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The Theoretical Study of External Magnetic Field Effect on Chemical Reactions in Solution

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External magnetic field effects on chemical reactions in solution are studied theoretically and consequently reactions through radical pairs are shown to be controlled by a magnetic field. Some conditions necessary for the occurrence of the magnetic field effects are discussed, the effects being classified into three types: (1) the electronic Zeeman effect ($\Delta g\beta H$), (2) the hyperfine interaction effect, and (3) the mixed effect.

Recently, magnetic field effects on dynamical processes of excited states have been extensively studied. The phenomena can be divided into two classes; intramolecular and intermolecular cases. The intramolecular phenomena include magnetic field effects on radiative[1] and nonradiative[2] decay processes, predissociation,[3] and reactivity of triplet sublevels.[4] The intermolecular phenomena are related with the selection rule of reactions induced by the collision of excited molecules or radicals with some spin multiplicities (*i.e.* triplet+triplet, triplet+doublet, doublet+doublet *etc.*). In actuality, the intermolecular magnetic field effect has been observed with delayed fluorescence,[5] photoconductivity,[6] chemiluminescence,[7] chemically induced dynamic electron and nuclear polarization (CIDEP and CIDNP).[8]

Concerning external magnetic field effects upon chemical reactions through excited states, reliable studies have scarcely been done. A magnetic field effect upon photo-decomposition has been observed with iodine molecules in gas phase.[3] Gupta and Hammond[9] reported magnetic field effects on some photoisomerization reactions through exciplexes in solution.[10]

Recently, the yields of some excited states produced by pulse radiolysis[11] and laser photolysis[12,13] have been found to be affected by a magnetic field. The Novosibirsk group[14,15] found an external magnetic field effect on the yield ratio of a cage product to a free radical product in some thermal reactions between alkyl lithium and alkyl halide. We also found an external magnetic field effect on the reaction yields of both the cage product and the free radical products in the singlet sensitized photolysis of dibenzoyl peroxide in solution.[16]

In this paper, we have developed a theory for the external magnetic field effect on chemical reactions through radical pairs in solution on the basis of the general formula for the spin hamiltonian of a weakly coupled radical pair which was developed in a previous paper[17] and was used as one of the basic theories for CIDNP.[8] The purpose of the present study is to clarify the conditions necessary for the magnetic field control of chemical reactions.

Theory

It has already been shown that the singlet-triplet conversion in a radical pair in solution is affected by an external magnetic field when the energy separation between the singlet and triplet ground states, $|2J,|$ is comparable to or smaller than the difference between the Zeeman energies of the component radicals or their hyperfine energies.[8] Therefore in this paper, we consider only a separated radical pair in solution. In the previous paper,[17] we obtained the matrix elements between the singlet $|\mathrm{S}_0;\ M>$ and triplet $|\mathrm{T}_m;\ M'>$ ($m=0,\ \pm1$) ground states of a radical pair. It can be expressed in general as follows:

$$v^m_{M'.M} = \langle \mathrm{T}_m;\ M'|\mathrm{H}_{\mathrm{st}}|\mathrm{S}_0;\ M\rangle, \tag{1}$$

where H_{st} in the second-order matrix element representing the interaction between the orbitally degenerate singlet and triplet states,[17] and M and M' stand for the sets of the nuclear states of the singlet and triplet ground states, respectively. The non-vanishing elements for the separated radical pair in solution are given as follows:

$$\begin{aligned}&\langle \mathrm{T}_m;\ M_i{}^{\mathrm{a}},\ M_j{}^{\mathrm{b}}|\mathrm{H}_{\mathrm{st}}|\mathrm{S}_0;\ M_i{}^{\mathrm{a}},\ M_j{}^{\mathrm{b}}\rangle = v_{\mathrm{N}}\\ &\qquad + (1-m^2)[(g^{\mathrm{a}}-g^{\mathrm{b}})\beta H+\sum A_i{}^{\mathrm{a}}M_i{}^{\mathrm{a}}-\sum A_j{}^{\mathrm{b}}M_j{}^{\mathrm{b}}]/2,\end{aligned} \tag{2}$$

$$\begin{aligned}&\langle \mathrm{T}_{\pm1};\ M_i{}^{\mathrm{a}}\mp1,\ M_j{}^{\mathrm{b}}|\mathrm{H}_{\mathrm{st}}|\mathrm{S}_0;\ M_i{}^{\mathrm{a}},\ M_j{}^{\mathrm{b}}\rangle\\ &\qquad = \mp A_i{}^{\mathrm{a}}[I_i{}^{\mathrm{a}}(I_i{}^{\mathrm{a}}+1)-M_i{}^{\mathrm{a}}(M_i{}^{\mathrm{a}}\mp1)]^{1/2}/(8)^{1/2},\end{aligned} \tag{3}$$

$$\begin{aligned}&\langle \mathrm{T}_{\pm1};\ M_i{}^{\mathrm{a}},\ M_j{}^{\mathrm{b}}\mp1|\mathrm{H}_{\mathrm{st}}|\mathrm{S}_0;\ M_i{}^{\mathrm{a}},\ M_j{}^{\mathrm{b}}\rangle\\ &\qquad = \pm A_j{}^{\mathrm{b}}[I_j{}^{\mathrm{b}}(I_j{}^{\mathrm{b}}+1)-M_j{}^{\mathrm{b}}(M_j{}^{\mathrm{b}}\mp1)]^{1/2}/(8)^{1/2}.\end{aligned} \tag{4}$$

Here g^ν (ν=a or b) is the average value of the three principal values of the $\boldsymbol{g}^\nu$ tensor, $A_k{}^\nu$ is the Fermi contact term of the k-th nucleus, and H is the strength of the external magnetic field. As is shown in Appendix, v_{N} is the usual matrix element for radiationless transition between the singlet and triplet ground states of the radical pair. This corresponds to the radiationless transition rate constant for a large molecule and may safely be assumed to be much samller than the second term on the right-hand side of Eq. 2 for the separated radical pair in solution as is shown in Appendix. Thus, we disregard v_{N} hereafter in the present paper.

According to the radical pair theory of CIDNP derived by Kaptein,[18] the yield, $P^{\Gamma}(H)$ (Γ=S(singlet), T(triplet), or F(free radical)) of the cage product through the singlet ground state[19] of a radical pair formed from a Γ-precursor is given for the case where the singlet-triplet transition rate, $k^m_{M'.M}$ is small ($k^m_{M'.M}=(1/\hbar)\ |v^m_{M'.M}| \ll 1/t_{\mathrm{d}}$):

$$P^{\mathrm{S}}(H) = (\lambda/N)\sum_m\sum_M\sum_{M'}(p-x^m_{M'.M}), \tag{5}$$

$$P^{\mathrm{T}}(H) = (\lambda/3N(1-p))\sum_m\sum_M\sum_{M'}x^m_{M'.M}, \tag{6}$$

$$\begin{aligned}P^{\mathrm{F}}(H) = (\lambda/4N)\sum_m\sum_M\sum_{M'}[1+\{p(1-\lambda)+\lambda x^m_{M'.M}\}/\\ (1-p\{1-\lambda(1-\lambda)/2\})].\end{aligned} \tag{7}$$

Here $k^m_{M'.M}$ is the transition rate between $|\mathrm{S}_0;\ M>$ and

$|T_m; M'\rangle$, t_d is the lifetime of the radical pair, λ is the probability for recombination during a singlet encounter, p is the total probability of at least one reencounter appearing in Noyes' reencounter function, $f(t) = m_0 t^{-3/2}\exp(-m_0 p^2/t)$[20] where m_0 is a constant with the dimension of $s^{1/2}$. N is the number of the nuclear states, $|S_0; M\rangle$, and $x^m_{M'.M}$ is given as follows:[18]

$$x^m_{M'.M} = m_0\pi^{1/2}(v^m_{M'.M})^2(\omega^m_{M'.M})^{-3/2}, \tag{8}$$

where

$$\omega^m_{M'.M} = [\{J+m(g^a+g^b)\beta H/2\}^2+(v^m_{M'.M})^2]^{1/2}. \tag{9}$$

For the case of large $k^m_{M'.M}$ we need a numerical calculation[11–13] for evaluation $P^\Gamma(H)$. But for the extreme case where $k^m_{M'.M}$ is very large ($k^m_{M'.M} \gg t_d^{-1}$, $(1/\hbar|J|)$, the singlet–triplet conversion rate is so fast that $|S_0; M\rangle$ and $|T_m; M'\rangle$($m=0$, ±1 for the zero field and $m=0$ for high field) are assumed to exist in equilibrium with each other. Therefore, we can derive the following equations for $P^\Gamma(0)$ and $P^\Gamma(H_\infty)$:

$$\begin{aligned} P^S(0) &= p\lambda(1+p(1-\lambda/4)+\cdots)/4 \\ &= p\lambda/[4(1-p(1-\lambda/4))], \end{aligned} \tag{10}$$

$$\begin{aligned} P^S(H_\infty) &= p\lambda(1+p(1-\lambda/2)+\cdots)/2 \\ &= p\lambda/[2(1-p(1-\lambda/2))], \end{aligned} \tag{11}$$

$$P^T(0) = P^S(0), \tag{12}$$

$$\begin{aligned} P^T(H_\infty) &= p(1+p(1-\lambda/2)+\cdots)/6 \\ &= p\lambda/[6(1-p(1-\lambda/2))]. \end{aligned} \tag{13}$$

Here $H_\infty \gg 2v^m_{M'.M}/(g^a+g^b)\beta$. In the above evaluation, we assumed, for simplicity, that the radicals escaped from the cage disappear so fast that no cage product is formed through the free radicals.

In order to compare the theory with experiments, we define the relative change in the yield for the cage product, $R^\Gamma(H)$, and that for the i-th free radical product, $Q^\Gamma_i(H)$, as follows:

$$R^\Gamma(H) = [P^\Gamma(H)-P^\Gamma(0)]/P^\Gamma(0), \tag{14}$$

$$Q^\Gamma_i(H) = [F^\Gamma_i(H)-F^\Gamma_i(0)]/F^\Gamma_i(0). \tag{15}$$

Here $F^\Gamma_i(H)$ is the yield of the i-th free radical product and can be expressed with the fraction, f_i, for giving the product from the escaped radical:

$$F^\Gamma_i(H) = f_i[1-P^\Gamma(H)]. \tag{16}$$

Therefore, $Q^\Gamma_i(H)$ can be rewritten as

$$Q^\Gamma_i(H) = -R^\Gamma(H)P^\Gamma(0)/(1-P^\Gamma(0)). \tag{17}$$

This equation means that $Q^\Gamma_i(H)$ is independent of f_i and has the opposite sign to $R^\Gamma(H)$.

Types of External Magnetic Field Effects on Chemical Reactions

As mentioned above, the matrix elements between the singlet and triplet states of a separated radical pair are expressed by the difference between the g factors and hyperfine interactions of the component radicals. Here we classify the external magnetic field effects on chemical reactions into the following three types: (1) effect of $\Delta g\beta H$ ($\Delta g = g^a - g^b \neq 0$ and $A_i^a = A_j^b = 0.$), (2) effect of hyperfine interactions ($\Delta g = 0$, $A_i^a \neq 0$, and $A_j^b \neq 0.$), and (3) mixed effect of $\Delta g\beta H$ and hyperfine interactions.

Effect of Electronic Zeeman Interaction ($\Delta g\beta H$). In this case, the following equations hold:

$$v^0_{M'.M} = \Delta g\beta H/2\delta_{M'.M} = v\delta_{M'.M}, \tag{18}$$

$$v^{\pm1}_{M'.M} = 0. \tag{19}$$

These equations show that the conversion occurs only between $|S_0; M\rangle$ and $|T_0; M\rangle$. At first, we consider a reaction through a singlet precursor. For a small v ($(1/\hbar)v \gg t_d^{-1}$), $R^s(H)$ can be given as follows:

$$R^S(H) = -fx/p. \tag{20}$$

Here f is the fraction with which a cage product is given through separated pairs,[21] $x = m_0\pi^{1/2}v^2\omega^{-3/2}$, and $\omega^2 = J^2+v^2$. For $v \ll |J|$ (case a) and $v \gg |J|$ (case b), x can be approximated to be $m_0\pi^{1/2}v^2|J|^{-3/2}$ and $m_0\pi^{1/2}v^{1/2}$, respectively. Thus we can derive the following equations:

$$\text{(case a)} \quad R^S(H) = -fm_0\pi^{1/2}(\Delta g\beta H)^2/(p|J|^{3/2}), \tag{21}$$

$$\text{(case b)} \quad R^S(H) = -fm_0\pi^{1/2}(\Delta g\beta H)^{1/2}/p. \tag{22}$$

For the extreme case where H is very large (case c), $R^s(H)$ can be given with the aid of Eqs. 5 and 11 as follows:

$$\text{(case c)} \quad R^S(H) = 1/[2(1-p(1-\lambda/2))]-1. \tag{23}$$

Equations 21—23, clearly show that $R^S(H)$ is proportional to H^2 at low fields and $H^{1/2}$ at higher field, but it saturates at much higher fields. This is shown in Fig. 1.

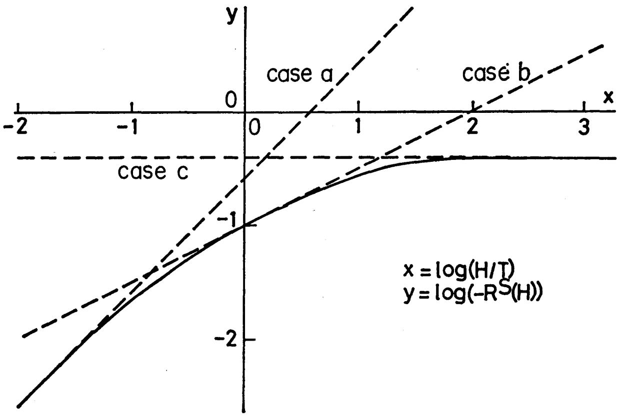

Fig. 1. The calculated contribution of the electronic Zeeman effect to the magnetic field dependence of $R^S(H)$: ——, plot of $\log(-R^S(H))$ *versus* $\log H$ for the whole magnetic field region; ----, plots of $\log(-R^S(H))$ *versus* $\log H$ for cases a, b, and c.

An example of this type of the magnetic field effect is the singlet sensitized photo-decomposition reaction of dibenzoyl peroxide in toluene.[16] It was observed that the yield of phenyl benzoate, the cage product of the reaction, decreased proportionaly to the square root of the applied field strength. This means that the reaction shows a case b type magnetic field effect. From the slope of the observed $R^S(H)$ for phenyl benzoate, *versus* $H^{1/2}$, fm_0/p was determined to be $1.08\times10^{-6}\ s^{1/2}$ with the aid of Eq. 22. Since $f \lesssim 1$, $0.5 < p < 1$, and $m_0 \approx 10^{-6}\ s^{1/2}$,[18] the theoretical value of fm_0/p agrees well with the experimental value.

As for the free radical products (2-methylbiphenyl, 4-methylbiphenyl, and 1,2-diphenylethane) in the reaction, their $Q_i^S(H)$ values were observed to be independent of f_i and increased by 2% in the presence of 4.3 T field.[16] Since $R^S(4.3\text{ T})$ and $P^S(0)$ were observed to be −0.08 and 0.12, respectively, for phenyl benzoate,[16,25] $Q_i^S(4.3\text{ T})$ was calculated to be 0.01 with the aid of Eq. 17. This value also agrees with the observed one (0.02)[16] within the limitations of experimental error.

Next, let us consider reactions through a triplet precursor. For a small v, $P^T(H)$ can be evaluated as follows:

$$P^T(H) = fx/[3(1-p)]. \tag{24}$$

This shows that $P^T(H)$ has the opposite sign to $R^S(H)$ (see Eq. 20). In the extreme case where v is very large, $P^T(H)$ is given by Eq. 13. The reaction showing an external magnetic field effect of this type has not yet been observed. We are now studying the triplet sensitized photo-decomposition reaction of dibenzoyl peroxide. This reaction may be the example of this type.

Effect of Hyperfine Interactions. The effects of hyperfine interactions on some reaction intermediates have been studied by Brocklehurst,[11] Michel-Beyerle *et al.*,[12] and Schulten *et al.*.[13] They evaluated numerically the effects for some ideal cases. Although it is impossible to derive a simple analytical expression for the effect, its qualitative features correspond fairly well to the extreme case where $k^m_{M',M}$ is very large. For this case, the singlet-triplet conversion occurs between $|S_0; M>$ and $|T_m; M'>$ ($m=0, \pm1$ for zero field and $m=0$ for high field, H_∞). Thus $P^\Gamma(H_\infty)$ for this case are given by Eqs. 10—13. According to these equations, the yield of the cage product from the singlet (triplet) precursor increases (decrease) on the application of a strong external magnetic field. Actually, H_∞ is less than 0.1 T for many cases.[11–13] On the other hand, the yield of each free radical product from the singlet (triplet) precursor is proved to decrease (increase) on the application of the field.

For a smaller $k^m_{M',M}$, the change in the yield of each product on the application of a strong field shows the same tendency as that for the strong limit case. But the degree of the change may be smaller than that of the strong limit case because of the diffusion of the radical pair to free radicals. An example of this type of the effect is the thermal reaction of benzylic chloride with butyllithium studied by Sagdeev *et al.*[14]

Mixed Effect of $\Delta g\beta H$ and Hyperfine Interactions. Although it is also difficult to obtain a simple analytical form for this case, qualitative analysis can be done for small $|J|$ ($|J| \ll v^m_{M',M}$) as follow. (1) At zero field, the conversion between $|S_0; M>$ and $|T_m; M'>$ ($m=0, \pm1$) occurs through hyperfine interactions. (2) At a higher field, H_1, where $A/g\beta \ll H_1 \ll A/\Delta g\beta$, and A and g are the orders of hyperfine interactions and g factors of the component radicals, respectively, only the conversion between $|S_0; M>$ and $|T_0; M>$ occurs through hyperfine interactions. Therefore, the yield of the cage product from the singlet (triplet) precursor is shown to increase (decrease) on the application of the field, H_1. (3) at a much higher magnetic field, H_2 (where $A/\Delta g\beta \ll H_2$), the conversion between $|S_0; M>$ and $|T_0; M>$ occurs through $\Delta g\beta H_2$ and hyperfine interactions as shown by Eq. 2. Thus the yield of the cage product at H_2 through the singlet (triplet) precursor is concluded to be smaller (larger) than that at H_1. From Eq. 16, the magnetic field dependence of $F^\Gamma_i(H)$ is also shown to be inverse to that of $P^\Gamma(H)$.

This type of the effect has been observed for the cage and free radical products in the thermal reaction of decafluorodiphenylchloromethane with butyllithium[15] and some free radical products (dimethylbiphenyls and tolyl benzoates) in the photo-decomposition reaction of dibenzoyl peroxide.[26]

The mixed effect at a high field, H ($H>H_1$) can easily be evaluated by taking the matrix element, $v^0_{M.M}$, between $|S_0; M>$ and $|T_0; M>$ as follows:

$$v^0_{M.M} = [(g^a - g^b)\beta H + \sum A_i^a M_i^a - \sum A_j^b M_j^b]/2. \tag{25}$$

In this case, with a method similar to that used for the electronic Zeeman effect, $P^S(H)$ can be given for small $v^0_{M.M}$ as follows:

$$P^S(H) = (\lambda/N)\sum_M (p - fx^0_{M.M}), \tag{26}$$

where

$$x^0_{M.M} = m_0 \pi^{1/2} (v^0_{M.M})^2 (\omega^0_{M.M})^{-3/2}$$

and

$$(\omega^0_{M.M})^2 = J^2 + (v^0_{M.M})^2.$$

In order to compare the theory with experiments, we define $R^S_{H_2}(H)$ as follow:

$$R^S_{H_2}(H) = [P^S(H_2) - P^S(H)]/[P^S(H_2) - P^S(0)]. \tag{27}$$

When H and H_2 are large enough, $P^S(H)$ and $P^S(H_2)$ can be evaluated by Eq. 26, and $P^S(0)$ can be assumed to be equal to λp. In actuality the $R^S_{4.3T}(H)$ values were calculated for phenyl benzoate in the photo-decomposition reaction of dibenzoyl peroxide, the high magnetic field approximation being adopted and the observed hyperfine coupling constants for *ortho*-(1.74 mT), *meta*-(0.59 mT), and *para*-(0.19 mT) protons of the phenyl radical[24] being used. Since no hyperfine structure was observed for the benzoxyl radical,[22] we did not consider its hyperfine interaction. The calculated $R^S_{4.3T}(H)$ values for various J values are plotted

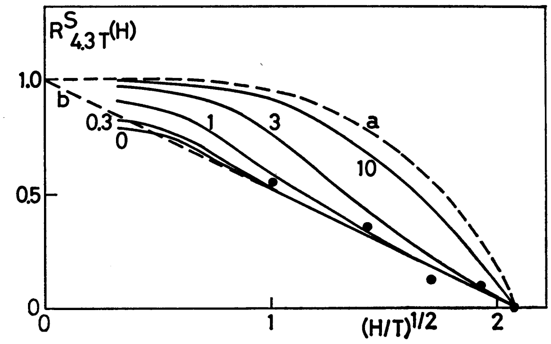

Fig. 2. The dependence of $R^S_{4.3T}(H)$ *versus* $H^{1/2}$ for phenyl benzoate as the photo-decomposition product of dibenzoyl peroxide: ——, the calculated dependence considering both the electronic Zeeman effect and the hyperfine interaction effect; $|J|=0$, 0.3, 1, 3, and 10 mT, for curves 0, 0.3, 1, 3, and 10 respectively; ----, the calculated dependence for case a (curve a) and for case b (curve b) considering only the electronic Zeeman effect: ●, the observed $R^S_{4.3T}(H)$ values for phenyl benzoate.[16]

as the function of $(H)^{1/2}$ in Fig. 2 (solid lines). In this figure are also shown the experimental results of phenyl benzoate (filled circle) and the $R^{S}(H)$-$H^{1/2}$ relationship corresponding to cases a and b of the electronic Zeeman effect (broken lines).

The $R^{S}_{4.3T}(H)$-$H^{1/2}$ plots for $|J|=0$ and $|J|=0.3$ mT agree well with curve b corresponding to case b. This means that in the small $|J|$ region the effect of the hyperfine interactions can safely be disregarded for this reaction compared with that of $\Delta g\beta H$. With increasing $|J|$, the $R^{S}_{4.3T}(H)$ dependence against H gradually deviates from curve b and approaches curve a corresponding to case a. The observed data fit to the curves for $|J|=0$ and $|J|=0.3$ mT (0.281×10^{-3} cm^{-1}). This shows that the magnetic field effect upon formation of phenyl benzoate is mainly due to the electronic Zeeman ($\Delta g\beta H$) effect.

Discussion

The magnetic field effect upon intramolecular processes of an excited state observed for small molecules in gas phase[2,3] is interpreted in terms of the enhancement of the non-radiative decay from the state into a quasi-continuum by the Zeeman interaction and also by the energy shift and broadening of rovibronic levels due to the Zeeman effect.[27,28]

A magnetic field effect on the dynamical process of an exciplex itself has been observed in solid phase[29] or in polymer.[30] This is the case where the acceptor and donor stay separately for a considerable time. In non-viscous solution, it seems difficult to observe any magnetic field effect on the dynamical process of an exciplex itself. The magnetic field effect in non-viscous solution, however, has been observed for reactions through the ion pair after exciplex formation.[12,13] This effect can be explained in terms of the radical pair theory treated in this paper. Recently, Hata observed a magnetic field effect on the photo-isomerization of isoquinoline *N*-oxide.[31] This might be due to a level-crossing[26] in an intermediate radical pair.

We summarize the conditions necessary for the magnetic field control of chemical reactions through raidcal pairs. (1) The magnetic field effect can be observed for reactions which proceed mainly through separated pairs, where $v^{m}_{M',M}\gg v_{N}$. It is believed that the reaction through close pairs shows no magnetic field effect.[18] (2) The conversion rate $k^{m}_{M',M}$ between $|S_0; M\rangle$ and $|T_m; M'\rangle$ should not be much smaller than the separation rate of radical pair to free radicals. As is shown in Eqs. 2—4, $k^{m}_{M',M}$ is large when Δg, hyperfine constants, and the number of the nuclei giving the hyperfine interactions are large. The second condition is the same as that necessary for CIDNP.[8,18] On the other hand, the first condition is not necessary for CIDNP because even a small amount of the product through a separated pair can give the strong CIDNP signal. The magnetic field effect on chemical reactions is useful not only for the determination of the reaction mechanism but also for the control of the product yields. This paper will give a theoretical guidance to the future investigation of the magnetic field effect upon chemical reactions.

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Appendix

Since we use a pure-spin BO representation[32] in this paper, the matrix elements between the singlet and triplet states for the usual radiationless transition ($H'_{mr,nt}$) and the hyperfine and electronic Zeeman interactions ($H_{mr,nt}{}^{S}$) can be written as follows:

$$\begin{aligned}H'_{mr,nt} = {}& \langle {}^1\psi_{mr}|H_{LS}|{}^3\psi_{nt}\rangle \\ &+ \sum\langle {}^1\psi_{mr}|T_N|{}^1\psi_{is}\rangle\langle {}^1\psi_{is}|H_{LS}|{}^3\psi_{nt}\rangle/(E_n-E_i) \\ &+ \sum\langle {}^1\psi_{mr}|H_{LS}|{}^3\psi_{is}\rangle\langle {}^3\psi_{is}|T_N|{}^3\psi_{nt}\rangle/(E_n-E_i),\end{aligned} \tag{A-1}$$

$$\begin{aligned}H^{S}_{mr,nt} = {}& \langle {}^1\psi_{mr}|H_{SI}|{}^3\psi_{nt}\rangle \\ &+ \sum\langle {}^1\psi_{mr}|H_{LZ}|{}^1\psi_{is}\rangle\langle {}^1\psi_{is}|H_{LS}|{}^3\psi_{nt}\rangle/(E_n-E_i) \\ &+ \sum\langle {}^1\psi_{mr}|H_{LS}|{}^3\psi_{is}\rangle\langle {}^3\psi_{is}|H_{LZ}|{}^3\psi_{nt}\rangle/(E_n-E_i),\end{aligned} \tag{A-2}$$

with

$${}^1\psi_{mr}(q, Q) = {}^1\phi_{m}(q, Q)\Lambda_{mr}(Q), \tag{A-3}$$

$${}^3\psi_{nt}(q, Q) = {}^3\phi_{n}(q, Q)\Lambda_{nt}(Q), \tag{A-4}$$

$${}^\mu\psi_{is}(q, Q) = {}^\mu\phi_{i}(q, Q)\Lambda_{is}(Q), \quad (\mu=1 \text{ or } 3), \tag{A-5}$$

where q and Q denote the sets of electronic, $\phi(q,Q)$, and vibrational, $\Lambda(Q)$, states, respectively. Here H_{LS}, H_{SI}, and H_{LZ} are the spin-orbit, hyperfine, and electronic Zeeman interaction terms, respectively, and T_N is the nuclear kinetic-energy term. Matrix elements v_P and v_F corresponding to the radiationless transitions $S_0 \leftarrow T_1$ and $T_1 \leftarrow S_1$, respectively, and the matrix element v_R corresponding to the singlet-triplet conversion of a separated radical pair can be given for a large molecule:

$$v_P = \sum_{r}\sum_{i}\sum_{s}(H'_{mr,n0}+H^{S}_{mr,n0}), \tag{A-6}$$

$$v_F = \sum_{t}\sum_{i}\sum_{s}(H'_{m0,nt}+H^{S}_{m0,nt}), \tag{A-7}$$

$$v_R = \sum_{i}\sum_{s}(H'_{m0,n0}+H^{S}_{m0,n0}). \tag{A-8}$$

Here we used a low-temperature approximation.

Concerning evaluation of v_P, $H'_{mr,n0}$ is usually approximated to be propotional to its Franck-Condon facter, $\langle\Lambda_{mr}|\Lambda_{n0}\rangle$[32], and $H^{S}_{mr.n0}$ can also be shown to be propotional to it. Thus v_P can be approximated as follows:

$$v_P = \sum_{r}(h'_{mn}+h^{S}_{mn})\langle\Lambda_{mr}|\Lambda_{n0}\rangle, \tag{A-9}$$

where $h'_{m,n}$ and h^{S}_{mn} are the propotional coefficients of $H'_{mr,n0}$ and $H^{S}_{mr.n0}$ respectively. They can be determined by the electronic wave functions at the equilibrium position for Q. Since βH is 0.467 cm^{-1} for $H=1$ T, and vibronic couplings are usually estimated larger than 100 cm^{-1}, h^{S}_{mn} can safely be ignored in the evaluation of v_P for usual experimental conditions. In a similar way, $H^{S}_{m0.nt}$ can also be shown to be disregarded for estimating v_F.

Concerning evaluation of v_R, $H^{S}_{m0.n0}$ is shown to be proportional to its Franck-Codon factor which may be assumed to be equal to unity for a separated raidcal pair. Therefore, $H^{S}_{m0.n0}$ in Eq. A-8 can be replaced by h^{S}_{mn} as are shown in Eqs. 2—4. On the other hand, $H'_{m0,n0}$, can be assumed to be much smaller than $\mathrm{H}^{\mathrm{S}}_{m0.n0}$ as is shown below. The first order term in $\mathrm{H}'_{m0,n0}$ vanishes since the singlet and triplet ground states have the same electronic structure. The second order terms are shown to be proportional to the following integral according to the promoting mode, Q_k:

$$\langle\chi_n^{k0}(0)|\mathbf{O}^1(Q_k)|\chi_i^{ks}(v_i^{ks})\rangle\langle\chi_i^{ks}(v_i^{ks})|\chi_m^{k0}(0)\rangle.$$

Here $\chi_p^{kq}(v_p^{kq})$ is the q-th vibrational wave function of the k-th promoting mode in the p-th electronic state with the vibrational quantum number, v_p^{ks}, and $\mathbf{O}^1(Q_k)$ is a linear operator according to Q_k Since $|\chi_n^{k0}(0)>$ is nearly the same as $|\chi_m^{k0}(0)>$ for the radical pair, the above integral vanishes for a harmonic oscillator. Thus this integral can safely be assumed to be much smaller than $h^{\mathrm{S}}_{mn}/h'_{mn}$. Therefore, $\mathrm{H}'_{m0,n0}$ in Eq. A-8 can safely be disregarded in estimating v_{R}, as is assumed in this paper. Of course there may be the case where it can not be disregarded.

References

1) W. B. Fowler, M. J. Marrone, and M. N. Kabler, *Phys. Rev. B*, **3**, 5909 (1973).

2) A. Matsuzaki and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **49**, 359 (1976); A. Matsuzaki and S. Nagakura, *Z. Phys. Chem.*, **101**, S283 (1976).

3) L. A. Turner, *Z. Phys.*, **65**, 464 (1930); E. O. Debenkolb, J. I. Steinfeld, E. Wasserman, and W. Klemperer, *J. Chem. Phys.*, **51**, 615 (1969).

4) M. Leung, and M. A. El-Sayed, *J. Am. Chem. Soc.*, **97**, 669 (1975).

5) R. C. Johnson and R. E. Merrifield, *Phys. Rev. B*, **1**, 896 (1970).

6) N. E. Geacintov, M. Pope, and S. Fox, *J. Phys. Chem. Solids*, **31**, 1375 (1970).

7) L. R. Faulkner and A. J. Bard, *J. Am. Chem. Soc.*, **91**, 209 (1969).

8) "Chemically Induced Magnetic Polarization," ed by A. R. Lepley and G. L. Closs, Wiley & Sons, New York (1973).

9) A. Gupta and G. S. Hammond, *J. Chem. Phys.*, **57**, 1789 (1972).

10) We reexamined their experiments with no effect to be observed; H. Hayashi, Y. Sakaguchi, and S. Nagakura, presented at the 26th International Congress of Pure and Applied Chemistry, Tokyo, Spetember 1977.

11) B. Brocklehurst, *J. Chem. Soc. Faraday Trans. 2*, **70**, 769 (1976).

12) M. E. Michel-Beyerle, R. Haberkorn, W. Bube, E. Bube, E. Steffens, H. Schroder, H. J. Neusser, and E. W. Schlang, *Chem. Phys.*, **17**, 139 (1976); R. Haberkorn, *ibid.*, **19**, 165 (1977).

13) K. Schulten, H. Staerk, A. Weller, H.-J. Werner, and B. Nicker, *Z. Phys. Chem.* **101**, S371 (1976).

14) R. Z. Sagdeev, T. V. Leshina, M. A. Mamkha, S. M. Shein, and Yu. N. Molin, *Org. Magn. Res.*, **5**, 603 (1973).

15) A. V. Podoplelov, R. Z. Sagdeev, T. V. Leshina, Yu. A. Grishin, and Yu. N. Molin, *Dokl. Akad, Nauk USSR*, **221**, 866 (1975).

16) Y. Tanimoto, H. Hayashi, S. Nagakura, H. Sakuragi, and K. Tokumaru, *Chem. Phys. Lett.*, **41**, 267 (1976).

17) K. Itoh, H. Hayashi, and S. Nagakura, *Mol. Phys.*, **17**, 561 (1969).

18) R. Kaptein, *J. Am. Chem. Soc.*, **94**, 6251 (1972).

19) In this paper, the products are assumed to be derived only from singlet states. The cases where some products are given through triplet states can be treated in a similar way.[11–13]

20) R. M. Noyes, *J. Am. Chem. Soc.*, **78**, 5486 (1956).

21) In the actual reaction, a cage product is considered to be given through not only separated pairs but also close pairs. For the latter case, x can safely be assumed to be zero because its $|J|$ value may be much large than v.

22) In the calculation, Δg was given by the difference between the g factors of the benzoxyl (2.0117)[23] and phenyl (2.0024)[24] radicals determined by ESR experiments.

23) N. J. Karck, E. T. Koh, B. L. Whitsel, and J. M. Mcbride, *J. Am. Chem. Soc.*, **97**, 6729 (1975).

24) P. H. Kasai, P. A. Clarke, and E. B. Whipple, *J. Am. Chem. Soc.*, **92**, 2640 (1970).

25) K. Tokumaru, A. Oshima, T. Nakata, H. Sakurai, and T. Mishima, *Chem. Lett.*, **1974**, 571; T. Nakata, and K. Tokumaru, *Bull. Chem. Soc. Jpn.*, **43**, 3315 (1970).

26) Y. Sakaguchi, H. Hayashi, and S. Nagakura, *Chem. Phys. Lett.*, to be published.

27) A. Matsuzaki, and S. Nagakura, *Helv. Chim. Acta*, **61**, 675 (1978).

28) P. W. Atkins, and P. R. Stannard, *Chem. Phys. Lett.*, **47**, 113 (1977).

29) R. P. Groff, A. Suna, P. Avakian, and R. E. Merrified, *Phys. Rev. B*, **9**, 2655 (1974).

30) K. Okamoto, A. Itaya, and S. Kusabayashi, *Chem. Lett.*, **1976**, 99.

31) N. Hata, *Chem. Lett.*, **1976**, 547.

32) B. R. Henry and W. Siebrand, "Organic Molecular Photophysics," ed by J. B. Birds, Wiley & Sons, New York (1975), Vol. 1, p. 153.