Theoretical Study of Relaxation Mechanism in Magnetic Field Effects on Chemical Reactions

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External magnetic field and magnetic isotope effects on the dynamic behavior of radical pairs in solutions have been studied theoretically, where the relaxation of their electron spins was taken into account. The decay observed with some radical pairs in micellar solutions under high magnetic fields is successfully interpreted in terms of the relaxation mechanism, and the magnetic field dependence of the relaxation rates is calculated for a model system.

Magnetic field effects on chemical reactions have been extensively studied during the last decade.[1-8] The effects observed for usual solvents are known to be classified and systematically explained in terms of the Δg, hyperfine coupling (HFC) and level-crossing (J) mechanisms[9] of the radical pair theory.[10,11]

Recently,we first succeeded in measuring the effect on photochemical reaction rates, taking the reactions of benzophenone (BP),[12-14] its derivatives,[15] and dibenzyl ketone (DBK)[14,16] in some micelles as examples. A similar effect was also observed in the reactions of 1,4-naphthoquinone (NQ) derivatives in a sodium dodecyl sulfate (SDS) micelle.[17] In these reactions, we have found some new external magnetic field and magnetic isotope effects on the decay of their intermediate radical pairs which cannot be explained in terms of only the Δg, HFC, and J mechanisms of the radical pair theory. The yields of their escaping radicals and reaction products were also found to show similar effects.

Among the new effects observed in the micellar solutions, the effects observed in the photodecomposition reaction of DBK[14] were explained in terms of the triplet (T) mechanism successfully applied to some chemically induced dynamic electron polarization (CIDEP).[18] On the other hand, the effects observed in the hydrogen abstraction reactions of BP's and NQ's could not be explained by this mechanism. In preceding papers,[14,15] we have suggested that the relaxation mechanism may explain these magnetic field effects. Brocklehurst studied theoretically the effect of the relaxation times (T_1 and T_2) of electron spins in a radical pair on the evolution of its singlet character.[19] However, it is not clear at present how the decay of the radical pair and the yields of escaping radicals and reaction products are influenced by a magnetic field when the relaxation mechanism is effective. Therefore, the purpose of the present study is to analyze theoretically the dynamic behavior of the radical pair through the relaxation mechanism and to explain the observed effects in micellar solutions with the developed theory.

Theoretical

Dynamic Behavior of Radical Pair. It has already been shown that a separated radical pair plays a very important role in the magnetic field effects on chemical reactions in solutions.[9,11,20] Thus, in the present paper, we also consider the dynamic behavior of the separated radical pair, in which the interaction between its component radicals (radicals a and b) is very small. In this paper, the separated radical pair is simply written as the radical pair.

The energy diagram of the radical pair is shown in Fig. 1. At the zero magnetic field, we assume that the energy (E_S) of its singlet state ($|S\rangle$) and that (E_{T_i}) of each sublevel (i=x, y, or z) of its triplet state are degenerate with each other. On this assumption, the singlet-triplet (S-T) separation ($2J$) of the radical pair and the energy splittings within the triplet sublevels are considered to be zero. This assumption is usually adopted for the theoretical studies of the above-mentioned mechanism except for the J one.

At a high field, where the high field approximation holds,[21,22] two of the triplet sublevels ($|T_{\pm 1}\rangle$) are shifted from the central one ($|T_0\rangle$) through the Zeeman effect. In usual radical pairs, the magnetic flux density (B) of 0.04 T is enough for the high field approximation.[9,20]

In order to analyze exactly the dynamic behavior of the radical pair, a stochastic Liouville equation must be solved.[20] However, it cannot be solved analytically and a tedious calculation is necessary for its solution. On the other hand, many nuclear spin states of a radical pair can interfere with one another and the overall dynamics of its singlet and triplet states become very simple. Thus we can use the first order rate equations

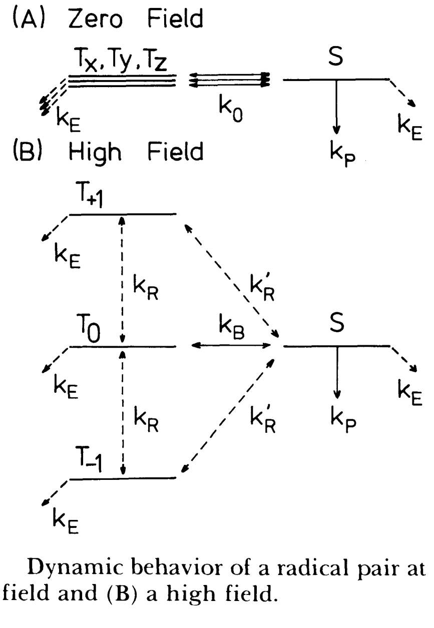

Fig. 1. Dynamic behavior of a radical pair at (A) the zero field and (B) a high field.

in order to understand the dynamics intuitively. In fact, all of the decay curves of radical pairs observed in micellar solutions with a laser-photolysis technique[13–17] have been expressed by combination of some exponential functions.

Therefore, we introduce rate equations for the populations of the singlet state and triplet sublevels ([S] and $[T_i]$) of a radical pair. At the zero field, they can be written as follows:

$$d[T]/dt = -(k_0+k_E)[T] + 3k_0[S], \tag{1}$$

$$d[S]/dt = k_0[T] - (k_P+3k_0+k_E)[S], \tag{2}$$

where $[T]=[T_x]+[T_y]+[T_z]$. Each rate constant (k_i) is shown in Fig. 1(A). The S-T conversion rate constant is written by k_0, which is determined by the HFC and has the order of 10^9—10^8 s^{-1}.[23] The reaction rate constant from the singlet state is written by k_P, which has the order of 10^{10}—10^7 s^{-1}.[23] The reaction from the triplet state is not considered in the present study for simplicity, although it is possible if necessary. The escaping rate constant of radicals from the radical pair, k_E, may have the order of 10^5 s^{-1} for the micellar solutions of BP's and NQ's. In usual solvents, it may be much larger.

At a high field, the following equations are introduced.

$$d[T_i]/dt = -\Big({\sum_{j\neq i}}' k_{ij}+k_{iS}+k_E\Big)[T_i] + \sum_{j\neq i} k_{ji}[T_j] + k_{Si}[S], \tag{3}$$

$$d[S]/dt = \sum_i k_{iS}[T_i] - \Big(k_P+\sum_i k_{Si}+k_E\Big)[S], \tag{4}$$

where i, $j=0$ or ± 1, k_{ij} is the conversion rate constant from the i-triplet sublevel to the j-one, and k_{Si} and k_{iS} are the S-T converson rate constants between the singlet state and the i-triplet sublevel. Since $k_{ij}=k_{ji}$,[21,22] and $k_{Si}=k_{iS}$,[9] Eqs. 3 and 4 are summarized as follows:

$$d[T']/dt = -(k_R+k_R'+k_E)[T'] + 2k_R[T_0] + 2k_R'[S], \tag{5}$$

$$d[T_0]/dt = k_R[T'] - (k_B+2k_R+k_E)[T_0] + k_B[S], \tag{6}$$

$$d[S]/dt = k_R'[T'] + k_B[T_0] - (k_P+k_B+2k_R'+k_E)[S], \tag{7}$$

where $[T']=[T_1]+[T_{-1}]$, $k_B=k_{S0}$, $k_R=k_{\pm 10}$, and $k_R'=k_{\pm 1S}$. As shown in Appendix, k_{10} is equal to k_{-10} and k_{1S} is equal to k_{-1S}. Each rate constant is shown in Fig. 1(B). It is noteworthy that the relaxation from the ±1-triplet sublevel to the singlet state must be taken into account besides that to the 0-one (see Appendix). In usual radicals, T_1^{-1} is 10^6—10^4 s^{-1}.[23] Thus k_R and k_R' may have similar values. According to the radical pair theory, k_B is based on the HFC and $\Delta g\beta B$ of the radical pair, where Δg is the difference between the isotropic g-values (g^a and g^b) of the component radicals and β is the electric Bohr magneton. Usually, k_B is larger than k_0.

Solution of Rate Equations. Equations 1 and 2 and Eqs. 5—7 are solved approximately for $k_P \gg k_0$, k_B (case a) and k_0, $k_B \gg k_P$ (case b), respectively. As already explained, in micellar solutions k_P, k_0, and k_B can be considered to be much larger than the other rate constants. This condition is considered in the present calculation. For the reaction from an S-precursor, the initial population ($[\ \ ]_0$) can be taken as follows: $[S]_0=1$, $[T]_0=0$, or $[T_i]_0=0$ ($i=0$ or ± 1). For the reaction from a T-precursor, the initial population can be taken as follows:[24] $[S]_0=0$, $[T]_0=1$, or $[T_i]=1/3$.

After calculation of [S], [T], [T′], and $[T_0]$, the total population of the radical pair ([R]) is obtained, where $[R]=[S]+[T]$ at the zero field and $[R]=[S]+[T']+[T_0]$ at a high field. The results are as follows:

S-precursor:

At the zero magnetic field:

$$\text{Case a } (k_P \gg k_0)\text{: } [R] = \exp[-(k_P+3k_0+k_E)t], \tag{8}$$

$$\text{Case b } (k_0 \gg k_P)\text{: } [R] = \exp[-(k_P/4+k_E)t]. \tag{9}$$

At a high magnetic field:

$$\text{Case a } (k_P \gg k_B)\text{: } [R] = \exp(-r_1 t), \tag{10}$$

$$\text{Case b } (k_B \gg k_P)\text{: } [R] = \exp(-r_2' t). \tag{11}$$

T-precursor:

At the zero magnetic field:

$$\text{Case a } (k_P \gg k_0)\text{: } [R] = \exp[-(k_0+k_E)t], \tag{12}$$

$$\text{Case b } (k_0 \gg k_P)\text{: } [R] = \exp[-(k_P/4+k_E)t]. \tag{13}$$

At a high magnetic field:

Case a ($k_P \gg k_B$):

$$[R] = (1/3)\exp(-r_2 t) + (2/3)\exp(-r_3 t), \tag{14}$$

Case b ($k_B \gg k_P$):

$$[R] = (1/3)\exp(-r_2' t) + (2/3)\exp(-r_3' t), \tag{15}$$

where r_1, r_2, r_3 r_2', and r_3' are given as follows:

$$r_1 = k_P + k_B + 2k_R' + k_E, \tag{16}$$

$$r_2 = k_B + 2k_R + k_E, \tag{17}$$

$$r_2' = k_P/2 + k_R + k_R' + k_E, \tag{18}$$

$$r_3 = r_3' = k_R + k_R' + k_E. \tag{19}$$

From these solutions, the following predictions can be given for the reaction from the S-precursor: (1) The decay of the radical pair can be expressed by a single exponential function for all the cases under consideration. (2) The decay rate constant at the zero field shows no or very little isotope effect because k_P and k_E usually show no magnetic isotope effect.[7] (3) For case a, the magnetically induced change of its decay rate constant is $k_B-3k_0+2k_R'$. This value is negative at a relatively low field and increases with increasing B. The magnetic field effect on the rate constant, however, is very small because the main component of r_1 is k_P. (4) For case b, the change is $k_P/4+k_R+k_R'$. This value is positive and the decay rate constant rapidly increases with increasing B in the low field region ($B<0.04$ T). On the other hand, in the high field region ($B>0.04$ T) its magnetically induced change becomes very small because k_P is a main term for the decay rate constant.

For the reactions from the T-precursor, the following predictions are made: (1) The decay of the radical pair can be expressed by a single exponential function at the zero field and by a combination of two eponential functions at a high field. (2) At the zero field, the decay rate constant can be represented by k_0+k_E for case a and by $k_P/4+k_E$ for case b. Therefore, its magnetic isotope effect can be expected for the former case but not for the latter. (3) For case a, the change from the decay rate constant at the zero field to the larger one in the high field region (r_2) is $k_B-k_0+2k_R$. Its magnetic field effect at a relatively low field is small but increases with increasing B. The smaller one (r_3) in the high field region is much smaller than the rate constant at the zero field. (4) For case b, the change from the decay rate constant at the zero field to r_2' is $k_P/4+k_R+k_R'$. This value is the same as that is given in the reaction from the S-precursor. On the other hand, the second component appears in the high field region for the reaction from the T-precursor. Its rate constant (r_3') is much smaller than that at the zero field.

The populations of one of the escaping radicals ([E]) and the product from the singlet radical pair ([P]) can also be obtained from the following equations:

$$d[E]/dt = k_E[R], \tag{20}$$

$$d[P]/dt = k_P[S]. \tag{21}$$

Results and Discussion

Summaries of Experimental Results. In the reactions of BP's and NQ's in micelles at room temperature,[12–15,17] the following characteristics were found for their magnetic field effects:

(a) The decay curves of their radical pairs observed at the zero field are expressed by single exponential functions. Some of the decay rate constants observed in an SDS micelle are listed in Table 1. They are about 3×10^6 s^{-1} for BP's and about 5×10^6 s^{-1} for NQ's. For BP, the magnetic isotope effect on the decay rate constant can scarcely be observed at the zero field.

(b) In the presence of a magnetic field above 0.04 T, the decay curves of the radical pairs are expressed by combinations of two eponential functions. The rate constants of the slow decay component observed with BP's and NQ's in the SDS micelle are listed in Table 1. They decrease with increasing B until 1.34 T at which the magnetic field effects become almost constant. They are about 2×10^6 s^{-1} at 0.04 or 0.05 T but are as small as about 3×10^5 s^{-1} at 1.34 T.

(c) As shown in Table 1, the magnetic isotope effects on the rate constants appeared clearly between 0.04 and 0.5 T, but the effects became small above 0.5 T again. Similar magnetic isotope effects were also obtained more accurately for the yields of the escaping radicals in the BP reaction.[15]

(d) The yields of the escaping radicals in the reactions of BP's and NQ's increase with increasing B until 1.34 T.[15,17]

The external magnetic field and magnetic isotope effects summarized above cannot be interpreted by the Δg, HFC, and J mechanisms for the following reasons: According to the Δg mechanism,[9] the decay rate constant of the radical pair in the reactions from the T-precursor should increase with increasing B. From the HFC mechanism,[9,20] the rate constant is expected to decrease with increasing B, which is saturated at a low magnetic field ($B \ll 0.1$ T).[20] According to the J mechanism,[9] the rate constant should increase at a level-crossing field. These predictions clearly contradict the observed results (see summary b).

The observed results cannot be explained also by the T mechanism for the following reason: The initial population of each sublevel of the triplet radical pair ($[T_i]_0$) can be influenced by a magnetic field through the T mechanism. However, this mechanism cannot explain appearance of the two decay components of the radical pair in the presence of a magnetic field and the magnetically induced changes of the slow decay component. The magnetic field effects on this component are the main problem of the present paper.

Application of Relaxation Mechanism. Now let us consider the observed magnetic field effects on the reactions of BP's and NQ's, taking account of the relaxation mechanism developed in the present paper. The observed numbers of the decay components of [R] in the absence (one) and presence (two) of a magnetic field agree well with the prediction for the reaction from the T-precursor. For case a, the observed decay rate constan at the zero magnetic field should correspond to k_0+k_E. As explained above, k_0 should have the order of 10^9—10^8 s^{-1} and should show a magnetic isotope effect. This prediction contradict the observed results (see summary a).

For case b, the rate constant at the zero magnetic field should correspond to $k_P/4+k_E$ and may not show any appreciable isotope effect. The magnitudes of k_P and k_E are also reasonable for explaining the observed rate constants. Thus we can conclude that case b is

TABLE 1. THE DECAY RATE CONSTANTS OF THE RADICAL PAIRS (k) OBSERVED WITH THE SDS SOLUTIONS OF SOME BP AND NQ DERIVATIVES

Magnetic field B/T	$k/10^6$ s^{-1}					
	BP[a]	BP-d_{10}[b]	BP-^{13}C[c]	BP-F_2[d]	NQ[e]	MNQ[f]
0	2.8[g]	2.8[g]	2.8[g]	2.9	4.7	4.1
0.04	2.2	2.1	2.4	—	—	—
0.05	—	—	—	—	2.4	1.9
0.07	1.9	1.9	2.2	—	—	—
0.10	0.9_1	—	1.1	1.3	1.7	1.4
0.20	0.7_1	—	0.8_9	0.7_5	1.3	0.9_5
0.50	0.4_9	—	0.5_3	0.4_5	0.8_5	0.7_7
1.00	0.3_7	—	0.3_8	—	—	—
1.34	0.3_7	—	0.4_2	0.3_0	0.5_2	0.6_5

a) Benzophenone; Refs. 13 and 15. b) Benzophenone-d_{10}; Ref. 13. c) Benzophenone-carbonyl-^{13}C; Refs. 13 and 15. d) 4,4′-Difluorobenzophenone; Ref. 15. e) 1,4-Naphtoquinone; Ref. 17. f) 2-Methyl-1,4-Naphtoquinone; Ref. 17. g) The values measured under a residual magnetic field (0.12 mT) are listed.

applicable to the reactions of BP's and NQ's in the micellar solutions and the rate constants of the fast and slow decay components are assigned to r_2' and r_3', respectively. This means that the magnetic field and magnetic isotope effects observed with the slow decay component are due to $r_3' = k_R + k_R' + k_E$ (see Eq. 19). Since k_E can be considered to be insensitive to a magnetic field below 1.34 T, the observed magnetic field and magnetic isotope effects are considered to be due to k_R and k_R'.

It is noteworthy that these effects are not due to such direct S-T conversion rate constant as k_0 and k_B. This is a new situation in the study of the magnetic field effects on chemical reactions through radical pairs. The effects through the other mechanisms have been shown to be due to k_0 and k_B.[9,20)]

Analytical Forms of Relaxation Rate Constants. The external magnetic field and magnetic isotope effects on k_R and k_R' of the radical pair have not yet been studied well. Therefore, we have undertaken to analyze them theoretically. The internal motions of a radical pair against the direction of an external magnetic field are shown in Fig. 2. Here Ω^i and Ω^{ab} represent the sets of the angular coordinates of the molecular axes of the i-th radical (X^i, Y^i, and Z^i) and the vector (r_{ab}) from an odd electron on radical b to that on radical a, respectively.

We have obtained the analytical forms of k_R and k_R' for the following simple model of a radical pair: (1) Each of the component radicals has its HFC with only one nucleus having spin 1/2. The principal values of the HFC tensor (A^i tensor) are given by A_X^i, A_Y^i, and A_Z^i. The nuclear spin quantum number is written by M^i. (2) The principal axes of the g tensor of the i-th radical (g^i tensor) are supposed to coincide with those of the A^i one. (3) The axial symmetry is assumed for g^i and A^i tensors. Their isotropic parameters are given by $g^i = g_{\parallel}^i/3 + 2g_{\perp}^i/3$ and $A^i = A_{\parallel}^i/3 + 2A_{\perp}^i/3$, respectively. Their anisotropic parameters are given by $\Delta g^i = g_{\parallel}^i - g_{\perp}^i$ and $\Delta A^i = A_{\parallel}^i - A_{\perp}^i$, respectively. Here $\parallel$ and $\perp$ represent the parallel and perpendicular components against the axis of symmetry, respectively. (4) The dipole-dipole interaction between the odd electrons is assumed to be due to that between the two points which are separated with each other by the averaged distance (R) of r_{ab}.

For the above model, k_R and k_R' are given as follows:

$$k_R = (1/4) \sum_{M^a} \sum_{M^{a\prime}} \sum_{M^b} \sum_{M^{b\prime}} P < T_{\pm 1}, M^a, M^b | T_0, M^{a\prime}, M^{b\prime} >, \quad (22)$$

$$k_R' = (1/4) \sum_{M^a} \sum_{M^{a\prime}} \sum_{M^b} \sum_{M^{b\prime}} P < T_{\pm 1}, M^a, M^b | S, M^{a\prime}, M^{b\prime} >, \quad (23)$$

where $P<m|\,l>$ is the transition probability from the m-th state to the l-th one. The derivations and analytical forms of the right sides of Eqs. 22 and 23 are given in Appendix.

Model Calculations of Relaxation Times. After hydrogen abstraction by the triplet state of BP or NQ from a micellar molecule, a radical pair of the ketyl or semiquinone radical with the alkyl one is produced. Thus the former and latter radicals can be written by radicals a and b, respectively.

Now let us calculate $k_R + k_R'$ numerically with the aid of Eqs. 22 and 23. Since many parameters in these equations have not yet been measured, they are assumed adequately. The following parameters are fixed: $g^a = g^b = 2.003$,[25)] $\Delta g^b = 0.002$,[25)] $\tau_a = 1 \times 10^{-10}$ s,[28)] and $\tau_b = 5 \times 10^{-9}$ s.[28)] The others are changed. The calculated contributions of the motions of radicals a and b (V^a and V^b) and the relative motion of the two radicals (V^{ab}) to $\log(k_R + k_R')$ are plotted against B in Fig. 3.

From Fig. 3, the following characteristics are found: (1) Curves a—e show the contributions of V^a for some sets of parameters. From curve a which shows the contribution of Δg of 0.002, this contribution is proved to be neglibly small. The increases from curve a to curves b—d show the contributions of the increases in $\Delta A^a/g\beta$ from 0 to 0.002, 0.004, and 0.006 T, respectively, where g is $(g^a + g^b)/2$. This contribution is

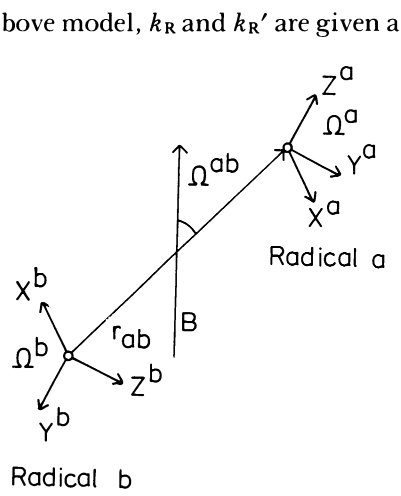

Fig. 2. Internal motions of a radical pair.

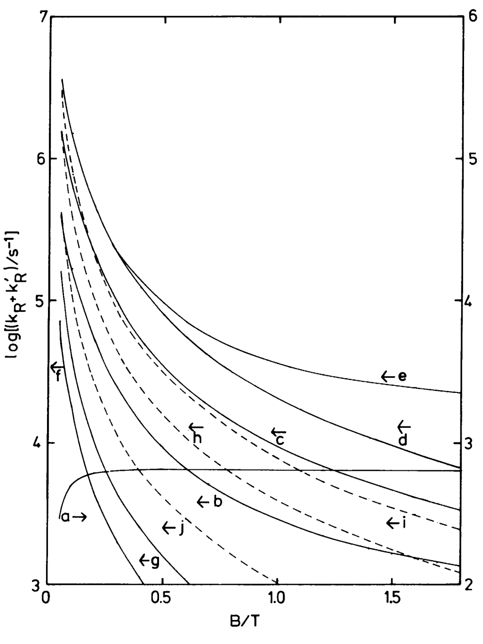

Fig. 3. Calculated contributions of V^a, V^b, and V^{ab} to $k_R + k_R'$ with the following parameters: V^a: $g^a = 2.003$ and $\tau_a = 1 \times 10^{-10}\,s^{-1}$ (a) $\Delta g^a = 0.002$ and $\Delta A^a/g\beta = 0$ T; (b) $\Delta g^a = 0.002$ and $\Delta A^a/g\beta = 0.002$ T; (c) $\Delta g^a = 0.002$ and $\Delta A^a/g\beta = 0.004$ T; (d) $\Delta g^a = 0.002$ and $\Delta A^a/g\beta = 0.006$ T; (e) $\Delta g^a = 0.01$ and $\Delta A^a/g\beta = 0.006$ T. V^b: $g^b = 2.003$, $\Delta g^b = 0.002$, and $\tau_b = 5 \times 10^{-9}$ (f) $\Delta A^b/g\beta = 0.004$ T; (g) $\Delta A^b/B\beta = 0.006$ T. V^{ab}: (h) $R = 0.8$ nm and $\tau_{ab} = 1 \times 10^{-9}$ s; (i) $R = 0.8$ nm and $\tau_{ab} = 5 \times 10^{-10}$ s; (j) $R = 1.0$ nm and $\tau_{ab} = 1 \times 10^{-9}$ s.

shown to be larger under low magnetic fields and to increase with increasing ΔA^a. This is the origin of the magnetic isotope effect on k_R+k_R' and the amount of the effect is also shown to decrease with increasing B because of the denominator $(1+\omega^2\tau_a^2)$ in Eqs. A7—A9. The differnce between curves e and d is the contribution of the increase of Δg from 0.002 to 0.01. This is also small.

(2) Curves f and g show the contribution of V^b. Thus the contribution of the alkyl radical is found to be negligibly small. This is due to the fact that its correlation time is assumed to be very long. Since this radical may take part in micellar formation, this assumption may be permitted.

(3) Curves h—j show the contribution of V^{ab}. This contribution is found to be comparable to that of V^a in magnitude. Thus this is also shown to play an important role in k_R. Figure 3 shows that this contribution decreases with inreasing B, R, and τ_{ab}. However, it is very difficult to determine the values of R and τ_{ab} from other experimental methods.

Comparison between the Observed and Calculated Rate Constants. In Fig. 4, the observed dependence of the decay rate constants on B is plotted for some typical reactions. In this figure, the rate constant values calculated for the adopted model are also shown. Here the contributions of V^a and V^{ab} are only taken into account because that of V^b has been shown to be much smaller than the former. The assumed parameters are as follows: $k_E=4\times10^5$ s^{-1}, $g^a=2.003$, $\Delta g^a=0.002$,[25] $\tau_a=1\times10^{-10}$ s, $R=0.8$ nm, and $\tau_{ab}=1\times10^{-9}$ s.[28] The value of ΔA^a is changed. The k_E, R, and τ_{ab} values are chosen in such a way as the calculated rate constant values agree with the observed ones. They seem to be reasonable for radical pairs considered in the present paper.

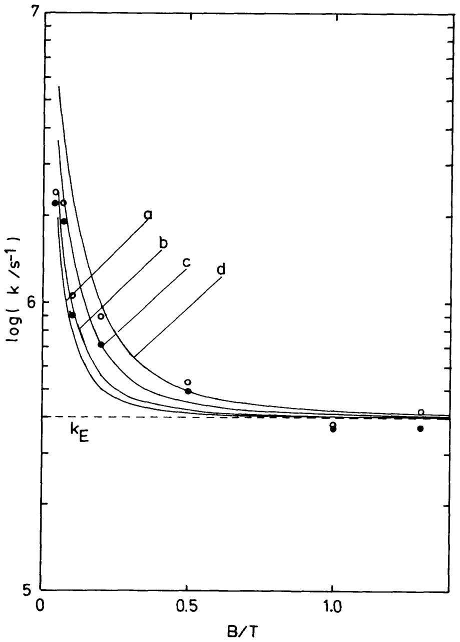

Fig. 4. The magnetic field dependences of the rate constants (k) of the slow decay components observed with the SDS solutions of (●) benzophenone and (O) benzophenone-carbonyl-^{13}C.[13,15] Calculated magnetic field dependences of the rate constants due to the combination of V^a and V^{ab} with the following parameters: (a) $\Delta A^a/g\beta=0$ T, (b) $\Delta A^a/g\beta=0.002$ T, (c) $\Delta A^a/g\beta=0.004$ T, and (d) $\Delta A^a/g\beta=0.006$ T. The other parameters are written in the text.

From the comparison among the results shown in Table 1 and Fig. 4, it is considered that this calculation can explain the observed characteristics of the decay rate constants in spite of the facts that the adopted model is very simple and that there are some ambiguities in assuming the parameters. The observed magnetic field dependence of the decay rate constant is well interpreted by the calculated k_R+k_R'. Its decrease with increasing B is due to the denominators in Eqs. A7—A9.

The observed magnitude of k_R+k_R' is also explained by this calculation. At magnetic fields below 0.1 T, the magnitude is calculated to be larger than 10^6 s^{-1}. At fields above 0.5 T, the magnitude is smaller than 10^5 s^{-1}. They agree well with the observed values if the observed decay rate constant at 1.34 T is nearly equal to k_E in each of the investigated reactions. The observed magnetic isotope effects on the decay rate constant in the BP reaction are also explained by the calculated curved in Fig. 4. They show that the decay rate constant increases with increasing ΔA^a and that the magnitude of the effects is appreciable at low magnetic fields and becomes small at high fields.

Thus the observed external magnetic field and magnetic isotope effects on the radical pair decay in each of the reactions of BP's and NQ's in micelles have been successfully interpreted in terms of the relaxation mechanism. At the zero magnetic field, the decay rate constant of the radical pair corresponds to $k_P/4+k_E$, which should not show any appreciable magnetic isotope effect. In the presence of a magnetic field where the high field approximation holds, the constant shows the external magnetic field and magnetic isotope effects which are due to the relaxations from the $\pm$1-sublevel of the triplet radical pair to the 0-sublevel (k_R) and the singlet state (k_R'). The analytical forms for a model system are derived and numerical values of k_R and k_R' are calculated. The magnetic field effects on the yields of the escaping radicals and reaction products observed in these micellar solutions are also explained by the relaxation mechanism. Details of the effects on the yields will be published elsewhere.[15,17]

Appendix

The transition probability, $P<m|n>$, under a time dependent perturbation ($V(t)$) is given as follows:[21]

$$P<m|n> = \hbar^{-2}|V_{mn}|^2\,2\tau_c/(1+\omega_{mn}{}^2\tau_c^2), \tag{A1}$$

where ω_{mn} is expressed by

$$\omega_{mn} = \hbar^{-1}(E_n-E_m), \tag{A2}$$

and $V(t)$ is supposed to take the form

$$V(t) = V\cdot f(t), \tag{A3}$$

where V is an operator which is independent of time and $f(t)$ is a fluctuating numerical factor. When the autocorrelation function ($G(\tau)$) of $f(t)$ decays exponentially with a correlation time of τ_c,

$$G(\tau) = \overline{f(t+\tau)f(t)} = \overline{f(t)^2} \exp(-|\tau|/\tau_c), \tag{A4}$$

Eq. A1 is obtained.

For a radical pair, various off-diagonal matrix elements among $|T_{\pm1}>$, $|T_0>$, and $|S>$ have been obtained previously (Eqs. 39 and 40 in Ref. 10b). They can be used for $V(t)$. In the presence of a magnetic field where the high field approximation holds, $P<T_{\pm1}|\Gamma>$ (Γ is T_0 or S) can be obtained as follows:

$$P<T_{\pm1}|\Gamma> = \sum_i \frac{|V^i|^2}{\hbar^2} \cdot \frac{2\tau_i}{1+\omega^2\tau_i^2} + \frac{|V^{ab}|^2}{\hbar^2} \cdot \frac{2\tau_{ab}\delta_{\Gamma T_0}}{1+\omega^2\tau_{ab}^2}, \tag{A5}$$

where $\delta_{T_0T_0}=1$ and $\delta_{ST_0}=0$. V^i (i=a or b) contains the contributions from the anisotropic terms of the g^i and A^i tensors and V^{ab} is due to the dipole-dipole interaction between radicals a and b. The correlation times of Ω^i and Ω^{ab} are given by τ_i and τ_{ab}, respectively. In this calculation, we consider the case where

$$\hbar\omega = |E_{T_{\pm1}} - E_{T_0}| = |E_{T_{\pm1}} - E_S| = (g^a+g^b)\beta B/2. \tag{A6}$$

From Eq. A5, the following equations can be derived: $k_{10} = k_{-10}$ and $k_{1S} = k_{-1S}$. It is shown that k_R' is comparable to k_R in magnitude. For the adopted model shown in the text, non-vanishing elements of P can be expressed as follows:

$$\begin{aligned} \hbar^2 P < T_{\pm1}, M^a, M^b | \Gamma, M^a, M^b > \\ = \sum (\beta B\Delta g^i + M^i \Delta A^i)^2 \tau_i / [30(1+\omega^2\tau_i^2)] \\ + D^2\tau_{ab}\delta_{\Gamma T_0}/[7.5(1+\omega^2\tau_{ab}^2)], \end{aligned} \tag{A7}$$

$$\begin{aligned} \hbar^2 P < T_{\pm1}, \pm 1/2, M^b | \Gamma, \mp 1/2, M^b > \\ = (\Delta A^a)^2 \tau_a / [30(1+\omega^2\tau_a^2)], \end{aligned} \tag{A8}$$

$$\begin{aligned} \hbar^2 P < T_{\pm1}, \mp 1/2, M^b | \Gamma, \pm 1/2, M^b > \\ = (\Delta A^a)^2 \tau_a / [180(1+\omega^2\tau_a^2)]. \end{aligned} \tag{A9}$$

$P<T_{\pm1}, M, M'|\Gamma, M, M''>$ has the same form as $P<T_{\pm1}, M', M|\Gamma, M'', M>$, where D is given as follow:[22]

$$D = -(3/2)(\mu_0/4\pi)(g^2\beta^2/R^3). \tag{A10}$$

Since k_R and k_R' are defined as the averaged transition probabilities about the nuclear spin states, they are given as shown in Eqs. 22 and 23.

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