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Solvent and Temperature Effects on the Proton hfs in the ESR Spectra of the Organic Radical

Shigeyuki AONO and Masahiko SUHARA

Department of Chemistry, Faculty of Science Kanazawa University, Maru-no-uchi, Kanazawa

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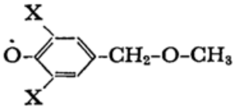
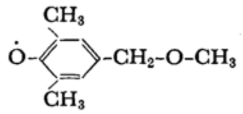
A theoretical investigation is made into the solvent and temperature effects on the proton hfs in the ESR spectra of such organic radicals as:



where X stands for the CH_3 group, in several solvents. Both effects are explained on the assumption that a molecular complex is formed between radical and solvent, so that the charge-transfer occurs from radical to solvent: The solvent effect is caused by the fact that, in various solvent molecules, slight changes take place in their lowest vacant levels, which are occupied by the electron transferred from the radical; on the other hand, the temperature effect is explained by the thermal motion of the molecules, which changes the probabilities of the radical being in the solvated state and in the free state.

Recently, experimental observations were made by Deguchi[1] of the proton hfs in the ESR spectra of such phenoxyl radicals as:



under various conditions. The results are shown in Table 1.

TABLE 1. THE METHYLENE PROTON HFS CONSTANTS

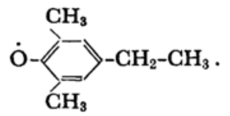
a) at room temperature and in various solvents

Solvent	Coupling const. (gauss)
n-Hexane	11.68
Benzene	12.00
Toluene	12.25
o-, *m*-, *p*-Xylene	12.50
Mesitylene	12.70

b) in tetrahydrofuran at two different temperatures

Temperature (°C)	Coupling const. (gauss)
−54	12.88
9	12.29

These results indicate, in short, that the proton fs constants increase with an increase in the number f methyl substituents in solvent molecules, and Sith a decrease in the temperature. However, o such behavior of the coupling constants was not observed in another type of radical:



Therefore, we can presume that these phenomena are responsible for the existence of the lone-pair electrons in the oxygen of the methoxy group. Further it should be pointed out that the solvents used here are known to be non-polar.

Mechanism

First of all, we assume that a sort of molecular complex between radical and solvent is formed. It then seems reasonable to assume that the charge-transfer from the oxygen lone-pair of the methoxy group in the radical to the lowest vacant level of the solvent molecule is a characteristic property responsible for the change in the proton hfs constants in the radical, since radicals which have no lone pair never behave thus. On the above assumptions, our theoretical procedures are as follows: The charge-transfer brings about a change in the coulomb term of oxygen by the amount of α'_O, which in turn alters the odd-electron density at the methylene proton by q'_M. Using the standard perturbation procedure, we then obtain:

$$q'_M = 2\alpha'_O c_{iO} c_{iM} \sum_{j \neq i} c_{jO} c_{jM} / (\varepsilon_i - \varepsilon_j), \qquad (1)$$

where ε_j is the orbital energy of the *j*th level, and where the *i*th level represents, especially, the level

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[1] Y. Deguchi, private communication.

for the odd electron, to the zeroth approximation. $c_{j\mathrm{O}}$ and $c_{j\mathrm{M}}$ are the LCAO coefficients of the jth orbital at the positions of the oxygen atom and the methylene H_2 group respectively. Here it must be noted that the H_2 or H_3 in the methylene or methyl group respectively gives a pseudo-π orbital constructed of 1s atomic orbitals. The radical in question is a π-radical, so that the odd electron occupies, to a good approximation, the highest occupied level of the mother molecule. In the perturbation calculation shown by Eq. (1), the main contributions should be those from the levels closest to the previous one. It follows from a simple investigation that the ith level is nearly the zero level, having a little of the bonding character due to the deeper coulomb terms of the oxygen in both the methoxy and phenoxy groups; the closest two levels, which are refered to the jth and j'th levels, corresponding to those occupied and vacant respectively, may be expected to show, roughly, the pairing property. Taking into account the facts that the contribution from the jth level exceeds than that from the j'th, and also that the oxygen atom of the methoxy group and the methylene H_2 belong to the same class (in the sense of classification to put star or unstar in the alternant hydrocarbon), the coefficient of α'_{O} in Eq. (1) must be positive. Therefore, we rewrite Eq. (1) as:

$$q'_{\mathrm{M}} = C_1\alpha'_{\mathrm{O}}, \quad C_1 > 0. \tag{2}$$

It can be seen that the sign of C_1 depends upon the position of the proton under consideration.

Since the value of the proton hfs is proportional to the odd-electron density at that position, a change in the latter produces one in the former with the same proportionality constants:

$$a'_{\mathrm{M}} = C_2 q'_{\mathrm{M}}, \quad C_2 > 0. \tag{3}$$

Next, let us discuss α'_{O} in relation to solvent molecules. It is assumed that the radical in question combines to some extent with the solvent molecule. There being several ways in which the molecular complex may originate, the charge transfer from radical to solvent will be picked up as a property responsible for the above-mentioned phenomena.

The ground-state wave function of this complex, to the zeroth approximation, is written as nonbonding, $\Psi_0(\mathrm{R}, \mathrm{S})$, where R and S represent radical and solvent respectively. In the higher approximation, the dative structure denoted by $\Psi_1(\mathrm{R}^+, \mathrm{S}^-)$ will mix with $\Psi_0(\mathrm{R}, \mathrm{S})$ to make a more accurate ground state[2]:

$$\Psi = \Psi_0(\mathrm{R}, \mathrm{S}) + \lambda\Psi_1(\mathrm{R}^+, \mathrm{S}^-)\,. \tag{4}$$

Here the mixing parameter, λ, is determined by the perturbation method to be:

$$\lambda = H_{01}/\Delta E_{01}\,, \tag{5}$$

where, using the electronic Hamiltonian H,

$$\left.\begin{aligned} E_{01} &= H_{00} - H_{11} - e^2/r\sigma\,, \\ H_{ij} &= (\Psi_i|H|\Psi_j). \end{aligned}\right\} \tag{6}$$

In the above, r is the distance between the radical and the solvent, and σ the dielectric constant of the solvent.

As a result, the charge density at the oxygen atom of the methoxy group is reduced by the factor of the normalization factor of Eq. (4), namely $(1+\lambda^2)^{-1}$. Then we have:

$$q'_{\mathrm{O}} \propto (1 + \lambda^2)^{-1} - 1 = -\lambda^2\,. \tag{7}$$

On the other hand, the charge density is related with the coulomb term by such a formula as:

$$\alpha = \alpha_1 - \alpha_2 q'_{\mathrm{O}}\,, \tag{8}$$

where α_1 and α_2 are constants. Hence:

$$\alpha'_{\mathrm{O}} \propto -q_{\mathrm{O}}'\,. \tag{9}$$

By combining Eqs. (2), (3), (7) and (9), we obtain:

$$a'_{\mathrm{M}} \propto \lambda^2\,. \tag{10}$$

That is to say, the formation of the charge-transfer complex results in an increase in the proton hfs coupling constant of the methylene group in the radical.

As to the ring proton at the meta position, since the carbon atom next to the proton belongs to a different class, the sign of C_1 in Eq. (2) must be reversed. However, in the relation:

$$a_{\mathrm{H}} = Qq \tag{11}$$

which relates the ring proton hfs constant, a_{H}, with the odd electron density on the neighboring carbon atom, the sign of the proportionality constant, Q, is negative, so that we also have the solvent effect, which increases the meta proton hfs constants in the radical. This is consistent with Deguchi's observation.[1]

Solvent Effect Depending on the Number of Substituent Groups

Since, in Eq. (5), the resonance integral in the charge-transfer process refers essentially to the interaction between the carbon and oxygen 2p atomic orbitals, in, respectively, the solvent and the radical, its value is nearly independent on the solvent species, but the denominator, ΔE_{01} is dependent on it. ΔE_{01} can be approximately rewritten, by using the oxygen lone-pair level, ε_0, and the lowest vacant level of the solvent molecule, $\varepsilon_1(n)$, as:

$$\Delta E_{01} = \varepsilon_0 - \varepsilon_1(n) - e^2/r\sigma\,, \tag{12}$$

where n represents the number of methyl substituents in the solvent molecule. We denote $\varepsilon_1(n)$ as a function of n:

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[2] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

$$\varepsilon_1(n) = \varepsilon_1(0) - \nu_n\delta, \quad \delta > 0, \tag{13}$$

in which δ is a small positive quantity: ν_n, the function of n, depending on the relative positions of the substituents, and $\varepsilon_1(0)$, the value for benzene. The last term in Eq. (13) arises from the very small perturbation due to the methyl substitution. Then:

$$\begin{aligned}\Delta E_{01} &= \varepsilon_0 - \varepsilon_1(0) - e^2/r\sigma + \nu_n\delta\,, \\ &= \Delta E_{01}(0)(1 - \nu_n\delta'),\end{aligned} \tag{14}$$

with:

$$\left.\begin{aligned}\Delta E_{01}(0) &= \varepsilon_0 - \varepsilon_1(0) - e^2/r\sigma\,, \\ \delta' &= -\delta/\Delta E_{01}(0) > 0\,.\end{aligned}\right\} \tag{15}$$

Considering that $|\nu_n\delta'| \ll 1$, we obtain:

$$\lambda^2 \propto \Delta E_{01}{}^{-2} \cong (1+2\nu_n\delta')/(\Delta E_{01}(0))^2\,. \tag{16}$$

Now we can define:

$$\Delta a(n) = (a'_{\mathrm{M}}(n) - a'_{\mathrm{M}}(0))/a'_{\mathrm{M}}(0)\,, \tag{17}$$

where $a'_{\mathrm{M}}(n)$ or $a'_{\mathrm{M}}(0)$ is the deviation of the proton hfs constant at the methylene group, when benzene or the n methyl-substituted benzene, respectively, is used as the solvent, from that with no solvent effect. Using Eqs. (9), (16) and (17), we get finally:

$$\Delta a(n) = 2\nu_n\delta'. \tag{18}$$

Thus, we conclude that, since ν_n should be positive, the proton hfs constants under consideration increase with an increase in the n value. In order to get a rough estimation, neglecting the position factors of the substituents, and by putting:

$$\nu_n \cong n, \qquad \delta' \cong 0.1 \tag{19}$$

say, $\Delta E_{01}(0)=1$, $\delta=-0.1$ in units of β, the resonance integral of benzene, we have $\Delta a(3)$ to be nearly 0.6. It should be noted that r is nearly 4 Å in usual molecular complexes, while σ is larger than 2 in the solvents under consideration. As to the empirical value, $a'(0)$, we might estimate it from Table 1a as:

$$a'(0) = a(\text{benzene}) - a(n\text{-hexane}) = 0.3 \text{ gauss}.$$

However, taking into account the fact that a(n-hexane) has some solvent effect, we have to use a little smaller value for the coupling constant in the bare state. If we take $a(\text{bare}) = 11.0$ gauss instead of $a(n\text{-hexane}) = 11.7$ gauss, we can obtain:

$$\Delta a(3) = (12.7 - 12.0)/(12.0 - 11.0) = 0.7$$

in accordance with the calculated value.

Temperature Effect

In discussing the temperature effect or the hfs constants of the solvated radical, it seems that two points are important; first, the equilibrium between the radical-solvent pair and the radical in the free (or loosely-combined) state,[3,4] second, the structural factor in the radical-solvent pair.[5] For the system under consideration, the first seems more important.

Let Ψ_{A} denote the solvated radical which corresponds to the ground state in the higher approximation, as has been discussed in the preceding section, of the radical-solvent pair formed by some sort of intermolecular forces, including the charge-transfer force, and let Ψ_{B} denote the radical in the free state, which was previously written as $\Psi_0(\mathrm{R, A})$. Assuming the rapid exchange between two states, the value of the hfs coupling constant is observed as:

$$\bar{a} = a_{\mathrm{A}}P_{\mathrm{A}} + a_{\mathrm{B}}P_{\mathrm{B}}\,, \tag{20}$$

where, for example, a_{A} and P_{A} are values of the coupling constant and the existing probability respectively of A state.

As has been shown in the preceding treatment,

$$a_{\mathrm{A}} = a_{\mathrm{B}} + a' \tag{22}$$

with a small positive quantity, a'. Then, considering that P_{A} and P_{B} are temperature-dependent, if we define such a quantity that:

$$\Delta a(T) = (a(T) - a(T_0))/a(T_0),$$

we can easily derive:

$$\Delta a(T) = (a'/a_{\mathrm{B}})(P_{\mathrm{B}}(T_0) - P_{\mathrm{B}}(T)), \tag{23}$$

where we have used the $a_{\mathrm{B}} \gg a'$ relation. Then, further, using $\Delta T = T - T_0$, we can rewrite Eq. (23) as:

$$\begin{aligned}\Delta a(T) &= (a'/a_{\mathrm{B}})\Delta T(P_{\mathrm{B}}(T_0) - P_{\mathrm{B}}(T))/\Delta T \\ &= -(a'/a_{\mathrm{B}})\Delta T\left(\frac{\partial P_{\mathrm{B}}}{\partial T}\right)_{T=T_0}.\end{aligned} \tag{24}$$

Therefore, if we can show that $(\partial P_{\mathrm{B}}/\partial T)_{T=T_0}$ has a positive value, it may be concluded that the hfs coupling constant tends to decrease with an increase in the temperature.

Now let us consider the perturbation causing the transition from the A state to the B state. It originates in the colliding motions of solvents against the radical; the perturbing Hamiltonian is written as:

$$V(t) = Vf(t), \tag{25}$$

where $f(t)$ is the time-dependent factor, which may reasonably be assumed to have a random property with an average value of zero, fluctuating many times in the time interval, t_0(actually the reciprocal of the hfs frequency).

Describing the wave function of the system under consideration as:

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[3] A. H. Reddoch, *J. Chem. Phys.*, **43**, 225 (1965).

[4] A. Crowly, N. Hirota and R. Kreilick, *ibid.*, **46**, 4815 (1967).

[5] S. Aono and K. Oohashi, *Prog. Theoret. Phys.*, **30**, 162 (1963); **32**, 1 (1964).

$$\Psi = C_A(t)\Psi_A e^{-i\omega_A t} + C_B(t)\Psi_B e^{-i\omega_B t} \tag{26}$$

with standard notations, we can obtain:

$$C_B(t) = -\frac{i}{\hbar} V_{BA}\int_0^t f(t')e^{-i\omega_{AB}t}\,dt', \tag{27}$$

$$\omega_{AB} = \omega_A - \omega_B, \tag{27a}$$

$$V_{BA} = (\Psi_B|V|\Psi_A). \tag{27b}$$

Here it should be noted that, since we have derived Eq. (27) under the initial conditions, $C_A(0)=1$ and $C_B(0)=0$, the existing probability of the B state is replaced by the transition probability from A to B. Therefore, we have:

$$P_B(t_0) = \frac{1}{\hbar^2}|V_{BA}|^2\int_0^{t_0} dt\int_{-t_0}^{t_0-t} d\tau \times f(t+\tau)f(t)e^{-i\omega_{AB}\tau}. \tag{28}$$

As in the case in the treatment of the NMR relaxation problem, the integral (28) is a random function, but the statistical average value of the expression:

$$G(\tau) = \overline{f(t+\tau)\,f(t)}$$

for a fixed τ generally has a definite value, independent of the time t. $G(\tau)$ is generally a rapidly decreasing function of τ, and when t_0 is large, the second integral in Eq. (28) (taking the statistical average) becomes almost independent of t_0, while integration with respect to t_0 gives a factor of t_0 in the answer:

$$P_B(t_0) = t_0 P_B, \tag{30}$$

in which P_B, the transition probability from A to B per unit of time, is:

$$P_B = \frac{1}{\hbar^2}|\overline{V}_{BA}|^2\int_{-\infty}^{\infty} G(\tau)e^{i\omega_{BA}\tau}\,d\tau. \tag{31}$$

Now, we assume that $G(\tau)$ decays exponentially with a characteristic correlation time τ_c:

$$G(\tau) = e^{-|\tau|/\tau_c}. \tag{32}$$

The transition probability per unit time then becomes:

$$P_B = \frac{1}{\hbar^2}|\overline{V}_{BA}|^2\frac{2\tau_c}{1+\omega_{BA}{}^2\tau_c{}^2}. \tag{33}$$

At this stage, we need to consider τ_c and ω_{BA} a little more deeply. Colliding motions of solvents against the radical will cause the translational and rotational motions of the radical, and their characteristic correlation times are known to be orders of 10^{-11} sec and 10^{-8} sec respectively, while the value of ω_{BA} may be estimated as the order of the activation energies for the corresponding motions, having values of a few kcal. Therefore, as we have the relation:

$$\omega_{AB}{}^2\,\tau_c{}^2 \gg 1$$

in our case, P_B in Eq. (33) is approximately:

$$P_B = \frac{1}{\hbar^2}\frac{|\overline{V}_{BA}|^2}{\omega_{AB}{}^2}\frac{2}{\tau_c}. \tag{34}$$

Since τ_c(rotational)$\ll\tau_c$(translational), it is obvious that the effect of the rotational motion predominates in our case.

According to Debye,⁶⁾ the rotational correlation time is:

$$\tau_c = \frac{4\pi\eta a^3}{3\boldsymbol{k}T}, \tag{35}$$

where $\boldsymbol{k}$ is the Boltzman constant, and where the assumption is made that the molecules are spheres with the a radius. η, the viscosity of the liquid, is also temperature-dependent; it is given, by the use of the Eyring transition state theory,⁷⁾ as:

$$\eta = nh\,e^{\Delta G^{\neq}/RT}, \tag{36}$$

where n is the number of molecules per unit of volume and $\Delta G^{\neq}$, the Gibbs free energy of the transition state.

Using the relation:

$$\Delta G^{\neq} = -\Delta S^{\neq}T + \Delta H^{\neq} \tag{37}$$

and substituting Eqs. (35) and (36) into Eq. (34), we obtain:

$$P_B = \frac{|\overline{V}_{BA}|^2}{(E_A-E_B)^2}\frac{3\boldsymbol{k}T}{2\pi nha^3}e^{\Delta S^{\neq}/R}e^{-\Delta H^{\neq}/RT}. \tag{38}$$

Inserting this into Eq. (24), we can obtain the temperature dependence of the hfs coupling constant in terms of macroscopic quantities. We may expect that these values, $\Delta S^{\neq}$ and $\Delta H^{\neq}$, negative in sign, will be several tens of eu and a few kcal respectively. As to the temperature-dependent factors, the exponential term should exceed the linear one, so that the value of the coupling constant will decrease with an increase in the temperature. However, it seems almost impossible to estimate it numerically because of the difficulty of determining the parameters, $\Delta S^{\neq}$, $\Delta H^{\neq}$, and so on.

Conclusion

We have presented some considerations concerning the solvent and temperature effects on the proton hfs coupling constants in the ESR spectra of the phenoxy radicals, on the assumption that the charge-transfer takes place from the oxygen lone pair of the radical to the vacant levels of the solvent. The increase in the values of the hfs constants with an increase in the number of the methyl substituents in the solvents is interpreted in terms of the lowering of the lowest vacant level of the solvent

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6) P. Debye, "Polar Molecules," Dover Publications, New York (1945), Chapter V.

7) J. O. Hirschfelder and C. F. Curtis, "Molecular Theory of Gases and Liquids," Wiley, New York (1945), p. 627.

due to the methyl substitution. In this case, we have used the rough proportionality which holds between the extent of the lowering in level and the number of methyl substituents.

On the other hand, the temperature effect has been explained by the use of an idea similar to those of Reddoch and Crowly *et al.* in some details. Using the time-dependent perturbation theory, we have obtained the hfs constant in terms of the rotational correlation time, or the liquid viscosity constant, from which the temperature-dependent factor arises. However, it was almost impossible for us to make a quantitative estimate because some parameters were difficult to determine.