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Influence of Large Magnetic Fields on the Dynamic Behavior of a Radical Pair Produced by Photoreduction of Benzophenone in a Micellar Solution

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The photochemical reaction of benzophenone in a micellar sodium dodecylsulfate solution was investigated under magnetic fields of 0–10 T. The decrease of decay rate of the ketyl radical and the increase of the yield of the escaped radical were saturated around 2 T. The contribution of the Δg mechanism was not observed below 10 T since the Δg value is very small for this system.

Magnetic field effects (MFEs) on physical and chemical properties have been attracting the interests of many scientists. The effects on chemical reactions have received considerable attention, since the magnetic interactions to invoke these effects are much smaller than the thermal fluctuation.[1)] This means that smaller magnetic fields than 1 T can change chemical reactions. Therefore, the reports applying much larger magnetic fields have been relatively scanty. We investigated the MFE of the product yields in the photodecomposition of dibenzoyl peroxide below 6 T.[2)] Turro *et al.* applied a field of 14.5 T for the MFE of the product yields in the photodecomposition of dibenzylketones.[3)] Boxer *et al.* investigated triplet yields of photosynthetic reaction centers below 5 T.[4)]

Because the MFEs on reaction yields were large in micellar solutions,[5)] we directly measured the effect on the radical pair decay below 1.34 T in the photoreduction of benzophenone in a micelle with a combination of a nanosecond laser photolysis apparatus and an electromagnet.[6,7)] Our result revealed that the effect was not saturated at 0.1 T. This could not be explained by the conventional hyperfine coupling mechanism (HFCM).[1)] We, therefore, proposed the relaxation mechanism (RM) to explain such an anomalous MFE.[8)]

There are some ambiguity about the MFEs in micellar solutions. In some reactions including the above one, the saturation of the MFE is not clear even at 1.34 T. On the other hand, some reactions, such as the photoreaction between xanthone and substituted phenols,[9)] show saturation below 0.5 T. This difference has not yet been explained clearly. Hence, we tried to investigate the former reaction under much larger fields. Large magnetic fields are attained by two distinct methods. One is a static field using a superconducting magnet and the other is a transient one using a pulsed magnet. For the kinetic analysis, the pulsed magnet is unfavorable since its transient response might compete the dynamic phenomena in question.

We constructed a nanosecond transient absorption measuring system including a superconducting magnet (Oxford 37057, PS120-10), the maximum field of which is 10 T. To avoid the influence of its magnetic field, we set our photomultiplier far from the magnet and guided our probing light by a quartz optical fibre. The output of the photomultiplier was measured by an HP54510A digitizing oscilloscope (1G sample/s) and then recorded by an NEC PC9801T computer. Magnetic fields (B) were measured by an F.W.Bell 9200 Gaussmeter with an FAR92-1815 probe. Other components are similar to those published previously.[10)]

Time profiles of the transient absorption ($A(t)$) were measured for the micellar sodium dodecylsulfate (RH, 8×10^{-2} mol dm^{-3}) solution of benzophenone (BP, 2×10^{-3} mol dm^{-3}) with the excitation of the 4th harmonic (266nm) of a Nd:YAG laser. In this case, the following reactions have been believed to occur:[7)]

$$\mathrm{BP} \xrightarrow{h\nu} {}^1\mathrm{BP}^* \rightarrow {}^3\mathrm{BP}^*$$

$$\begin{tikzcd} {}^3\mathrm{BP}^* + \mathrm{RH} \arrow[r] & {}^3(\mathrm{BPH}\bullet\ \bullet\mathrm{R}) \arrow[r] \arrow[d, shift right] & \mathrm{BPH}\bullet + \mathrm{R}\bullet \quad \text{(escaped radicals)} \\ & {}^1(\mathrm{BPH}\bullet\ \bullet\mathrm{R}) \arrow[r] \arrow[u, shift right, "\Leftarrow \text{magnetic field}"'] & \mathrm{BPH{-}R}, \text{etc.} \quad \text{(recombination)} \end{tikzcd}$$

Here, BPH• and R• are the BP ketyl and alkyl radicals, respectively. The triplet-singlet (TS) conversion of the radical pair (BPH• •R) is affected by magnetic fields.

$A(t)$ curves at 525 nm were measured under magnetic fields of 0-10 T. Those at B=0, 1, and 10 T are shown in Fig. 1. Each of the $A(t)$ curves can be represented by a combination of a decay part and a nearly constant one in this time region. The former is attributed to the radical pair decay and the latter is to the yield of the escaped ketyl radical. Figure 1 shows that the decay becomes slower with increasing B and that the yield increases with increasing B.

The radical pair decay above 0.04 T can be represented by a biexponential function, but the decay at B=0 T by a single exponential one.[8)] The slower rate constant (k_S) of the radical pair decay above 1 T and the rate constant at B=0 T (k_0) are shown in Fig. 2. These values have mutual errors of ±10% and the absolute values have errors of ±50% owing to the slower decay of the escaped radical. They are somewhat different from the previous ones,[8)] which may be due to the difference of the concentration of benzophenone (previously 1×10^{-3} mol dm^{-3}). Owing to experimental conditions inside the superconducting magnet, we could not use such a dilute solution. As the decay rate of the radical pair becomes slower, the yield of the escaped radicals increases. The magnetic field dependence of the relative yield of the escaped ketyl radical (R(B)) can be estimated from the $A(t)$ curves, and the value $R(\mathrm{B})=A(5\ \mu\mathrm{s}, \mathrm{B})/A(0\ \mu\mathrm{s}, \mathrm{B})$ is plotted in Fig. 3. The errors of these values are smaller than ±0.02.

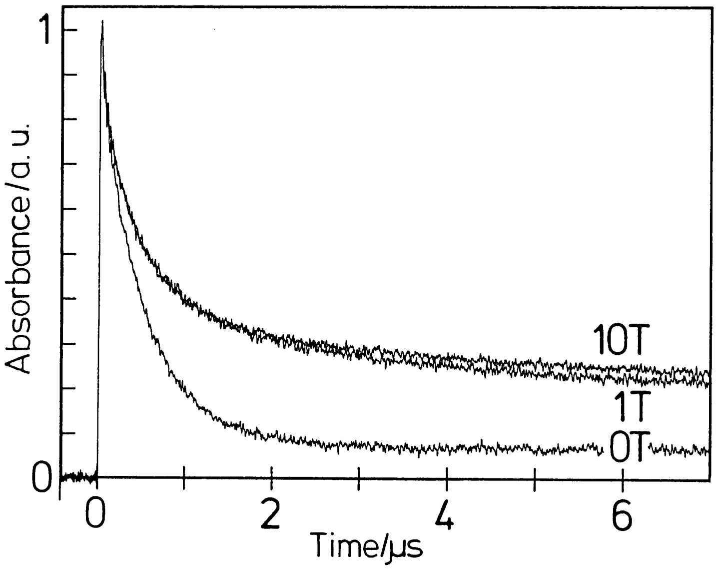

Fig. 1. $A(t)$ curves observed at an ambient temperature at 525 nm under the magnetic field of 0, 1, and 10 T for a micellar sodium dodecyl sulfate (8×10^{-2} mol dm^{-3}) solution of benzophenone (2×10^{-3} mol dm^{-3}).

As shown in Figs. 2 and 3, the MFEs on the rate constant and the yield were found to be saturated around 2 T and attained saturated values above it. This result indicates that the previous measurement up to 1.34 T was only slightly short of the field to describe the complete dependence and we need not seriously change previous discussion.[8] Consequently, the present results can be interpreted by the RM. According to the RM,[8,11,12] the k_S value can be represented as follows:

$$k_S = k_R + k_R' + k_E + k_{SO} \qquad (1)$$

Here, k_R is the relaxation rate constant between the $T_{\pm 1}$ and T_0 levels of a radical pair,[8] k_R' is the one between the $T_{\pm 1}$ and S levels of a radical pair,[8] k_E is the escape rate constant of radicals from a radical pair,[8] and k_{SO} is the recombination rate constant of a contact triplet radical pair.[12] k_E and k_{SO} are independent of B, but k_R and k_R' should decrease with increasing B.[8] At a very large magnetic field, the contribution of the anisotropic part of the g-term to k_R and k_R' should approach to limited values ($k_R(\infty)$ and $k_R'(\infty)$),[11] but the contributions of the anisotropic part of the HFC term and the spin-spin dipolar interaction between two radicals should tend toward zero.[11] Thus, the k_S value at a large field ($k_S(\infty)$) can be given as follows:

$$k_S(\infty) = k_R(\infty) + k_R'(\infty) + k_E + k_{SO} \qquad (2)$$

The $k_S(\infty)$ value of this case was estimated as the average of k_S between 3 and 10 T and was found to be $7.6\text{x}10^5\ \text{s}^{-1}$. This value can only be obtained with such large fields as used in the present study.

Under a magnetic field as large as 10 T, the contribution of the Δg mechanism (ΔgM)[1] should become much more important than under much smaller fields. Here, Δg is the difference of the isotropic g-values between the component radicals in a radical pair. A time resolved ESR spectrum of this reaction gave an anomalous alternating phase pattern.[13] This was able to be explained in terms of a spin-correlated radical pair.[14] In this spectrum, the Δg value between the ketyl and alkyl radicals was almost zero. If we overestimate that the difference is 0.05 mT at 0.34 T (the ESR field), it becomes no more than 1.5 mT at 10 T. On the other hand, the alkyl radical has four 2.5 mT β-protons and one 2.1 mT α-proton. Thus the ESR spectrum of the alkyl radical has a width of 12.1 mT which can be taken as a measure of hyperfime coupling interaction in the MFE. Consequently, the contribution of the Δg term on the ESR spectrum and hence that on the MFE through the ΔgM should be negligibly small, which well corresponds with the present results.

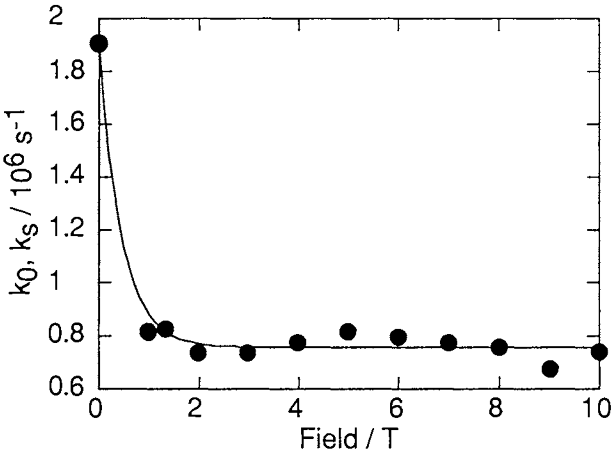

Fig. 2. Magnetic field dependence of the radical pair decay rate. In the presence of magnetic fields, the slower ones are plotted. (See text.)

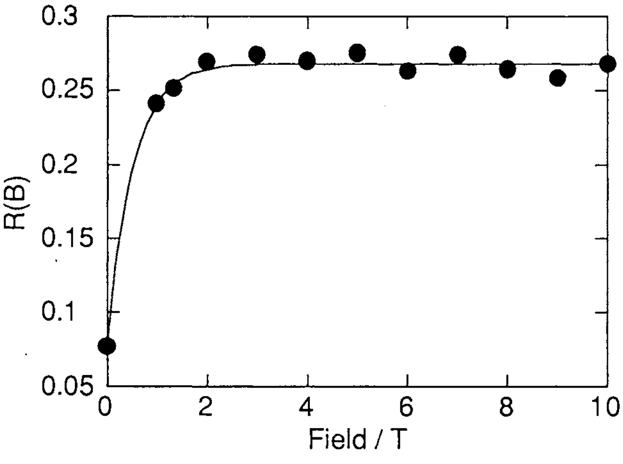

Fig. 3. Magnetic field dependence of the ratio $R(B) = A(5\ \mu s,B)/A(0\ \mu s,B)$ observed at 525 nm.

Another important contribution at larger fields is due to the anisotropy of the magnetic susceptibility. In general, a long molecule has an anisotropy in the magnetic susceptibility in the directions of its length and width. Consequently, such a molecule tends to align along a large magnetic field.15) Surfactant molecules are relatively long and flexible. Thus, the thermal turbulence disturbs the alignment of single molecule but it is possible that micelles might align under large fields. It seems from the present results, however, that this alignment effect is negligible below 10 T for such a spherical micelle as is obtained at a low surfactant concentration in the present case.

We also reported the MFEs of the photoreduction of naphthoquinone in a micellar solution.10) In this case, the Δg values of the naphthosemiquinone and alkyl radicals are as large as 0.0016,13) which is much larger than that of the benzophenone ketyl and alkyl radicals. Consequently, the contribution of the ΔgM can be expected for the former reaction. This experiment and the improvement of the measuring system are now in progress.

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