HYDROGEN BOND FORMATION IN RADICALS WITH PARTICIPATION OF THE UNPAIRED ELECTRON

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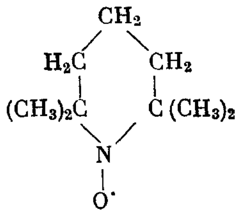
It is shown that stable nitroxide radicals form hydrogen bonds with water, methyl alcohol, and acetic acid molecules. A special feature of the hydrogen bond is that the unpaired electron particpates in its formation. The formation of the hydrogen bond changes the hyperfine splitting constant and the g-factor of the radical. The dynamics and the equilibrium of hydrogen bond formation have been studied, and the equilibrium constants and the bond energies have been determined. It is shown that under certain conditions the unpaired electron may participate in the formation of intermolecular hydrogen bonds in radicals.

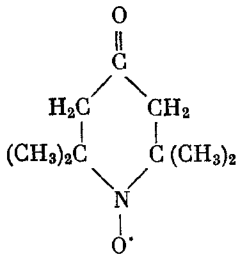
In several studies on organic free radicals in the liquid phase it was noted that the hyperfine splitting in the electronic paramagetic resonance (EPR) spectra of these radicals depends essentially on the nature of the medium in which the radicals are located. Obviously, this effect is solely due to the properties of the medium and was considered in [1-4] to be a solvation effect. However, the nature of the solvation and the structure of the solvates have not been investigated, and the concept of solvation is too general and lacks a precise meaning.

The interaction with the medium is interesting, since it may be used to study the properties of the unpaired electron, the latter playing an important role in the behavior and reactivity of the radical. First of all it is necessary to find out whether the above-mentioned effects are related to the dielectric properties of the medium as a whole, or are due to specific localized interactions between the radical and solvent molecules.

For this purpose we studied the EPR spectra of two stable nitroxide radicals (I) and (II), in which the unpaired electron (indicated by a dot near the oxygen atom) is delocalized by transfer to the N-O bond:



I



II

The EPR spectra in various solvents were taken in the EPR-2 spectrometer of the Institute of Chemical Physics, Academy of Sciences USSR [5]. All measurements were done with evacuated samples. The results are given in Table 1, where a_N denotes the hyperfine splitting of the line due to the N^{14} nucleus (in Oe).

Analysis of the a_N values shows that the solvents mentioned in Table 1 can be divided into two groups. In the first group – in water, methanol, acetic acid – the splitting of the nitrogen line varies, whereas in all other solvents the splitting is constant independent of the dielectric properties of the medium. This proves that the dielectric

TABLE 1. Distance between the Components of the Triplet in the EPR Spectrum of Radicals (I and (II)

Solvent	a_N ($\pm$ 0.2 Oe)	
	I	II
Acetone	15.6	15.6
Heptane	15.6	15.6
Carbon Tetrachloride	15.6	—
Benzene	15.6	—
Tetrahydrofuran	15.6	—
Water	17.1	17.1
Nitrobenzene	15.7	—
Methyl alcohol	16.3	16.3
Acetic acid	16.6	—
Chloroform	15.6	—

properties of the medium are not essential with regard to the effects observed, and that localized interactions between the radical and the surrounding molecules play a decisive role. It should be noted that a special feature of the solvents of the first group is their capacity to form hydrogen bonds with the radical.

To determine the variations of a_N to a sufficient accuracy, we used the following experimental procedure. In the resonator of the EPR spectrometer we placed two thin ampoules containing radical solutions of equal concentration in different solvents, and the EPR spectra were recorded simultaneously (sometimes even together with the signal produced by polycrystalline diphenylpicrylhydrazyl). By way of example, two such records are shown in Fig. 1. The lower record is the superposition of the spectra of radical (I) in acetone and in carbon tetrachloride. It is evident that the components of the two spectra exactly coincide. The upper record is the superposition of the spectra of the same radical in acetone and water. Here, only the triplet components at the lowest field strength coincide in the two solvents. The recorded intensity of these components is nearly twice the intensity of the individual components. The components at higher field strengths are spaced apart, the central one by $\Delta a = a_2 - a_1$, where a_2 and a_1 are the splittings in water and in acetone, respectively, and the outer components (at the highest field strength) by $2\Delta a$. Consequently, comparison of the EPR spectra of the radical in water and acetone proves that formation of a hydrogen bond with the radical in water and acetone proves that formation of a hydrogen bond with the radical changes the hyperfine splitting constant and the g-factor.

Figure 2 shows the superposed spectra of radical (II) in acetone and water. Here, all three components of the spectrum in acetone do not coincide with those of the spectrum in water, in other words, the formation of a hydrogen bond changes the a_N value and also the g-factor of this radical. The same happens when radicals (I) and (II) form hydrogen bonds with methyl alcohol, acetic acid, and other molecules capable of forming these bonds. In all other solvents the positions of the psectral components coincide exactly.

From the shifts of the components in the spectra taken in various solvents we can calculate the a_N values and the g-factors of the radicals in these solvents. When the shifts were small, they were analyzed with the aid of an

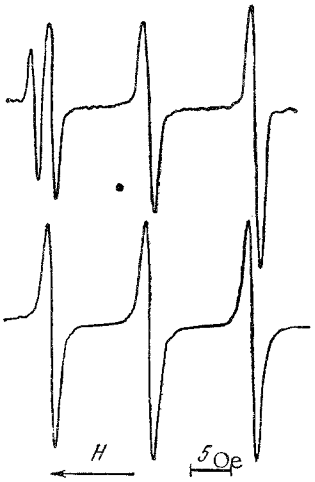


Fig. 1. Superposed EPR spectra of radical (I) in various solvents (see the text).

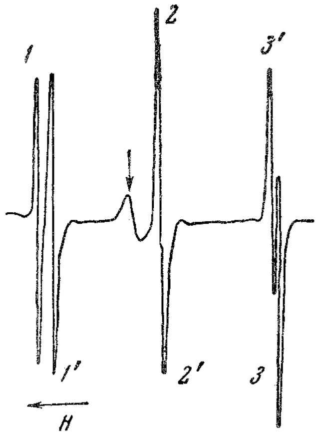


Fig. 2. Superposed EPR spectra of radical (II) dissolved in water and acetone (the line produced by DPPH is indicated by an arrow).

TABLE 2. A_N Values and G-Factors of Radicals (I) and (II) in various Solvents

Solvent	I		II	
	a_N, Oe	g-factor	a_N, Oe	g-factor
Carbon tetrachloride	15.6	2.0065	–	–
Acetone	15.6	2.0065	15.6	2.0065
Methyl alcohol	16.3	2.0060	16.3	2.0060
Acetic acid	16.6	2.0058	–	–
Heavy water (D_2O)	16.9	2.0056	–	–
Water	17.1	2.0054	17.1	2.0059

atlas of EPR spectra [6]; larger shifts were determined directly from the spectra. The g-factors were measured with reference to the values in solvents which do not form a hydrogen bond. The main results are reported in Table 2.

The data given in Tables 1 and 2 prove that a hydrogen bond having the special feature that the unpaired electron participates in this bond, form from the radical and the solvent molecule. This increases the magnitude of the isotropic splitting constant of nitrogen, either because the spin density near the nitrogen atom is altered, or because the hybridization of the bonds changes and the contribution of the s-state to the wavefunction of the unpaired electron rises. The g-factor drops simultaneously with the rise of a_N, the former decrease being due either to an increased absolute magnitude of the spin-orbital bond constant, or to a larger distance between the levels of the orbitals. Consequently, the unpaired electron participates in the formation of a hydrogen bond, which confirms the ideas on the donor-acceptor nature of the hydrogen bond which were proposed and worked out by Sokolov in 1947 [7].

It can be supposed that solvation of the free radical by hydrogen-bonding to the solvent S is a reversible reaction proceeding according to the scheme

$$R_0 + nS \overset{K}{\rightleftarrows} R_S, \qquad (1)$$

where K denotes the equilibrium constant; n the coordination number of the complex. It is of interest to study the nature of this equilibrium.

If the frequency at which the hydrogen bond forms and breaks is lower than the difference between the splitting distances of free and solvated radicals (in frequency units), then, components due to the two types of radicals will be found in the spectra. If however, this frequency is much higher than the difference between the splitting distances, then, the spectrum will consist of components characterized by an averaged splitting distance $\bar{a}$ which lies between the a_N values of the free and the solvated radicals. The parameter $\bar{a}$ is determined by Bloch's equations and equals

$$\bar{a} = a_0 p_0 + a_S p_S, \qquad (2)$$

where a_0 and a_S denote the a_N values of the radicals R_0 and R_S [see equation (1)], and p_0 and p_S the fractions of radicals R_0 and R_S in the solution. Substituting (2) into the equation for the equilibrium constant of (1), we easily find that

$$K[S]^n = (\bar{a} - a_0) / (a_S - \bar{a}). \qquad (3)$$

Equation (3) can be easily transformed to the convenient interpolation formula [2]

$$\bar{a} = \frac{1}{2}(a_0 + a_S) + \frac{1}{2}\rho(a_S - a_0), \qquad (4)$$

where

$$\rho = \frac{K[S]^n - 1}{K[S]^n + 1} \qquad (5)$$

varies from -1, if all radicals are unsolvated R_0 radicals, to $+1$, if all radicals are solvated; $[S] = (1/K)^{1/n}$ at $\rho = 0$.

We studied equilibrium (1) in the solvent mixtures acetone – water and heptane-methanol. Here, as in the previous measurements, two ampoules were placed simultaneously in the resonator of the EPR spectrometer: one am-

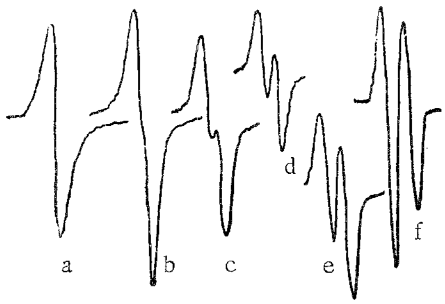


Fig. 3. Superposed outer components of the EPR spectra produced by radical (I) dissolved in acetone and in acetone – water mixtures with the following water: acetone ratios: a) 0.06; b) 0.40; c) 0.50; d) 0.67; e) 1.00; f) water without acetone.

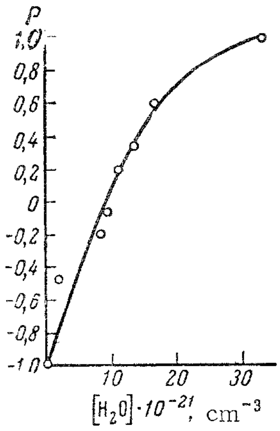


Fig. 4. Plot of ρ of radical (I) in water-acetone solutions versus the water concentration.

poule being filled with a solution of the radicals in acetone or heptane, the other with solvent mixtures of various compositions. By way of example, several double lines, which are the superposed outer components produced at higher field strengths by radical (I) in acetone and in mixtures of various proportions of acetone and water, are shown in Fig. 3. It will be seen that mixtures produce only a single component characterized by an averaged parameter $\bar{a}$ whose magnitude increases with the water concentration in the solution. This indicates that the frequency at which the hydrogen bond forms and breaks is much higher than the difference in splitting distance. For this same reason, no splitting caused by the proton of the water molecule participating in the hydrogen bond is observed.

Using equation (4) and substituting $a_0 = 15.6$ and $a_S = 17.1$* Oe, we may calculate ρ from the experimental value of $\bar{a}$. Values of $\bar{a}$ and ρ for radical (I) at various water concentrations in the mixture are given in Table 3.

In Fig. 4 the ratio ρ of radical (I) in water – acetone mixtures is plotted versus the water concentration. Assuming $n = 1$ and using equation (5), we can calculate the equilibrium constant by using the ordinate of the point where the curve in Fig. 4 intersects the axis of abscissas $\rho = 0$; this yields $K = 1.25.10^{-22}$ cm^3. In fact, according to equation (3) there would exist a linear relationship between $(\bar{a}-a_0)/a_S-\bar{a})$ and [S], if $n = 1$. Fig. 5 confirms that this relationship exists. Hence, we may take that the coordination number of the complex with the hydrogen bond equals unity.

The temperature dependence of the equilibrium constant and the energy of the hydrogen bond between the radical and a water molecule can be derived from measurements of $\bar{a}$ in acetone – water mixtures at various temperatures. By way of example, Fig. 6 shows lg K for the hydrogen bond between radical (I) and water plotted versus the inverse temperature. The energy of the hydrogen bond is 2.4 ± 1.0 kcal/mole, and the equilibrium constants equals

$$K = 2.10^{-24} \exp(2400/RT) \text{ cm}^3.$$

TABLE 3. Values of $\bar{a}$ and ρ of Radical (I) in Mixtures of Water and Acetone

$[H_2O]\cdot 10^{-21}$, cm^{-3}	$\bar{a}$, Oe	ρ	$[H_2O]\cdot 10^{-21}$, cm^{-3}	$\bar{a}$, Oe	ρ
0	15,6	—1,00	11,1	16,5	0,20
2,0	16,0	—0,47	13,4	16,6	0,33
8,6	16,2	—0,20	16,6	16,8	0,60
9,5	16,3	—0,07	33,3	17,1	1,00

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* In pure solvents the parameter a_N does not vary with the temperature. This suggests that in water, alcohol and acetic acid the parameter a_S equals a_N.

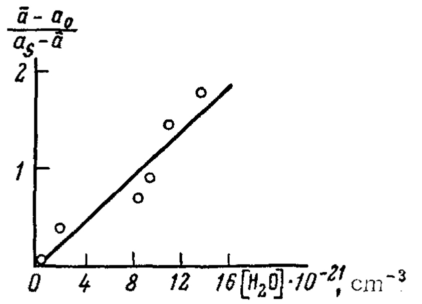


Fig. 5. Ratio $(\bar{a}-a_0)/(a_S-\bar{a})$ for radical (I) as a function of the water concentration.

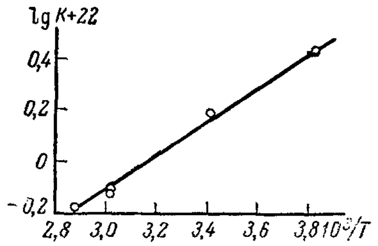


Fig. 6. Plot of lg K of the hydrogen bond between radical (I) and water molecules versus 1/T.

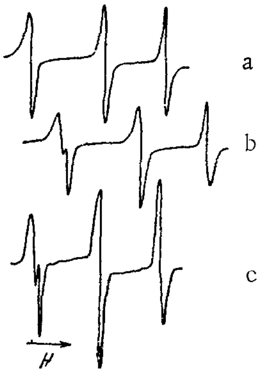
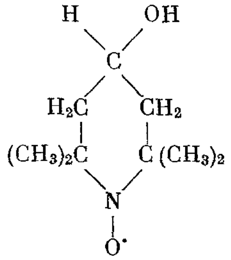


Fig. 7. Superposed EPR spectra of radicals (II) and (III) in heptane: a) 22°; b) −20°; c) −30°.

In a similar way it was found that the equilibrium constant of the complex formed from radical (II) and water equals $0.7 \cdot 10^{-22}$ cm^3 at 20°, and that the equilibrium constant of the complex with methyl alcohol is $2 \cdot 10^{-22}$ cm^3 at the same temperature. The energies of the hydrogen bonds between radical (II) and water, and methanol, amount to 4 ± 2 and 4.5 ± 2.0 kcal/mole. The high inaccuracy of the hydrogen bond energies are due to the difficulties arising in an accurate analysis of the shifts of the components in the EPR spectra. In the radical we also detected formation of an intermolecular hydrogen bond with methyl alcohol. The values of the g-factor and the hyperfine splitting constant in n-heptane and methyl alcohol at T = 22° were determined: in heptane g = 2.0067, a_0 = 15.6 Oe, in methanol g = 2.0063, a_S = 16.2 Oe.


III

Radical (III), which in an inert solvent (for example, in heptane) may form either intermolecular hydrogen bonds with the OH group of other radicals or an intramolecular hydrogen bond, is of particular interest as regards participation of the unpaired electron in hydrogen bond formation. For this reason we simultaneously recorded in EPR spectra of radicals (II) and (III) in heptane by employing the above procedure at concentrations so low that the formation of intermolecular bonds may be ignored. Such records taken at various temperatures are shown in Fig. 7. No noticeable shifts of the components occur at room temperature; at lower temperature the shifts appear and increase with decreasing temperature. This is due to the formation of an intramolecular hydrogen bond in the radical at low temperatures. Here, it is difficult to calculate the equilibrium constant, and the energy of the hydrogen bond from the EPR data, since the values of the parameters a_0 and a_S for the intermolecular bond are not known. A characteristic feature of the intramolecular hydrogen bond in (III) is that the corresponding g-factor is larger than the g-factor of the radical without a hydrogen bond. This distinguishes the intramolecular hydrogen bond in (III) from the intermolecular hydrogen bonds in (I) and (II). Formation of an intramolecular hydrogen bond affects a_N of radical (III) in the same way as does formation of intermolecular hydrogen bonds. It is possible that the anomalous behavior of the g-factor during the formation of an intramolecular bond in (III) is due to the circumstance that the latter forms between the hydrogen atom of a hydroxyl group and the nitrogen atom of the N-O bond, whereas in the other cases the hydrogen bond is evidently attached to the oxygen atom. It should be noted that the formation of an intramolecular bond in (III) was proved also by the methods of optical spectroscopy [9].

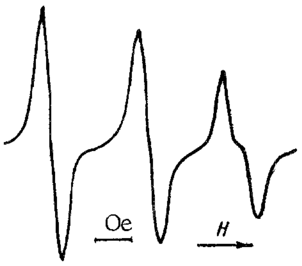
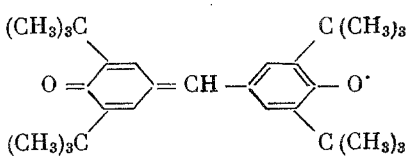


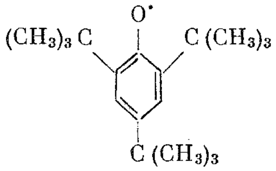
Fig. 8. Superposed EPR spectra of radical (IV) in heptane and methanol.

Besides the nitroxide radicals (I)-(III), Coppinger's radical



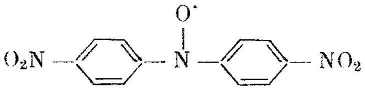
was also studied.

It was found that the EPR spectra of this radical in heptane and in methyl alcohol do not differ. Consequently, even if this radical can form a hydrogen bond in which the unpaired electron participates, the equilibrium in pure alcohol already lies on the side of the free radical. This conclusion, derived from our measurements, agrees with the conclusion of paper [10], where it was shown from kinetic data that the radical



whose structure is similar to that of Coppinger's radical, is not solvated in methyl alcohol.

Participation of the unpaired electron in the formation of a hydrogen bond is typical not only of aliphatic, but also of aromatic nitroxide radicals. This is illustrated in Fig. 8 by the superposed EPR spectra of the radical



IV

in heptane and methyl alcohol. Here, we also observe variations of a_N and the g-factor: in haptane a_N = 11.7 Oe, in methanol 12.7 Oe, the g-factors being 2.0065 and 2.0059, respectively. The parameter a_N varies also in other aromatic radicals (for example, in diphenylnitroxide [11]).

Our results and conclusions on the formation of hydrogen bond in radicals are essential for clarifying the characteristics of the reactivity of the radicals, since polar factors greatly influence the reactivity. The hydrogen bond produces the largest polar effects, particularly if it is formed in the activated complex of the reaction.

The results reported may be of interest also for the theory of the hydrogen bond.

In conclusion the authors acknowledge E. G. Rozantsev, who provided some radicals, and M. B. Neiman for his interest in our study and for a discussion.

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