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PROTOLYTIC REACTIONS OF 3,6-DI-*tert*-BUTYL-2-HYDROXYPHENOXYL WITH NITROGEN BASES

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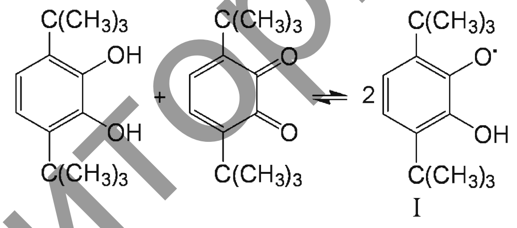
Stable phenoxyl radicals were used as spin probes for the EPR spectral determination of the kinetic basicity of amines, nitrogen heterocycles, alkaloids, and of rate constants for rapid intermolecular proton exchange with various NH-acids in nonaqueous media. An analysis was carried out on the effect of the solvation properties of the medium on the EPR spectral parameters of the components of acid–base reactions required for spectral kinetic investigations.

Key words: *phenoxyl radical, protolytic reactions, nitrogen bases, EPR spectra, hyperfine coupling constants, proton transfer rate constant, proton exchange rate constant, ion pairs.*

3,6-Di-*tert*-butyl-2-hydroxyphenoxyl (I), which is a stable radical formed upon mixing solutions of the corresponding spatially-hindered pyrocatechol and *ortho*-quinone:



(1)

may be used as a spin probe for the EPR spectral study of the kinetic basicity of organic proton acceptors such as aliphatic and aromatic amines, nitrogen heterocycles, and natural alkaloid bases [1, 2]. The high sensitivity of the hyperfine coupling constants (HCC) of the unpaired electron with the proton of the hydroxyl group in I to the acid–base properties of the medium also permits us to determine the specific rate constants of the rapid proton exchange of this radical with various organic OH- and NH-acids in nonaqueous solutions from dynamic EPR spectra of this hydroxyphenoxyl radical [2]. A characteristic feature of I as well as substituted *o*-hydroxyphenoxyls, namely, 4,6-di-*tert*-butyl-3-chloro-2-hydroxyphenoxyl (II) and 4-triphenylmethyl-6-*tert*-butyl-3-chloro-2-hydroxyphenoxyl (III) is rapid intramolecular and homolytic hydrogen atom migration within the five-membered HOCCO$^{\bullet}$ chelate bridge [2, 3]. The degenerate and nondegenerate tautomerism or proton transfer in these radicals gives rise, in turn, to the dual protolytic reactivity of these paramagnetic OH-acids.

In light of the nanosecond degenerate intramolecular proton transfer ($A \rightleftharpoons A'$) in the stable 3,6-di-*tert*-butyl-2-hydroxyphenoxyl radical (I), the scheme for the rapid and reversible protonation of organic bases Y by this compound in

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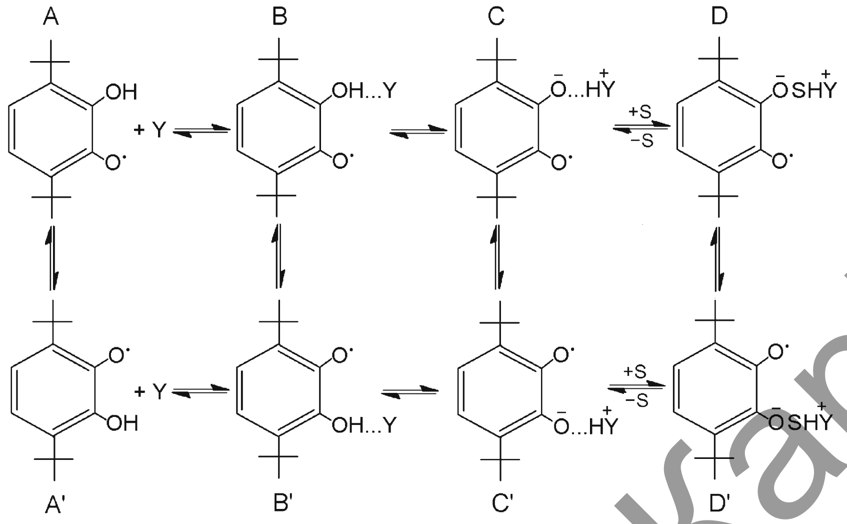
various media S through two independent channels A ⇄ B ⇄ C ⇄ D and A′ ⇄ B′ ⇄ C′ ⇄ D′ may be represented by scheme (2) [2].



(2)

The scheme presented for the two-channel protolytic reaction of substituted hydroxyphenoxyl I also illustrates such tautomeric transformations in the reaction system as hydrogen transfer in the starting compounds (A ⇄ A′) and cation transfer in the final products (C ⇄ C′ and D ⇄ D′) as well as tautomeric transitions in intermediates of this acid–base reaction, namely, hydrogen-bonded intermolecular complexes (HBC) (B ⇄ B′), which may appear specifically in the EPR spectra of the paramagnetic systems studied [2, 3].

TABLE 1. Kinetic and Thermodynamic Parameters for Proton Transfer from I to Various Bases

Base	K_e(293 K), L/mol	$-\Delta H \pm 3.0$, kJ/mol	k_1(293 K), L/mol·s	$E_1 \pm 6.0$, kJ/mol	k_{-1}(293 K), s^{-1}	$E_{-1} \pm 3.0$, kJ/mol
Triethylamine	9.7	37.7	$7.7\cdot10^{8}$	10.5	$8.7\cdot10^{7}$	48.2
Tributyl	2.2	36.0	$1.7\cdot10^{8}$	13.0	$7.6\cdot10^{7}$	49.3
Dimethyl-*tert*-butylamine	7.8	38.0	$5.7\cdot10^{8}$	5.4	$7.3\cdot10^{7}$	43.9
Dimethylallylamine	1.2	30.1	$4.8\cdot10^{8}$	2.9	$3.8\cdot10^{8}$	33.0
Pseudoephedrine	11.3	8.2	$1.8\cdot10^{9}$	28.0	$1.5\cdot10^{8}$	36.2
4-Methylpyridine	$1.3\cdot10^{-2}$	54.3	$2.4\cdot10^{8}$	2.1	$1.9\cdot10^{6}$	56.4
Thebaine	1.8	25.3	$5.4\cdot10^{8}$	16.8	$3.0\cdot10^{8}$	42.2
Triethylamine*	6.6	28.0	$3.6\cdot10^{8}$	18.4	$5.5\cdot10^{7}$	46.0
Atropine*	9.6	33.0	$7.5\cdot10^{8}$	2.5	$3.7\cdot10^{7}$	85.5
Quinine*	26.3	26.7	$1.7\cdot10^{8}$	32.2	$6.3\cdot10^{6}$	58.9

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*Experimental data taken in tetrahydrofuran as the medium.

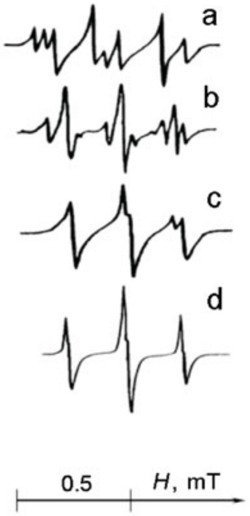
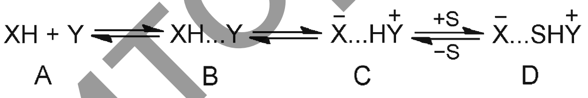


Fig. 1. Superposition of EPR spectra: a, b) radical I and ion pairs I′ with the thebaine counterion at 253 K in toluene and at 263 K in tetrahydrofuran, respectively, c) contact and loose ions pairs of I′ with triethylammonium cation at 263 K in tributyl phosphate, d) contact and loose ions pairs of I′ in triethylamine.

Scheme (2) may be rewritten in more convenient form taking account of the equivalence of both protolysis channels for hydroxyphenoxyl radical I:



$$\underset{A}{XH + Y} \rightleftharpoons \underset{B}{XH...Y} \rightleftharpoons \underset{C}{\overset{-}{X}...H\overset{+}{Y}} \underset{-S}{\overset{+S}{\rightleftharpoons}} \underset{D}{\overset{-}{X}...SH\overset{+}{Y}} \qquad (3)$$

Here, XH indicates a paramagnetic OH-acid or stable hydroxyphenoxyl radical I acting as a spin probe.

Contact ion pairs of organic radical-anions with various counterions such as 3,6-di-*tert*-butyl-*o*-semiquinone (I′) with ammonium cations C (see scheme (3)) may undergo solvation accompanied sometimes by their loosening or dissociation by the action of molecules of the medium S [4]. In this case, EPR spectroscopy is used to establish that if the formation of molecular HBC A ⇄ B between radical I and proton acceptor molecules binding its hydroxyl group such as tetrahydrofuran or tributyl phosphate affects only the rate of hydrogen transfer B ⇄ B′ (see scheme (2)) but does not alter the position of the EPR signal of the substituted hydroxyphenoxyl in the magnetic field, then liquid-phase C ⇄ D processes in ionic HBC are accompanied by changes in the *g*-factor of the semiquinone radical-anion I′. Taking account of these factors is important in determining the kinetic basicity of tertiary amines (Y) by dynamic EPR spectroscopy using stable hydroxyphenoxyl I as an acid spin probe for these purposes [7].

Calculations for the rate constants of the forward A ⇄ C (k_1) and reverse reactions C ⇄ A (k_{-1}) of the reversible protonation, for example, of tertiary amines by radical I were carried out using formulas based on modified Bloch equations relating these constants with line broadening of the hyperfine structure (HFS) of the EPR spectrum ($\Delta(1/T_2)$) due to rapid acid–base reactions in the paramagnetic liquid-phase systems studied [5]:

$$\Delta\frac{1}{T_2}=\frac{\gamma_e\alpha(1-\alpha)(\Delta a)^2}{k_1[\mathrm{Y}]+k_{-1}} \tag{4}$$

where γ_e is the gyromagnetic ratio of an electron, α and $(1-\alpha)$ are the mole fractions of paramagnetic species I and I′, while Δa is the distance between the hyperfine structure lines of EPR spectrum of I and I′ broadened due to the protolytic A ⇄ C reaction in magnetic field units.

Simulation of the dynamic ESR spectra in the liquid-phase protolytic system with the rapid A ⇄ C reaction may be carried out using a program proposed by Chen and Hirota [6] for a four-jumping model adapted for current versions of PGI Visual Fortran. Table 1 gives some of our previously obtained physicochemical parameters of the reversible protonation for various tertiary amines by acid spin probe I in toluene and tetrahydrofuran [7, 8].

In the present work, major attention is focused on analysis of the EPR spectra of the products of the protolysis of hydroxyphenoxyl radical I formed in nonaqueous solutions of various organic bases, which we studied previously relative to the kinetics of their rapid proton transfer reactions and exchange with paramagnetic H-acid I.

The dependence of the EPR spectral parameters such as the HCC and *g*-factor of radicals I and I′ on the solvation properties of the medium affects the value of Δa in Eq. (4) and HFS line broadening of the EPR spectra of the paramagnetic participants in rapid bimolecular protolytic reactions. Our EPR spectral study showed that the formation of molecular HBC of the semiquinone radical I with various proton acceptors (even with such strong acceptors as hexamethylphosphoric triamide) does not lead to marked change in the hyperfine structure and *g*-factor of the EPR spectrum of I (g_1 = 2.00435 in toluene solutions of I) although hexamethylphosphoric triamide forms strong complexes with the hydroxyradical and significantly hinders hydrogen transfer B ⇄ B′ in these complexes in comparison with the rate of intramolecular tautomerism for A ⇄ A′ in more inert solvents such as hexane or in toluene itself (see scheme (1)) [7]. However, the magnetic moment of radical-ion I′ in the final salt products of protolytic reaction (1) is markedly diminished with loosening of the contact ion pair by the solvating molecules of the liquid medium S through the channel C ⇄ D. Figure 1 shows the variations of the superpositioning of the EPR spectra of radicals I and I′ depending on the nature of the ammonium cation and solvating properties of the reaction medium.

The EPR spectrum of semiquinone radical I is a triplet of doublets displaying hyperfine coupling constants of the unpaired electron with two magnetically-equivalent benzene ring protons and with the hydroxyl group proton, a_H = 0.392 mT and a_H^OH = 0.162 mT, respectively [7]. Semiquinone radical-anion I′ has an EPR spectrum with hyperfine coupling constant of the unpaired electron with two magnetically-equivalent ring protons a_H = 0.335 mT. The loss of the acidic hydroxyl proton in I, for example, to a tertiary amine leads to the disappearance of a_H^OH in the ion pair of I′ with the protonated base.

If the value of the *g*-factor for I′ in the contact ion pair with the ammonium cation of the protonated alkaloid, thebaine, in toluene is g'_I = 2.00450, then this would appear as a superposition of the right-hand component of the triplet EPR spectrum of I′ and the downfield component of the doublet hydroxyl splitting of the analogous triplet EPR spectrum of semiquinone radical I as presented in Fig. 1a.

Such positioning of the HFS lines of radicals I and I′ permits us to take Δa in Eq. (4) equal to $\Delta a = a_\mathrm{H}^\mathrm{OH}$ = 0.162 mT in determining the kinetic basicity of many proton acceptors with the tertiary nitrogen atom in relatively inert solvents such as toluene or hexane.

The contact ion pair of I′ with the thebaine cation becomes looser even in tetrahydrofuran, and Fig. 1b illustrates the superposition of the EPR spectra of the components of the slow protolytic reaction A ⇄ D ($v \le \gamma_e\Delta a$) (scheme (2)) [5]. This scheme shows that the EPR spectrum of the corresponding loose ion pair is shifted upfield by 0.080 mT relative to the spectrum of the contact ion pair (Fig. 1a). A similar loosening of the stronger tight ion pair of I′ with the triethylammonium cation may be seen in tributyl phosphate, which has stronger solvating properties than tetrahydrofuran. Figure 1c demonstrates superposition of the EPR spectra of two ion pairs corresponding to the slow reaction C ⇄ D (see scheme (3)). It is interesting to note that there is loosening of the corresponding ion pair of I′ with the triethylammonium cation in pure triethylamine but the EPR spectrum of this product is shifted downfield (see Fig. 1d). The slight increase in the *g*-factor of the ion pair solvated by this base is apparently a consequence of some contribution of the unshared electron pair of the triethylamine nitrogen atom to the total magnetic moment of the 3,6-di-*tert*-butyl-*o*-semiquinone radical-anion.

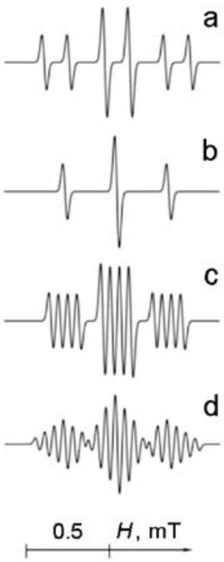


Fig. 2. EPR spectra of radical I and its derivatives at 293 K in toluene: a) hydroxyphenoxyl I, b) 3,6-di-*tert*-butyl-*o*-semiquinone radical-anion (I′), c) contact ion pair of I′ with a lithium cation, d) dimer of the contact ion pair of I′ with a lithium cation.

A feature of ions pairs of 3,6-di-*tert*-butyl-*o*-semiquinone with various cations including metal cations is a tendency of their nonaqueous solutions to aggregate upon standing. In particular, in previous work [9], we showed that EPR spectra of intermolecular radical pairs with the corresponding dipole–dipole interactions of the unpaired electrons are recorded in toluene solutions of several contact ion pairs of I′ with ammonium cations at low temperatures.

The EPR spectral processes for aggregation of ion pairs of I′ are more easily followed in salt products with smaller alkali metal cations than with bulky protonated alkaloid molecules such as thebaine. Single-valence metallic lithium, sodium and sodium bases, having lower ionization potentials than multiatomic organic proton acceptors, form ion pairs both in reactions with I and with 3,6-di-*tert*-butyl-*o*-quinone corresponding to this radical [10].

The EPR spectrum of I is a triplet of doublets with the abovementioned hyperfine coupling constants of the unpaired electron with the magnetic nuclei of the radical (see Fig. 2a). The reduction of I or the related *ortho*-quinone by single-valence alkali metal (M) base leads to the formation of an ion pair of the semiquinone radical-anion I′ with the corresponding cation C, whose EPR spectrum (Fig. 2b) is already a triplet with hyperfine coupling constants of the unpaired electron only with two magnetically-equivalent ring protons equal to $a_H = 0.335$ mT. The EPR spectrum of the contact ion pair of I′ with alkali metal cations may show hyperfine structure from these cations as a quartet with hyperfine coupling constant $a_M = 0.060$ mT (see Fig. 2c) [4]. Upon standing, aggregation of these ion pairs to give dimers occurs in their toluene solutions. The EPR spectra of these dimers show splitting already from two magnetically-equivalent alkali metal cations as the corresponding septet with $a_M = 0.050$ mT (see Fig. 2d). The ring protons of radical-anion I′ in monomeric and dimeric forms of the ion pairs, as seen from the EPR spectra (Fig. 2), also retain their magnetic equivalence, which indicates rapid cation exchange $C \rightleftarrows C'$ in these species (see scheme (1)).

Figure 3a shows the dynamic EPR spectra of the reaction pair of semiquinone radical I and anabasine alkaloid obtained in relatively inert toluene. Since anabasine is an alkaloid with both tertiary and secondary nitrogen base sites and the more basic piperidinyl substituent has NH-acidity, the EPR spectrum shown in Fig. 3a illustrates the dynamics of rapid intermolecular

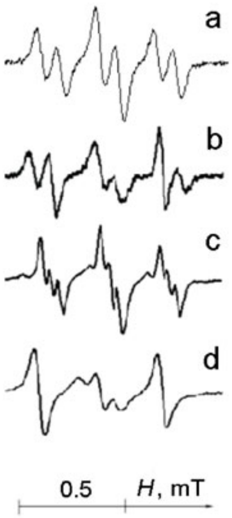
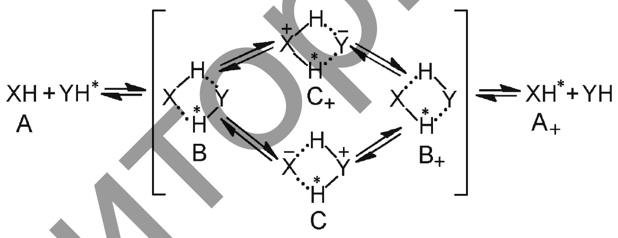


Fig. 3. EPR spectra of a mixture of I and anabasine in toluene solution at 310 (a), 255 (b), 238 (c), and 183 K (d). [Y] = 0.04 mol/L.

proton exchange A ⇄ A_+ between semiquinone radical I and this molecule. The general scheme for this exchange may be represented as follows [8]:



(5)

where the asterisk indicates an acid proton with different nuclear spin orientation.

The rate of the rapid intermolecular proton exchange between the paramagnetic OH-acid (I) and diamagnetic NH-acidic anabasine v_{ex} from similar spectra is calculated using the well-known formula [5]:

$$v_{ex} = \frac{\gamma_e \tilde{a}_H^{OH}}{2\sqrt{2}}\left[1-\left(\frac{\tilde{a}_H^{OH}}{a_H^{OH}}\right)^2\right]^{1/2} \tag{6}$$

where $\tilde{a}_H^{OH}$ is the effective hydroxyl splitting constant in the EPR spectrum of I as the result of rapid intermolecular proton exchange in this system, which, in the absence of such a reaction, is $a_H^{OH} = 0.162$ mT. Table 2 gives some kinetic parameters of the rapid intermolecular proton exchange between hydroxyphenoxyl I and various secondary amines, which display NH-acidity in toluene [7, 8].

We may note that while the alkaloid, ephedrine, is a typical NH-acid, its isomer, pseudoephedrine, may also display properties of a tertiary amine since the acidic proton in this molecule is linked by means of an intramolecular hydrogen bond in this proton acceptor molecule (see Table 1).

TABLE 2. Kinetic Parameters of the Proton Exchange of I with Some NH-Acids in Toluene

Base	k_{ex}(293 K), L/mol·s	k^0_{ex}, L/mol·s	E_a, kJ/mol
Diethylamine	$(3.1 \pm 0.7)\cdot 10^{9}$	$(1.7 \pm 0.6)\cdot 10^{9}$	4.0 ± 0.4
Piperidine	$(6.3 \pm 1.0)\cdot 10^{8}$	$(5.9 \pm 0.8)\cdot 10^{9}$	5.5 ± 0.5
Ephedrine	$(3.7 \pm 0.2)\cdot 10^{9}$	$(3.7 \pm 0.3)\cdot 10^{9}$	2.3 ± 0.5
Anabasine	$(8.7 \pm 0.1)\cdot 10^{8}$	$(7.5 \pm 0.1)\cdot 10^{9}$	5.3 ± 0.3
α,β′-Dipiperidyl	$(1.7 \pm 0.1)\cdot 10^{9}$	$(1.3 \pm 0.1)\cdot 10^{10}$	4.9 ± 0.4
Ethylenediamine	$(6.8 \pm 0.1)\cdot 10^{9}$	$(4.9 \pm 0.1)\cdot 10^{11}$	10.4 ± 0.2
2,3-Diaminobutane	$(6.1 \pm 0.1)\cdot 10^{9}$	$(3.4 \pm 0.1)\cdot 10^{11}$	9.8 ± 0.8
Hexamethylenediamine	$(7.2 \pm 0.1)\cdot 10^{9}$	$(2.6 \pm 0.1)\cdot 10^{11}$	8.7 ± 0.9

The EPR spectrum in Fig. 3b demonstrates the intermolecular dynamics of the rapid reversible proton transfer in the system containing I and anabasine, which proceeds through the channel A ⇄ C on the condition of low-temperature decomposition of the cyclic complexes due to two hydrogen bonds B and B_1, providing for rapid proton transfer in this protolytic acid–base system. The formation of an intermediate as a linear complex with one hydrogen bond as shown in scheme (2) is sufficient for proton transfer.

Figure 3c illustrates the EPR spectrum of radical-anion I′ with the anabasine cation, in which there is hyperfine structure from the hyperfine coupling of the unpaired electron with the nucleus of the nitrogen atom of the piperidine substituent of the base with hyperfine coupling constant a_N = 0.030 mT. The pyridine substituent of anabasine has less thermodynamic basicity and does not form an ammonium cation with paramagnetic acid I [7]. However, as in the case of the alkaloid, thebaine, similar superposition of the EPR spectra of two types of ion pairs of the corresponding ammonium cation with 3,6-di-*tert*-butyl-*o*-semiquinone I′ is observed at low temperatures in a toluene mixture of semiquinone radical I with anabasine (see Fig. 3d). This finding should apparently be attributed to the high asymmetry of the protonated base sites in these alkaloids. In this case, the cation transfer C ⇄ C′ is markedly hindered in one of the ion pairs of this reaction system (see scheme (1)), and the EPR spectrum of such a paramagnetic ammonium salt is a doublet of doublets with hyperfine coupling constant of the unpaired electron with the *para* and *meta* ring protons in I′ a_H = 0.37 mT and a_H = 0.30 mT, respectively.

The structure of the second contact ion pair apparently does not hinder rapid intramolecular cation transfer, and the EPR spectrum of this structure is a triplet with hyperfine coupling constant of the unpaired electron with two magnetically-equivalent ring protons equal to a_H = 0.335 mT (see Fig. 3d). We should note that among the various alkaloids studied, the abovementioned spectral effects are observed only in ion pairs of I′ with cations of protonated thebaine and anabasine.

Diamines such as ethylenediamine (EDA) and hexamethylenediamine (HMDA) have NH-acidity characteristic for primary and secondary amines and undergo rapid intermolecular proton exchange with hydroxyphenoxyl I [8, 11]. This behavior is also found for polyethylenimine (PEI), which already is a polymeric NH-acid. EPR spectra of the corresponding ion pairs are seen at low temperatures in such reaction systems and display the abovementioned triplets from two magnetically-equivalent ring protons of radical-anion I′ (see Fig. 4b).

The formation of new paramagnetic products is seen in toluene mixtures of I with PEI and HMDA upon standing. The EPR spectra of these products are shown in Fig. 4c, d. We should note that this effect is not observed in toluene solutions of EDA and other aliphatic diamines. A computer simulation of these isotropic EPR spectra using the Bruker WINEPR program

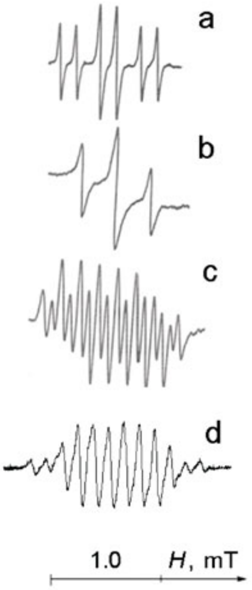


Fig. 4. EPR spectra of 3,6-di-*tert*-butyl-2-hydroxyphenoxyl (a), ion pair of 3,6-di-*tert*-butyl-*o*-semiquinone with the cation of protonated polyethylenimine (PEI) (b), ion pair of I′ chelated by polyethylenimine (PEI) molecules (c), and ion pair of I′ chelated by hexamethylenediamine (HMDA) molecules (d) at room temperature.

indicated that they correspond to ion pairs of the 3,6-di-*tert*-butyl-*o*-semiquinone radical-anion with counterions of protonated HMDA and PEI molecules chelated with excess molecules of the corresponding bases present in the solution. The hyperfine structure of the EPR spectra of these chelates is attributed to hyperfine coupling of the unpaired electron with two ring protons of I′ and two nitrogen atom magnetic nuclei of protonated HMDA and PEI molecules.

In particular, a computer simulation of the chelate complex of the ion pair of I′ with the hexamethylenediamine cation permits the formation of 12 absorption lines in the EPR spectrum (Fig. 4d) due to hyperfine coupling of the unpaired electron of the paramagnetic species with two magnetically-equivalent ring protons in I′ with coupling constant $a_H = 0.335$ mT and with two magnetically-equivalent nuclei of the ammonium cation nitrogen atoms with coupling constant $a_N = 0.100$ mT. Similar modelling of the EPR spectrum of the chelate product formed in the reaction mixture of I and PEI (Fig. 4c) could be carried out with possible coupling of the unpaired electron of I′ with two nuclei of cation nitrogen atom to give coupling constants $a_{N1} = 0.080$ mT and $a_{N2} = 0.140$ mT and retention of the magnetic equivalence of the ring protons in I′. The hyperfine coupling of these ring protons with the unpaired electron of the semiquinone radical-anion is described by the abovementioned constant.

Thus, the spatially-hindered stable phenoxyl radical, 3,6-di-*tert*-butyl-2-hydroxyphenoxyl (I), which we use as a paramagnetic H-acid or spin probe for the EPR spectral determination of the kinetic basicity of various organic proton acceptors and rates of rapid protolytic reactions of OH- and NH-acids in nonaqueous media can also be used to study salt formation processes in various acid–base systems proceeding in organic solvents.

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