

Magnetic Field Effects on Photoreduction Reaction of 2-Methyl-1,4-Naphthoquinone in Brij 35 Micellar Solution with Additional Radical

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A study was made of magnetic field effects (MFEs) on the photoreduction reaction of 2-methyl-1,4-naphthoquinone (MNQ) in Brij 35 micellar solution containing 4-lauroylamino-TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl) radical (L-R•) under magnetic fields below 1.75 T by a nanosecond laser flash photolysis technique. The triplet MNQ mainly underwent the hydrogen abstraction from Brij 35 molecule to give a radical pair. The escaped radical yield increased with magnetic fields from 0 to 0.62 T and then saturated from 0.62 to 1.75 T. MFEs for both systems can be explained by the relaxation mechanism. However, it was supposed that additional radical, L-R• affected the MFEs mainly through enhancing the spin-spin interactions of radical pairs. The effect of the micelle size on MFEs of the studying system was also discussed.

Keywords magnetic field effects, micellar solution, 2-methyl-1,4-naphthoquinone, laser photolysis

Introduction

In the past three decades, many groups have been concerning and studying magnetic field effects (MFEs) on photoreduction reaction of carbonyl compounds such as benzophenone, benzoquinone and anthraquinone derivatives in micellar solutions. The radical pair lifetime and the escaped radical yield increased with the increase of magnetic field strength. The observed MFEs for these systems could be successfully explained by the relaxation mechanism (RM), where the spin relaxation due to the anisotropic g -factor, hyperfine and dipole-dipole interactions play important roles.¹⁻⁴ Reactions taking place in micellar solutions are of special interest since they show both very large and quite unusual dependence on the strength of an external magnetic field.⁵

In our previous paper,⁶ the photoexcited triplet of 2-methyl-1,4-naphthoquinone (MNQ) in SDS (sodium dodecyl sulphate) micellar solution containing 4-lauroylamino-TEMPO radical (L-R•) was studied, and MFEs studies showed that the effects of the presence of L-R• on the photoreduction of MNQ in SDS micellar solution were attributed not only to the enhancement of the spin relaxation of the radical pair (RP) but also to the occurrence of additional chemical reactions. In the present study, we investigated the photoreduction reaction of MNQ in Brij 35 (polyoxyethylene (35) lauryl ether) micellar solution containing L-R• radical. Our aim was to understand how MFEs change in Brij 35 system and how the micelle itself affects MFEs, and

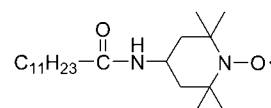
also to make sure that the presence of additional radical truly affects the spin relaxation of the radical pairs (RPs) and spin dynamic behavior of RPs in this photoreduction process.

Experimental

Materials

MNQ was recrystallized from benzene and heptane (1 : 1, V/V). Brij 35 was used as received. 4-Lauroylamino-2,2,6,6-tetramethyl piperidine-1-oxyl (L-R•, Scheme 1), was prepared from lauroyl chloride and 4-amino-TEMPO in anhydrous benzene in the presence of pyridine under nitrogen atmosphere. The structure of L-R• was confirmed by IR and ¹H NMR (300 MHz, in CDCl₃). Steady-State ESR measurement showed that L-R• was stable in micellar solution. Distilled water was obtained from Cica-Merck and purified in Iwaki UP-100 ultrapure water system by ion exchange and ultrafine filtering.

Scheme 1



Apparatus

Laser flash photolysis experiments were performed

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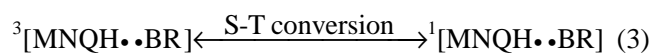
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at 298 K. The third (355 nm) harmonic of a Quanta-Ray GCR-103 Nd : YAG laser was used as the excitation light source. The concentrations of MNQ, L-R•, and Brij 35 were 3×10^{-4} , 1×10^{-4} mol•L⁻¹ and 5% (wt), respectively. Under these concentrations, the absorbance of L-R• at 355 nm is negligible compared with that of MNQ. Distilled water was carefully deoxygenated by bubbling with nitrogen for at least 30 min before making up solutions, and all micellar solutions were made by sonication. Each of the sample solutions was stored under a nitrogen atmosphere during experiments, and the solutions flowed through an optical quartz cell. The magnetic fields (0–1.75 T) were generated by a Tokin SEE-10W electromagnet. The other experimental conditions were similar to those described elsewhere.⁶⁻⁸

Results and discussion

Photochemical reaction scheme

In the case of MNQ in Brij 35 micellar solution, the reaction scheme can be represented as follows:⁹⁻¹¹



where, ISC means intersystem crossing, ${}^1\text{MNQ}^*$ and ${}^3\text{MNQ}^*$ represent the singlet and triplet states of MNQ, BRH denotes a micellar molecule, and ${}^1[\]$ and ${}^3[\]$ are the singlet and triplet radical pairs, respectively.

In order to clarify the photochemical reaction process of MNQ in Brij 35 micellar solution containing L-R• (MNQ/L-R•/Brij 35 system), we measured the transient absorption spectra of laser excitation of this system and those of the sample without L-R• (MNQ/Brij 35 system) under the same conditions.

Figure 1 (a, b) shows the typical spectra obtained at different delay time after excitation of MNQ/L-R•/Brij 35 and MNQ/Brij 35 systems, respectively. The spectra observed for these systems showed similar features. The absorption peak at 370 nm observed at 80 ns after excitation was assigned mainly to the T-T absorption^{12,13} of ${}^3\text{MNQ}^*$ and the absorption band of MNQH• also contributed to it.⁹ The absorption band around 410 nm, assigned to the absorption of MNQH•, was observed in either of the systems. These results indicated that the

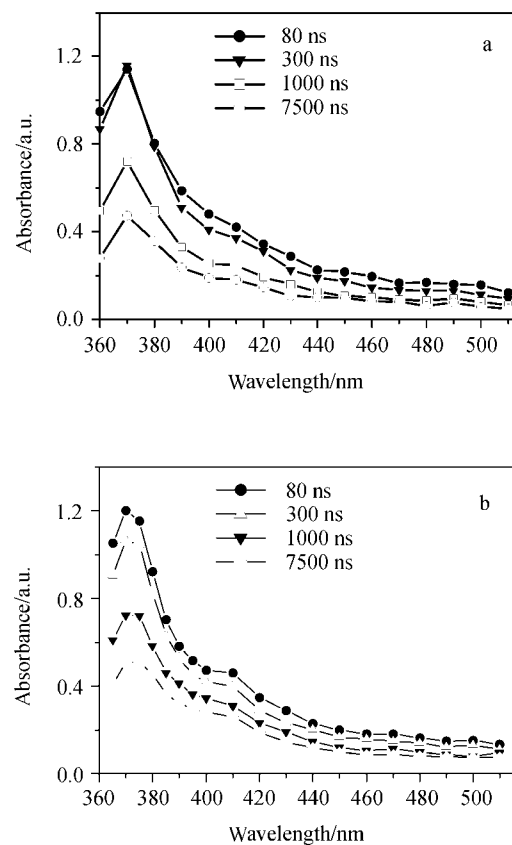


Figure 1 Transient absorption spectra observed for (a) MNQ/Brij 35 and (b) MNQ/L-R•/Brij 35 after various delay time following laser excitation in the absence of a magnetic field (0 T).

H-abstraction of ${}^3\text{MNQ}^*$ yielding MNQH• took place as the major reaction process in MNQ/L-R•/Brij 35 system, as in MNQ/Brij 35. We could also observe that the absorption peak at 410 nm was formed very quickly after laser excitation for MNQ/L-R•/Brij 35 system, and a little difference from that for MNQ/Brij 35 system, which implied that H-abstraction of ${}^3\text{MNQ}^*$ yielding MNQH• was due to not only the reaction of ${}^3\text{MNQ}^*$ with Brij 35 but also the reaction of ${}^3\text{MNQ}^*$ with L-R•. It was possible that L-R• is much more oxidative than Brij 35.

MFEs on decay kinetics for MNQ/L-R•/Brij 35 system

We reported remarkable MFEs on the decay processes of the RPs for MNQ/SDS system below 1.75 T and successfully explained the observed MFEs in terms of the relaxation mechanism (RM).^{2,6,9} In the present study, we measured MFEs for MNQ/L-R•/Brij 35 and MNQ/Brij 35 systems below 1.75 T.

Figure 2 shows the time profiles of the transient absorbance, $A(t)$ curves, monitored at 380 nm for MNQ/L-R•/Brij 35 system under various magnetic fields. The initial decaying part ($80 \text{ ns} < t < 1 \mu\text{s}$) of each of the $A(t)$ curves represents the absorption of both the RP and the escaped radicals, while the remaining part ($1 \mu\text{s} < t < 15 \mu\text{s}$) corresponds to only that of the escaped ones. With increasing magnetic field strength, the decay of the $A(t)$

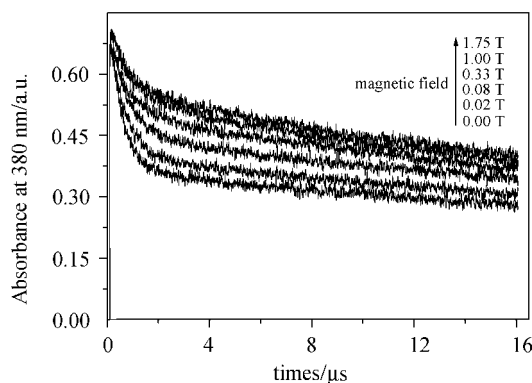


Figure 2 $A(t)$ curves observed at 380 nm for MNQ/L-R•/Brij 35 system under various magnetic fields.

curve became slower and the yield of the escaped radical was increased. The tendency of the field dependence was similar to that observed for MNQ/Brij 35 system.

According to RM theory,^{11,14} the decay curves $A(t)$ of RPs generated in the present reactions in the absence or presence of a magnetic field can be given as follows:

$$B=0\text{ T}; A(t)=A_0\exp(-k_0t) \quad (6)$$

$$B > 0\text{ T}; A(t)=A_f\exp(-k_f t)+A_s\exp(-k_s t)+C \quad (7)$$

The decay rate constant (k_0) at zero field and the fast (k_f) and slow ones (k_s) are represented by:

$$k_0=(k_{\text{rec}}/4)+k_{\text{esc}} \quad (8)$$

$$k_f=k_{\text{rec}}/2+k_s \quad (9)$$

$$k_s=k_r+k_r'+k_{\text{esc}} \quad (10)$$

Here, k_f and k_s correspond to the short-lived (fast decay) and long-lived (slow decay) components of RPs, respectively; k_{rec} is the recombination rate constant; k_r and k_r' are spin relaxation rate constants between $T_{\pm 1}-T_0$ and $T_{\pm 1}-S$, respectively; and k_{esc} is the escape rate constant of RPs.

From Eqs. (6)–(10), and according to the method given by reference,¹⁵ we could determine the related rate constants for MNQ/L-R•/Brij 35 and MNQ/Brij 35 systems, which are listed in Table 1.

MFEs were observed on the yields of the escaped radicals (Y_{esc}). Judging from the $A(t)$ curves shown in Figure 2, it was supposed that the absorbance at 380 nm at $t > 15.0\ \mu\text{s}$ was mainly due to the escaped MNQH•.

Table 1 Rate constants for the processes of RPs obtained for MNQ/L-R•/Brij 35 and MNQ/Brij 35 systems at 298 K

Rate Constants	MNQ/L-R•/Brij 35 (MNQ/Brij 35)	MNQ/L-R•/SDS (MNQ/SDS)
$k_0/(10^6\ \text{s}^{-1})$	1.24 (1.6)	4.69 (4.18)
$k_{\text{Esc}}/(10^5\ \text{s}^{-1})$	3.27 (3.93)	9.3 (6.7)
$k_{\text{rec}}/(10^6\ \text{s}^{-1})$	3.65 (4.83)	15 (14)

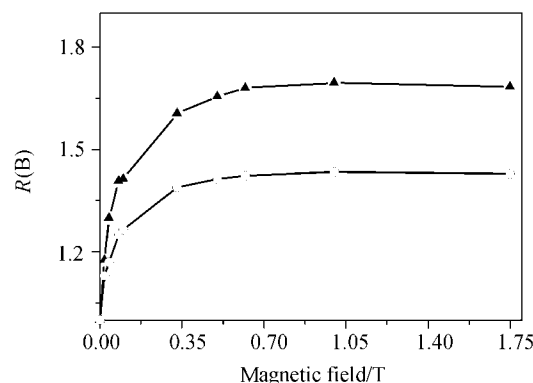


Figure 3 Magnetic field dependence of the escaped radical yields, $R(B)=A_{380}(15\ \mu\text{s}, B)/A_{380}(15\ \mu\text{s}, 0)$ obtained for \circ , MNQ/L-R•/Brij 35 and \blacktriangle , MNQ/Brij 35.

The $R(B) [A_{380}(15.0\ \mu\text{s}, B)/A_{380}(15.0\ \mu\text{s}, 0\ \text{T})]$ value was used to present the magnitude of the MFEs on the Y_{esc} values. Here, $A_{380}(15.0\ \mu\text{s}, B)$ and $A_{380}(15.0\ \mu\text{s}, 0\ \text{T})$ are the absorbance values at 380 nm measured at $t=15.0\ \mu\text{s}$ in the presence and absence of a magnetic field of B , respectively. Figure 3 showed the magnetic field dependence of the $R(B)$ values for MNQ/L-R•/Brij 35 and MNQ/Brij 35 systems. The $R(B)$ were values increased with increasing B from 0 to 0.62 T, and then MFEs were almost saturated from 0.62–1.75 T for both the systems.

Mechanism of the MFEs observed for MNQ/L-R•/Brij 35 system

The characteristic features of the MFEs observed for MNQ/L-R•/Brij 35 system were summarized as follows: (i) The field dependence of the RP and $R(B)$ values was quite similar to that observed for MNQ/Brij 35 system. Based on this similarity, the MFEs observed for MNQ/L-R•/Brij 35 system were also explained by RM theory, as the case of MNQ/Brij 35.¹⁵ (ii) The magnitude of the MFEs on the $R(B)$ value observed for MNQ/L-R•/Brij 35 system was smaller than that observed for MNQ/Brij 35 system. (iii) MFEs in Brij 35 systems were smaller than that in SDS systems.⁶

Feature (ii) can be understood as follows: the Y_{esc} value at zero field, $Y_{\text{esc}}(0\ \text{T})$, and that in the presence of a magnetic field of B , $Y_{\text{esc}}(B)$, can be expressed by Eqs. (11) and (12), respectively.

$$Y_{\text{esc}}(0\ \text{T}) \approx k_{\text{esc}}/k_0=k_{\text{esc}}/(k_{\text{rec}}/4+k_{\text{esc}}) \quad (11)$$

$$Y_{\text{esc}}(B) \approx (2/3)k_{\text{esc}}/k_s=(2/3)k_{\text{esc}}/(k_{\text{rlx}}+k_{\text{esc}}) \quad (12)$$

On the one hand, because the k_{esc} value for MNQ/L-R•/Brij 35 system is larger than that for MNQ/Brij 35 system, the $Y_{\text{esc}}(0\ \text{T})$ value for the former system is higher than that for the latter one. On the other hand, in the presence of a magnetic field of B , the larger the k_{rlx} value for MNQ/L-R•/Brij 35 system is, the lower the $Y_{\text{esc}}(B)$ value is, which is lower than that for MNQ/Brij

35 system. Thus, the $R(B)$ [$Y_{\text{esc}}(B)/Y_{\text{esc}}(0\text{ T})=A_{380}(15.0\ \mu\text{s}, B)/A_{380}(15.0\ \mu\text{s}, 0\text{ T})$] value obtained for the former system is lower than that for the latter one.

Feature (iii) could be attributed to the confinement of RPs, and the micelle size and surroundings might affect MFEs of the radical pairs. The size of micelle is different from each other for Brij 35 and SDS. The former micellar size (Brij 35 about 60—100 Å) is larger than that of the latter one (SDS about 10—30 Å).^{16,17} Another reason might be attributed to that SDS micelle is more compatible with MNQ and additional radical than Brij 35 is, so the overall spin-evolution process is very different. Thus, MFEs in Brij 35 system became smaller.

Conclusion

The magnetokinetic method can be used as a tool for investigating MFEs on photo-induced chemical reaction mechanism concerning more than one kind of hydrogen donor/or electron donor. In this experiment, it was believed that several factors can be contributed to MFEs in the Brij 35 system. Firstly, the competition interaction of triplet precursor with other hydrogen donor or electron donors (other than micelle itself) affected the MFEs in the system, and this competition interaction might decrease the RPs lifetime and increase the inter-radical coupling, allowing smaller scope of spin-evolution. Secondly, the confinement of the RPs, and the consequently diffusive motions that affect the overall spin-evolution process are of a different nature from those systems in which only one kind of RPs was generated. Thirdly, through comparison with the MFEs results between Brij 35 and SDS micellar systems, it could be concluded that different micellar cage gave rise to a very different MFEs. Our analysis of the MFEs measured by optical techniques could be affirmed by ODESR (optical-detected ESR) techniques, which

might give the details of RPs generation or degeneration.

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