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Paramagnetic Quenching of the Inverted Magnetic Field Effects Observed in the Photoreduction of Decafluorobenzophenone in a Brij35 Micellar Solution

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The inversion of magnetic field effects (MFEs) observed in the photoreduction of decafluorobenzophenone was studied in the absence and presence of a paramagnetic Gd^{3+} ion. The MFEs appearing at both low ($B \leq 2$ T) and high ($2\ T < B \leq 10$ T) fields were simultaneously quenched by the addition of Gd^{3+}. For the present reaction, it is concluded that the inversion of the MFEs is due to the relaxation mechanism.

Magnetic field effects (MFEs) on chemical reactions of radical pairs and biradicals have received considerable attention during the last two decades.[1-3] Recently, we have found anomalous inversions of MFEs on the dynamic behavior of radical pairs generated by hydrogen abstraction of triplet pentafluoroacetophenone[4] and decafluorobenzophenone[5] in Brij35 micellar solutions. It is possible to explain such inversions of MFEs (1) by the relaxation mechanism (RM)[6] through the anisotoropic hyperfine and Zeeman interactions[4] or (2) by a combination of the hyperfine coupling and the relaxation mechanisms (HFCM and RM) in a low field region and the Δg mechanism (ΔgM) in a high field region.[7] From the view point of experiments, however, the mechanism of such inversions of MFEs has not yet been clear. It is noteworthy that a paramagnetic ion can quench the MFEs due to the RM.[8,9] In this paper, we first prove that the inversion of the MFEs observed in the reaction of decafluorobenzophenone ($(C_6F_5)_2CO$) in a Brij35 micellar solution is not due to the ΔgM but due to the RM.

In the absence and presence of a gadolinium ion (Gd^{3+}) as a paramagnetic quencher, laser flash photolysis (266 nm) was performed at room temperature on a degassed Brij35 (5.0×10^{-2} mol dm^{-3}) micellar solution containing $(C_6F_5)_2CO$ (5.0×10^{-5} mol dm^{-3}). In the present system, the following reaction has been believed to occur:[5]

$$(C_6F_5)_2CO \xrightarrow{h\nu\ (266\ \mathrm{nm})} {}^3(C_6F_5)_2CO^* \tag{1}$$

$${}^3(C_6F_5)_2CO^* + RH\ (\mathrm{Brij35}) \longrightarrow (C_6F_5)_2COH\bullet + R\bullet \tag{2}$$

Here, ${}^3(C_6F_5)_2CO^*$ and $(C_6F_5)_2COH\bullet$ represent the triplet excited state of decafluorobenzophenone and decafluorobenzophenone ketyl radical, respectively. RH is a hydrogen donor which is a micellar molecule. R• is an alkyl radical ($-O\dot{C}HCH_2-$) generated from RH. The transient absorption bands of $(C_6F_5)_2COH\bullet$ was observed at 280-340 and 450-550 nm.[5]

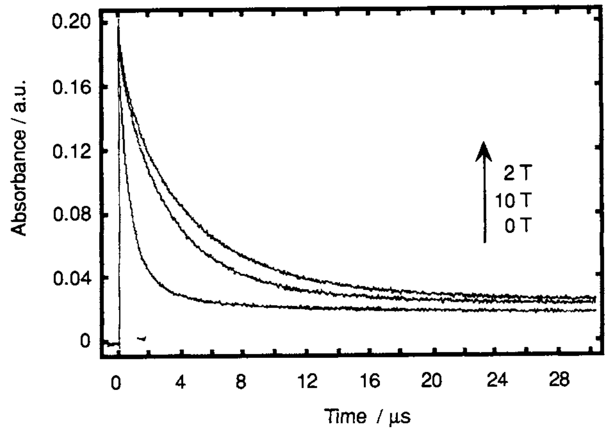

Fig. 1. A(t) curves observed at 320 nm in the absence of Gd^{3+} under magnetic fields of 0, 2, and 10 T for the Brij35 micellar solution of $(C_6F_5)_2CO$.

Time profiles of the transient absorption (A(t)) were measured at 320 nm in the absence and presence of Gd^{3+} under magnetic fields of 0-10 T. Some typical curves obtained at 320 nm are shown in Fig. 1. The A(t) curves had fast and slow decay components. In comparison with the results reported in the previous paper,[4] the fast component corresponds to the radical pair decay and the slow component to the yield of the escaped radicals. We can see from Fig. 1 that the A(t) curves are appreciably changed by the magnetic fields. The escaped yield of $(C_6F_5)_2COH\bullet$ increased with increasing magnetic field (B) in a low field region ($B \leq 2$ T), but decreased again with increasing B in a high field region ($2\ T < B \leq 10$ T). Because the lifetime of the fast component is within a range of 2.7-5.0 μs, the A(20 μs) / A(0 μs) ratio (=Y) can safely represent the relative yield of the escaped $(C_6F_5)_2COH\bullet$ at t = 20 μs. Thus, we can see that the Y(B T) / Y(0 T) ratio (= R(B)) can give the MFE on the yield of the escaped radical. The R(B) values obtained in the absence and presence of Gd^{3+} are plotted in Fig. 2.

In the absence of Gd^{3+}, as shown in Fig. 2, the R(B) value increases steeply with increasing B in the low field region ($B \leq 2$ T), but decreases gradually with increasing B in the high field region ($2\ T < B \leq 10$ T). We can clearly see from this figure that the magnetically induced increases in R(B) observed at low and

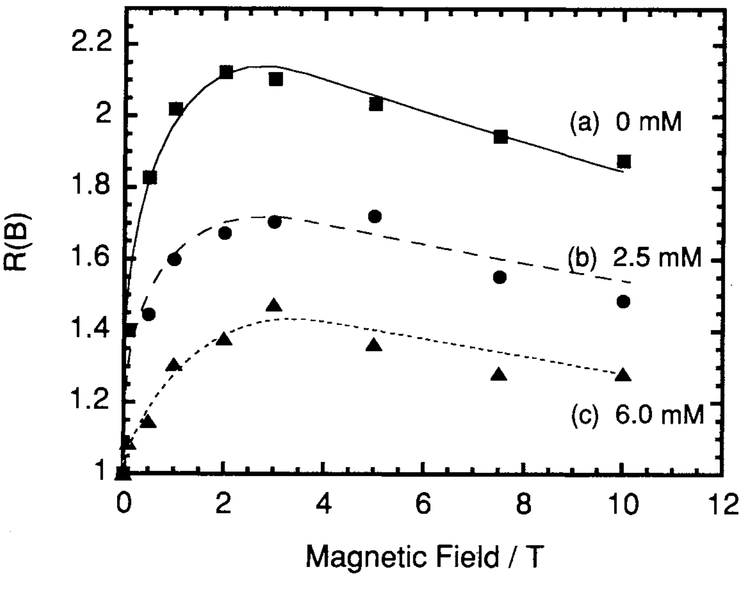

Fig. 2. Magnetic field dependence on the relative yield (R(B)) of the escaped $(C_6F_5)_2COH\bullet$ observed at 320 nm under the magnetic field region of 0-10 T for the Brij35 micellar solution of $(C_6F_5)_2CO$ in the absence (a) and presence of Gd^{3+}; (b) 2.5×10^{-3} mol dm^{-3} (c) 6.0×10^{-3} mol dm^{-3}. The standard deviations of R(B) values are within ± 0.03.

high fields decrease with increasing Gd^{3+} from 0 to 6.0 x 10^{-3} mol dm^{-3}. The MFEs observed in both low and high field regions are simultaneously quenched by the addition of Gd^{3+}. Since the R(B) values at various Gd^{3+} concentrations (0-6.0 x10^{-3} mol dm^{-3}) reached their maximum values at 2-3 T, the ratio R(10 T) / R(3T) gives a degree of the inverted MFEs. If the MFEs observed in both low and high field regions are due to the same mechanism, the R(10 T) / R(3 T) ratio should not be influenced by Gd^{3+}. On the other hand, as described in the previous paper,7) the R(10 T) / R(3 T) ratio increases with increasing Gd^{3+}, when the MFEs are ascribable to a combination of the RM (low field) and the ΔgM (high field). The obtained R(10 T) / R(3 T) ratios are listed in Table 1. Although the magnetically induced increase in R(B) at each field decreases with increasing Gd^{3+}, Table 1 shows that the degree of the inverted MFEs is not influenced by the addition of Gd^{3+}. This fact indicates that the MFEs observed in the low and high field regions should be explained by the same mechanism.

When we used a diamagnetic Lu^{3+} ion of 6.0 x 10^{-3} mol dm^{-3} for comparison, the obtained MFEs were similar to those observed in the absence of Lu^{3+} (or Gd^{3+}). This means that the MFEs are not influenced by the addition of Lu^{3+}. We can conclude, therefore, that the reduction of the MFEs by Gd^{3+} is not due to ionic effects but due to paramagnetic effects. These paramagnetic Gd^{3+} ions would enhance the $T_{\pm 1}$-T_0 (or S) relaxation of the electron spins in triplet radical pairs as proved in the previous papers.8,9)

Table 1. The degree of the inverted MFEs, R(10 T) / R(3 T), observed in the absence and presence of Gd^{3+}

Conc. of Gd^{3+} a)	R(10 T) / R(3 T)b)
0	0.88
1.0	0.86
2.5	0.90
6.0	0.90

a) in 10^{-3} mol dm^{-3}. b) The standard deviations of R(10 T) / R(3 T) ratios are within ± 0.05.

The MFEs observed in the low and high fields are ascribable to the RM from the following reasons: (1) As mentioned above, the MFEs observed in the low and high fields should be explained by the same mechanism. (2) The MFEs due to the ΔgM cannot be quenched by a small amount of paramagnetic ions,7) but the MFEs due to the RM can be removed with the addition of Gd^{3+}.8,9) (3) For the generated radical pair of $(C_6F_5)_2COH\cdot$ (g=2.0032)5) and $R\cdot$ ($-O\dot{C}HCH_2-$; g=2.0033),10, 11) Δg value is almost zero (=0.0001). In conclusion, we first proved experimentally that the inversion of the MFEs observed in the reaction of decafluorobenzophenone ($(C_6F_5)_2CO$) in Brij35 is not due to the ΔgM but due to the RM. The present MFEs can be interpreted by the RM through the anisotoropic hyperfine and Zeeman interactions as explained in the previous paper.4) Further studies on the paramagnetic effects on the MFEs of the radical pair decays are also in progress.

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