hfs) constants  $a^N$  for these radicals range between 9 and 17 Oe [3, 4]. If we employ the relation connecting the values of the hfs constant  $a^N$  in nitroxyl radicals with  $\pi$ -electron density on the nitrogen atom that is frequently used in practice,  $a^N = 35.5 \rho_N^\pi$  [3], the value of  $\rho_N^\pi$  for these radicals varies between 0.25 and 0.47. The wide variation of the electronic structure of the  $\text{>N}-\dot{\text{O}}$  radicals investigated, and also the existence of the self-association of the Ionol in solution [5] made these systems convenient models for studying the influence of the electronic nature of the free radical on associative interactions with a diamagnetic molecule.

We have studied the concentration and temperature dependences of the chemical shift  $\tau^{\text{OH}}$  in systems consisting of one of the radicals (I-VII), Ionol, and  $\text{CCl}_4$  by the NMR method. The concentration of radicals was varied in the range of  $10^{-3}$ - $10^{-1}$  M and of Ionol between 0.05 and 0.5 M, and the temperature was varied between  $-10$  and  $+60^\circ\text{C}$ . The experimental results obtained from the NMR spectra were treated by the method described previously [6] using the relation

$$A = K\Delta\tau - KAD_0, \quad (1)$$

where A is the tangent of the angle of slope of the linear relationship  $\delta\tau^{\text{OH}} = f(R_0)$ , where  $\delta\tau$  is the change in the chemical shift  $\tau^{\text{OH}}$  at the given concentration of Ionol caused by the addition of the radical to the system, K is the equilibrium constant of the formation of the radical-Ionol complex,  $D_0$  and  $R_0$  are the initial concentrations of Ionol and of the radical, respectively, and  $\Delta\tau$  is the chemical shift due to complex-formation.

As an example, Fig. 1 gives relationships describing Eq. (1) for the radical (III)-Ionol- $\text{CCl}_4$  system at various temperatures. Similar relationships have been obtained for all the systems investigated in this work. The heat  $\Delta H$  and entropy  $\Delta S$  of formation of the radical-Ionol complexes were determined from the temperature dependence of the equilibrium constants K and the values of the hfs constants  $a^{\text{OH}}$  calculated from the relation [7]

$$a^{\text{OH}} = - \frac{\Delta\tau^{\text{OH}} (\text{Hz}) \cdot T^{\circ}\text{K}}{1328460} (\text{Oe}). \quad (2)$$

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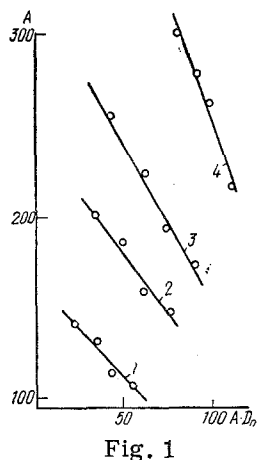


Fig. 1

Fig. 1. Dependence of the values of A on  $AD_0$  for the radical III-Ionol system: 1) 315°K; 2) 297°K; 3) 281°K; 4) 270°K.

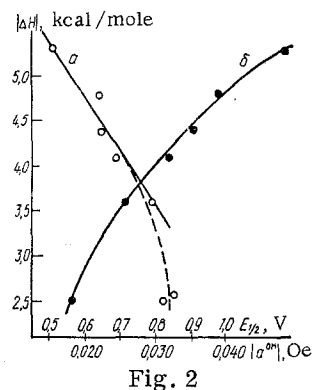


Fig. 2

Fig. 2. Dependence of the strength of the radical-Ionol complexes: a) on the half-wave potential of the oxidation of the radicals,  $E_{1/2}$ ; b) on the value of hfs constant  $a^{\text{OH}}$  in the complex.

As in our previous investigations [6, 8], the value of the constant  $a^{\text{OH}}$  in the paramagnetic complexes studied decreases linearly with a rise in the temperature. The spectral and thermodynamic parameters of the complex-formation of the radicals (I-VII) with Ionol found in this way are given in Table 1.

The presence of four methyl or two phenyl groups close to the  $\text{>N}-\dot{\text{O}}$  fragment and also the strong steric screening of the hydroxyl group of the Ionol by the voluminous ortho-tert-butyl substituents gives grounds for assuming that a substantial influence on the parameters of complex-formation in the system must be exerted by the steric factor. In actual fact, it has been shown previously for diamagnetic [9] and paramagnetic [8] complexes that both the length of hydrogen bond and the strength of H complexes depend to a large degree on the steric screening of the reaction centers of the interacting molecules.

To evaluate this influence from information on the geometrical structures of the radicals (I-VII) [3] and of the Ionol molecule and taking into account van der Waals radii of the methyl, phenyl, and tert-butyl groups, we have calculated the minimum distances  $R_{\text{O} \dots \text{O}}$  to which the molecules in the complex may approach. For all the radical-Ionol pairs studied, this distance proved to be practically the same (of the order of  $3.0 \pm 0.1 \text{ \AA}$ ), so that the observed changes in the values of  $\Delta H$  and  $a^{\text{OH}}$  are not due to a change in the distance  $R_{\text{O} \dots \text{O}}$  between the radical and the Ionol. This is shown by the linear relationship that we have found between the values of  $\Delta H$  and  $\Delta S$

$$|-\Delta H| = 0.05 + 0.31|-\Delta S|, \quad (r = 0.987) \quad (3)$$

which is generally observed in the interaction of molecules with comparable steric factors. In addition, the changes found in the strength of the paramagnetic complexes of radicals (I-VII) with Ionol do not correlate with the change in the  $\pi$ -electron density on the oxygen and nitrogen atoms of the  $\text{>N}-\dot{\text{O}}$  fragments of the radicals [3].

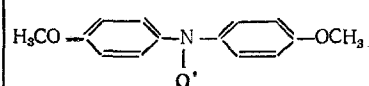
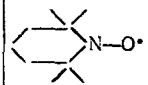
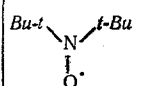
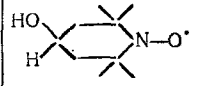
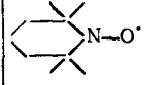
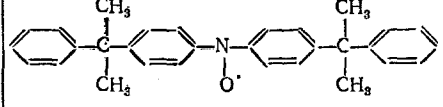
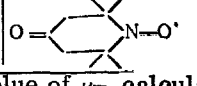
The explanation of the observed changes in  $\Delta H$  and  $a^{\text{OH}}$  must apparently be sought in the different electron-donating capacities of the nitroxyl radicals investigated, as a measure of which the ionization potential  $I$  is usually used. Unfortunately, information on the ionization potentials of free radicals is extremely limited [3]. We therefore evaluated their electron-donating properties in solution on the basis of the values of the half-wave potentials of polarographic oxidation  $E_{1/2}$ , which are proportional to the energy of detachment of an electron from the highest occupied molecular orbital and, in the case of reversible one-electron oxidation, are connected with the ionization potential by the relation [10]

$$E_{1/2} = I + \Delta E_{\text{solV}} + \text{const}, \quad (4)$$

in which the term  $\Delta E_{\text{solV}}$  takes the influence of the solvent into account.

To find the value of  $E_{1/2}$  for the oxidation of the radicals we used the method of voltamperometry at solid electrodes. Since in all measurements we used the same solvent, the contribution of  $\Delta E_{\text{solV}}$  to the value

TABLE 1. Spectral and Thermodynamic Characteristics of the Formation of Complexes Between Nitroxyl Radicals and Ionol

$N_6$	Radical	$E_{1/2}$ , V	$a_N$ , Oe	$-\Delta H$ , kcal/mole	$-\Delta S$ , e.u.	$-a^{OH}$ , Oe	$\mu_R \cdot D$	$-\Delta H_{DA}$ , kcal/mole
I		0,51	10,1	5,3	17,4	0,048	3,85	3,6
II		0,64	15,1	4,8	14,2	0,038	3,14	3,4
III		0,65	15,7	4,4	14,3	0,036	3,08	3,0
IV		0,69	14,6	4,1	13,4	0,032	3,12	2,9
V		0,79	14,2	3,6	11,8	0,026	2,90*	2,3
VI		0,81	9,5	2,5	8,3	0,018	0,8*	2,1
VII		0,85	14,6	2,6	8,6	0,014	1,36	1,8

\*Value of  $\mu_R$  calculated from Eq. (6)

of  $E_{1/2}$  may be considered as practically constant, which permits the assumption of a linear interrelationship between  $E_{1/2}$  and I. The stability of the nitroxyl radicals investigated in the electrolyte solutions used was confirmed by the invariability of the ESR signals in control experiments.

It has been shown [3] that the unshared pair of electrons of the oxygen atom of the radical (electron donor) and the 1s orbital of the hydrogen atom of the proton-donating group (electron acceptor) participate in the formation of paramagnetic complexes of a nitroxyl radical and a diamagnetic molecule containing OH, NH, or SH groups. It must be mentioned that with a fall in  $E_{1/2}$  of the radical the conditions for the transfer of electron density from the unshared pair of the oxygen atom or the radical to the vacant orbital of the acceptor (Ionol) in donor-acceptor complexes become more favorable [11]. At the same time, the strength of the complex must increase which is in harmony with the experimental results (see Table 1).

Since as a consequence of the presence of an unpaired electron in the  $\rho_N^\pi$  orbital of the radical the electron density on the unshared pair of electrons of the oxygen atom is spin-polarized [12], it must be expected that on complex-formation with one and the same proton donor a symbatic relationship will be observed between the values of  $E_{1/2}$  and the constants  $a^{OH}$  in the hydroxy group of the Ionol. Such a relationship is in fact observed and has a linear nature

$$|-a^{OH}| = 0.099 - 0.1 E_{1/2}, \quad (r = 0.989) \quad (5)$$

which may be evidence in favor of the donor-acceptor model of the H bond in the paramagnetic nitroxyl radical-phenol complex.

It was mentioned above that in the paramagnetic associates investigated the distance between the oxygen atoms of the radical of the Ionol is about 3.0 Å. It is usually assumed [11] that at such distances the contribution of donor-acceptor interaction (short-range, i.e., requiring the overlapping of the orbitals of the molecules forming the complex) to the strength of a H complex is very small and the contribution of the electrostatic - long-range - interaction is predominating. The linear relationship that we have observed between the values of  $a^{OH}$  and  $E_{1/2}$  (5) is one of the few indications of the existence of a donor-acceptor bond between molecules located at large distances from one another.

For paramagnetic donor-acceptor complexes, as for diamagnetic complexes [11], one should apparently expect a linear relationship between the values of  $\Delta H$  and  $E_{1/2}$  which, however, is not observed experimentally

(Fig. 2). The greatest deviation from linearity is observed in the region of large values of  $E_{1/2}$ , i.e., in the region of small donor-acceptor interactions. This shape of the  $|\Delta H| = f(E_{1/2})$  relationship is probably due to the fact that a dipole-dipole (electrostatic) interaction also makes a contribution to the strength of the radical-Ionol complex, and at the same distance between the molecules in the complex with one and the same proton donor this must be proportional to the dipole moment of the molecule of the base (the radical). In actual fact, it follows from the figures given in Table 1 that the strength of complexes of the radicals (I-VII) with Ionol falls with a decrease in the dipole moment of the radical,  $\mu_R$ , but there is no linear relationship between these magnitudes.

The existence of an electrostatic contribution to the heat of formation of paramagnetic H complexes of a radical and Ionol is also in harmony with the absence of a linear relationship between the magnitude  $\Delta H$  and  $a^{OH}$  (Fig. 2b). As has been shown previously [8] the value of the latter is due to the transfer of spin density from the radical to the Ionol as a consequence of overlapping between the  $2p_\sigma$ -hybridized (intermediate between trigonal and tetragonal) molecular orbital of the unshared pair of the oxygen atom of the radical and the  $1a$  orbital of the hydrogen atom of the phenolic hydroxyl, i.e., it is determined only by donor-acceptor interaction.

We have established that the interconnection between the magnitude  $\Delta H$ ,  $E_{1/2}$ , and  $\mu_R$  is described by the relation

$$|\Delta H| = 6.27 - 5.14E_{1/2} + 0.45\mu_R,$$

in which the first two members correspond to the donor-acceptor contribution ( $\Delta H_{DA}$ ) and the third to the electrostatic contribution ( $\Delta H_\mu$ ). It can be seen from Table 1, that, as was to be expected [11], with a rise in  $E_{1/2}$ , i.e., with a decrease in the donor capacity of the radicals, the value of  $\Delta H_{DA}$  decreases, which also explains the observed decrease in the degree of transfer of spin density from the radical to the Ionol molecule. In actual fact, the values of  $a^{OH}$  and  $\Delta H_{DA}$  are connected with one another by the linear relation

$$-a^{OH} = -0.019 + 0.18|\Delta H_{DA}|, \quad (r = 0.996) \quad (6)$$

the value of the free member of which is apparently due to the change in the hfs constant  $a^{OH}$  both through the delocalization of the spin density from the hydroxy group to the aromatic ring of the Ionol [6] and through the electrostatic interaction of the dipole moments of the radical and the Ionol.

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