# Magnetic-Field-Dependent Spin Adduct Yield in the Photoreduction of Naphthoquinones in SDS Micellar Solution

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A spin trapping method was applied to probe the radical pair model in the magnetic-field-dependent photoreduction of naphthoquinones in a SDS micellar solution. In these systems a spin adduct of the SDS radical was detected, and the adduct yield was strongly dependent on the static magnetic field. The magnetic-field-dependent adduct yield varied with spin traps, quinones, and concentrations of the quinones. In addition, quenching of stable nitroxides, added to the system instead of the spin trap, during the photoreduction of a naphthoquinone in a SDS micellar solution was also dependent on the magnetic field. These results were analyzed with a kinetic model of this reaction system. The present method, using ESR spectroscopy with a spin trapping technique, is superior to other methods because with the former method intermediate transient radicals can be accumulated and detected directly under various magnetic fields. Another advantage of our method is that many different kinds of spin traps can be employed to elucidate the detailed behaviors of the transient radicals. A magnetic-field effect for a final product yield.

#### Introduction

Many magnetic-field-dependent chemical reactions have been found in this decade.<sup>1</sup> This magnetic-field dependency of chemical reactions in the liquid phase has been described in terms of the radical pair (RP) model of CIDNP.<sup>2</sup> This magnetic-field dependence in chemical reactions not only has its own relevance to chemistry, but also has the possibility of being applied to some important fields, such as isotopic separation<sup>3</sup> and control of reaction paths to obtain novel products, etc. So that exact knowledge about many magnetic-field-dependent reactions<sup>4</sup> can be obtained and advantage of this interesting phenomenon can be made, it is very important to study the details of the mechanism and to obtain direct experimental evidence for it. Such detailed (and deep) knowledge about the phenomenon would be a guide for the design of reaction systems which are highly dependent on magnetic fields.

Many kinetic studies<sup>5</sup> with flash photolysis have been undertaken, and valuable kinetic data with transient radicals were obtained. Time-resolved ESR methods, although the magneticfield dependence cannot be obtained, were also applied to detect and identify the transient species during (magnetic-field-dependent) reactions.<sup>6</sup>

In the present study,<sup>7</sup> we applied a spin-trapping technique<sup>8</sup> to detect transient radicals as functions of the magnetic field. With this method, transient unstable radical intermediates are converted and accumulated as stable nitroxide radicals which can be observed afterward. The advantages of this method are the following: (1) Transient radicals, which are difficult to detect and identify because of their low concentrations and because their absorptions lie in an undetectable range and/or in an absorption range of other molecules for other techniques such as UV spectrophotometry, can be directly detected and identified for the reactions under the various magnetic fields. (2) By use of different kinds of spin traps under different conditions, detailed information about these transient species can be obtained. (3) A very large magnetic field effect can be obtained (in this study more than 300% of the magnetic field effect in the spin-adduct yield was obtained), and this method is promising for the application of these magneticfield-dependent reactions as a preparative method to other fields such as isotopic separation, etc.

In our study, spin traps are required to be water-soluble and photostable, and it is prefered to use multiple spin traps. Most spin traps are classified as nitrones or nitroso compounds. A number of nitrone traps had been synthesized with hydrophilic or amphiphilic character<sup>8</sup> and used widely. The ESR spectra of nitrone spin adducts are generally less informative than those obtained by nitroso spin traps.<sup>9</sup>

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On the other hand, to our knowledge only three water soluble nitroso compounds are known, i.e., an aliphatic spin trap, 2-(hydroxymethyl)-2-nitrosopropane (HMNP),<sup>10</sup> and aromatic spin traps, 3,5-dibromo-4-nitrosobenzenesulfonate as well as its deuterio analogue<sup>9</sup> and perdeuterio-2,4-dimethyl-3-nitrosobenzenesulfonate (DMNS).<sup>11</sup> HMNP like 2-methyl-2-nitrosopropane (MNP), which is slightly soluble in water, is very sensitive to visible light.<sup>9</sup> DMNS is a photostable spin trap like nitrosodurene which is also characterized by its wide scattering of  $\beta$ -hydrogen splitting constants and its high trapping rate constants with alkyl radicals.<sup>12,13</sup> We chose phenyl-tert-butylnitrone (PBN), which is the most widely used nitrone trap, and DMNS, which is an interesting nitroso spin trap as mentioned above.

Yields of the spin adducts during the photoreduction of menadione (MD; 2-methylnaphthoquinone, vitamine  $K_3$ ) and naphthoquinone (NQ) were determined, and magnetic-field dependences of the yields (of the spin adducts of the SDS radical) under various conditions are described in detail. A kinetic analysis was also performed based on a reaction mechanism. In addition, taking advantage of the fact that stable nitroxide radicals react with transient species during a reaction,<sup>14</sup> we observed the magnetic-field-dependent life spans of several nitroxide radicals during the photoreduction of these quinones. The yields of the spin adducts of the SDS radical and the decay rates of the stable nitroxide radicals under many conditions could be explained systematically with a kinetic model and with the dynamic properties of a micelle and the solubilized reactant molecule.

#### **Experimental Section**

Naphthoquinone (NQ) was obtained from Wako Pure Chemicals (Osaka, Japan) as a guaranteed grade reagent and recrystallized twice from ethanol. Menadione (MD) was used as supplied from the same company. Sodium dodecyl sulfate (SDS) was obtained from Nakarai Chemicals (Kyoto, Japan) as electrophoresis grade. Phenyl-tert-butylnitrone (PBN) was purchased from Aldrich Chemicals (Milwaukee, WI) and spin labels, i.e. 2,2,5,5-tetramethylpiperidine-1-oxyl-4-ol (TEMPOL), 2,2,5,5tetramethylpiperidine-1-oxyl (TEMPO), 5-doxylstearic acid (5-SAL), and 12-doxylstearic acid (12-SAL) were purchased from Syva Corp. (Palo Alto, CA). All these latter chemicals were used without further purification. Perdeuterio-2,4-dimethyl-3nitrosobenzenesulfonate (DMNS) was synthesized.<sup>11</sup>

The sample solutions were made by dissolving these reagents in a 50 mM phosphate buffer (90 mM NaCl, 50 mM sodium phosphate, pH 7.4). The concentration of SDS was 0.4 M unless otherwise specified. The sample solution was deaerated by flushing with humidified nitrogen gas for more than 1 h with stirring. The sample solution was charged into a quartz flat cell in the ESR cavity as described in the preliminary report<sup>7</sup> and photolyzed with a ultrahigh-pressure mercury lamp (UH-500D, Ushio, Tokyo, Japan) with a CuSO<sub>4</sub> filter (3 g of CuSO<sub>4</sub>·5H<sub>2</sub>O in 10 mL of  $H_2O$ ), which cut the UV light 50% at 330 nm and 90% at 320 nm.



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Figure 1. ESR spectra (X-band, at 338 mT) of the spin adduct in the photoreduction of MD (0.10 mM) in SDS micellar solution with either PBN (A) or DMNS (B) as the spin trap under a magnetic field of 500 (upper) or 7.5 mT (lower).

ESR spectra were obtained with a ESR spectrometer (E-3, Varian, Palo Alto, CA) at room temperature  $(21 \pm 1 \text{ °C})$ . The absolute concentration of spin adducts were determined by comparing the double integrated area of the spectra with that of a standard sample solution which was made by dissolving purified TEMPO in the 0.4 M SDS micellar solution. Magnetic-field strength was calibrated with an aqueous solution of  $K_2(SO_3)_2NO$ (Fremy's salt) buffered with 50 mM  $K_2CO_3$ .<sup>16</sup>

UV spectra were recorded after photoirradiation in various magnetic fields as follows. The sample solution was put into a UV cell (quartz, light path 1.0 cm) and deaerated by bubbling humidified nitrogen and then sealed. The UV cell with the sample solution was placed in a sample holder, whose temperature was kept at 37 °C, and irradiated in a magnetic field. After photolysis in the magnetic field, the UV spectra were observed with a UVvisible spectrophotometer (type-124, Hitachi, Tokyo, Japan), whose sample holder was also kept at 37 °C.

#### **Results and Discussion**

I. Spin Adduct Yield. Figure 1A shows the ESR spectra of the spin adduct obtained during the photoreduction of MD in a SDS micellar solution in the presence of PBN as the spin trap. The ESR pattern is the same as that in the photoreduction of NQ and has been already assigned to the adduct of the SDS radical (with PBN as the spin trap) in a preliminary report.<sup>7</sup> The yield of this spin adduct was very much dependent on the magnetic field under which the (simultaneous) photoirradiation was made, but the ESR pattern was not dependent on the magnetic field as shown in the figure. Figure 1B shows the ESR spectra of the spin adduct of the SDS radical in the same reaction in the presence of DMNS as the spin trap.<sup>7</sup> The hyperfine coupling constants (hfc's) for  $^{14}$ N and  $^{1}$ H are 1.470 ± 0.010 and 0.949 ± 0.026 mT (1 T = 10<sup>4</sup> G), respectively, and the g factor of the radical is 2.0059. These values are similar in magnitude to those of the alkyl spin adducts reported by Konaka and Sakata.<sup>11</sup>

Figure 2 shows the magnetic-field-dependent yields of the spin adducts of the SDS radical in the photoreduction of NQ (left) and MD (right), respectively, with the two spin traps, PBN (A) and DMNS (B). These two graphs indicate that the magnetic



Figure 2. Magnetic-field dependence of the spin adduct yield ( $C_{adduct}$ ) in the photoreduction of NQ (left) and MD (right) in a SDS micellar solution with a spin trap of either PBN (A, 17 mM) or DMNS (B, 1.0 mM). Both the concentrations of NQ and MD were 0.10 mM. Three independent and random ordered observations were made at each magnetic field ( $B_0$ ), under which the UV irradiation was made. Averaged values and standard errors are shown.



Figure 3. Magnetic-field dependence of the spin adduct yield ( $C_{adduct}$ ) in the photoreduction of MD (0.10 mM) in isopropyl alcohol with PBN (17 mM) as the spin trap. Three independent and random ordered observations were made at each magnetic field ( $B_0$ ), under which UV irradiation was made. Averaged values and standard errors are shown.

field modifies the yield to a larger extent in the case of MD than in the case of NQ. It is also evident that, in both reaction systems, the magnetic-field effects in the spin adduct yields are larger with DMNS than with PBN. It is noteworthy that the magnetic-field effect in the spin adduct yield exceeds 300% for the system containing MD and DMNS.

Figure 3 shows the spin adduct yield in the photoreduction of MD in isopropyl alcohol in the presence of PBN as the spin trap, at various magnetic fields. The hfc's of the adduct (with PBN as the spin trap) are 1.54 and 0.36 mT for <sup>14</sup>N and <sup>1</sup>H ( $\beta$  proton from the NO group), respectively. These parameters are in good agreement with the values in the literature<sup>17</sup> for the spin adduct (with PBN) of the isopropyl alcohol radical in the same (solvent) alcohol. Although the reaction begins with the abstraction of a hydrogen from the solvent by the excited NQ in the triplet state, in the same manner as the reaction in the SDS micellar solution, no magnetic field effects on the yield of the spin adduct were observed in this case. Therefore, the observed magnetic field effect on the spin adduct yield of the reaction in SDS micellar solution should be due to the radical pair interaction in the micelle and not to other factors (common to the systems both in SDS micellar solution and in isopropyl alcohol) such as a change in the yield of the excited quinone in the triplet state.

Sakaguchi et al.<sup>18</sup> observed semiquinones in the photoreduction of naphthoquinones in a SDS micellar solution and found a quite similar dependence on the magnetic field in the semiquinone decay kinetics. Since in our case the concentration of the SDS radical was monitored, these results, Sakaguchi's and ours, complement each other. Because there may be no magnetic field dependence in the spin-trapping process, these observations shown in Figures 2 and 3 are solid evidence for the hypothesis that the free radical intermediates form pairs, and the yield of the product within the pair (cage product) is varied by the magnetic field through the magnetic interaction between the pairing radicals. Many magnetic-field-dependent reactions have been explained with the radical pair interaction between a radical from the photosensitizer and the SDS radical.<sup>4i,5a-d,h,i,k,18</sup> However, it was difficult to detect the SDS radical at various magnetic fields.

Recently, it was found that microwave irradiation at particular magnetic fields reduces the spin adduct yield.<sup>19</sup> This reduction in the spin adduct yield as the function of the static magnetic field revealed the ESR patterns of the SDS radical and the semiquinone (protonated) radical, i.e., the microwave field induces the transition between the triplet and the singlet levels of the radical pair, and the spin adduct yield is modified by this extra kinetic process. This also reinforces the radical pair model.

*II. Reaction Mechanism.* To discuss further the magnetic-field dependence of the above reaction, we postulate the following reaction scheme based on the literature:<sup>18</sup>

$$NQ \rightarrow {}^{1}NQ^{*} \rightarrow {}^{3}NQ^{*}$$
(1)

$$^{3}NQ^{*} + SDS \rightarrow ^{3}(NQH \cdot SDS) \xrightarrow{k_{ISC}} ^{1}(NQH \cdot SDS)$$
 (2)

$$^{3}(NQH \cdot SDS) \xrightarrow{k_{E}} NQH \cdot + SDS \cdot$$
 (3)

$$^{1}(NQH \cdot SDS) \xrightarrow{r_{p}} cage product$$
 (4)

$$T-NO + \cdot SDS \xrightarrow{\kappa_T} T(SDS)N-O.$$
 (5)

Naphthoquinone (NQ; we use this symbol both generically and specifically) is promoted to the excited triplet state ( ${}^{3}NQ^{*}$ ) by UV irradiation via the excited singlet state (reaction 1).  ${}^{3}NQ^{*}$  abstracts a hydrogen atom from a SDS molecule, and the triplet radical pair composed of protonated semiquinone (NQH\*)<sup>6,19</sup> and the SDS radical (SDS\*) is formed. This triplet radical pair is converted to the singlet radical pair and vice versa (reaction 2). One or both of the component radicals of the radical pair escape from the triplet radical pair (reaction 3). Cage products are formed through the singlet radical pair (reaction 4). The spin trap TNO captures a SDS radical, and the spin adduct T-(SDS)NO\* is formed (reaction 5). Because the concentration of

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Figure 4. Time course of the ESR signal growth of the spin adduct during the photoreduction of MD (0.10 mM) in a SDS micellar solution with the spin trap DMNS (1.0 mM), at a magnetic field of 38 (top) or 338 mT (bottom). These are well approximated as a function of  $S = S_0(1 - \exp(-t/\lambda))$  with the time constants ( $\lambda$ ) of 22.4 and 27.4 s for the top and the bottom, respectively. In the case of low-field observation, averaged values and standard errors of three independent observations at each magnetic field are shown.

SDS is almost constant, and the light intensity is constant, we can set one kinetic constant to the production of the triplet radical pair. Thus

$$NQ \xrightarrow{\gamma} {}^{3}(NQH \cdot {}^{5}SDS)$$
(6)

In this reaction, NQ is partly recovered by both the disproportionation of the (protonated) semiquinone and the reaction between the radicals in the singlet radical pair (we pay attention to this process separately among the several cage product formations).

$${}^{1}(\text{NQH} \cdot \text{SDS}) \xrightarrow{k_{\text{rec}}} \text{recovery of NQ}$$
(7)

$$2NQH \xrightarrow{k_{D}} NQ + NQH_{2}$$
(8)

Assuming steady-state conditions for the transient species, we obtain the following equations (see Appendix) for the concentration of quinone in the present simplified reaction system:

$$[NQ] = [NQ_0] \exp(-\xi t)$$
(9)

$$\xi = (y - k_{\rm rec}q - k_{\rm E}p/2) \tag{10}$$

where p and q represent the ratios of the steady-state concentrations of triplet and singlet radical pairs to the concentration of NQ, respectively (i.e.  $[{}^{3}\text{RP}] = p[\text{NQ}]; [{}^{1}\text{RP}] = q[\text{NQ}]).$ 

According to reaction 5, the differential equation for the production of the spin adduct may be written as

$$d[TRNO^{\bullet}]/dt = k_{T}[TNO][SDS^{\bullet}] = \Phi k_{E}p[NQ] \quad (11)$$

where  $\Phi$  is the ratio of SDS radicals which are trapped by the spin trap to the total SDS radical which have escaped.

III. Time Course of the Reaction. The time course of the signal growth for the system containing MD and DMNS at two magnetic fields (38 and 338 mT) is shown in Figure 4. Those two curves are approximately expressed in the form  $S = S_0\{1 - \exp(-t/\lambda)\}$  as predicted in eq 9 and 11. The time constants ( $\lambda$ ) are 22.4 s for 38 mT and 27.5 s for 338 mT. This result indicates that the photoreduction of naphthoquinones proceeds faster at lower magnetic fields. Figure 5 shows changes in the UV spectrum during the course of photoreduction of MD in SDS micellar solution. As seen in Figure 5, the reduction of the absorption at about 340 nm (due to MD) is larger, and the increase of the absorption at about 390 nm (due to the semiquinone<sup>18</sup>) is smaller at the residual magnetic field compared with those at a high magnetic field.



Figure 5. Magnetic-field effects on the UV spectral changes during the photoreduction of MD in a SDS micellar solution at 37 °C: (A) at 2.0 mT, (B) at 80 mT.

Therefore, the kinetic constant for the decrease of quinone ( $\xi$ in eq 10) should be larger at lower magnetic fields. Because *p* becomes larger and *q* becomes smaller when the magnetic field is increased, the recycling process of quinone through the singlet radical pair (eq 7) is considerably smaller than that through the disproportionation process of escaped protonated semiquinone (eq 8). Since disproportionation of the semiquinone anion is usually slow at this pH,<sup>20</sup> the protonated semiquinone which has escaped from the triplet radical pair may be trapped by another micelle and disproportionate at a relatively high rate upon colliding<sup>21</sup> with another protonated semiquinone.

Without the quenching process<sup>22</sup> of the spin adduct by the transient radicals and postulating that a part ( $\Phi$  in eq 11) of the SDS radical is trapped by the spin trap, the concentration of the spin adduct can be expressed by the following equation by integrating eq 11 using eq 9:

$$[TRNO]_{t} = k_{E} p \Phi[NQ_{0}] \{1 - \exp(-\xi t)\} / \xi$$
(12)

The final concentration of the spin adduct ([TRNO<sup>•</sup>] is expressed as eq 13 with the assumption that  $k_p$  dominates other terms.<sup>5a,e,f,j</sup>

$$[TRNO^{\bullet}] = \Phi[NQ_0] / \{1/2 + (k_{ISC}/k_E)\}$$
(13)

Therefore at the maximum  $k_{\rm E}$  and minimum  $k_{\rm ISC}$ , and if there is no loss of SDS radical by the other reactions ( $\Phi = 1$ ), we obtain the spin adduct concentration which is twice the initial concentration of the quinone. Equations 12 and 13 indicate another important relation that the larger the rate  $k_{\rm ISC}/k_{\rm E}$ , the smaller the spin adduct yield, and the larger the recycling of quinone by the disproportionation, the larger the spin adduct yield at infinite magnetic field.

The large difference between the absolute yields of the spin adducts for the two spin traps may be caused by a large difference in  $\Phi$  (in eq 11), i.e. the kinetic constant of the spin trapping process for DMNS is much larger than that for PBN.<sup>13</sup>

*IV. Magnetic Field Dependence of the Spin Adduct Yield. (A) Dependence on Quinone.* Spin adduct formation in the case of MD is more dependent on the magnetic field than in the case of

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 (22) At low concentrations of quinone (10<sup>-4</sup> M), in the presence of a spin

<sup>(22)</sup> At low concentrations of quinone  $(10^{-4} \text{ M})$ , in the presence of a spin trap at high concentrations, the quenching rate is small as evidenced by the time course of the signal (Figure 4). However, with increasing concentration of quinone, the signal decreases after reaching the maximum intensity due to quenching.

NO (Figure 2). Because menadione is not soluble in water but NQ is slightly soluble, the solubility in water of naphthosemiquinone may be larger than that of semiquinone from MD. Therefore the lifetime of the radical pair may be longer, and thus the yield of the spin adduct of the escaped radical is smaller in the case of MD than in the case of NQ. The larger expected rate of  $T_0 - S_0$  mixing in the former case (because  $\sum_i A_i^2 I_i (I_i + 1)$  for semiquinone from MD is larger than that of naphthosemiquinone, where  $A_j$  and  $I_j$  are the hfc and spin quantum number of j'thnucleus of a radical) may be another cause for the smaller spin adduct yield for the MD system at zero field. At high magnetic fields, the spin adduct yield for MD is expected to be smaller than that for NQ for the same reason mentioned above. However, the results shown in Figure 2 contradict this prediction. As mentioned in section III, at a high magnetic field there may be considerable recycling of the quinone from the escaped semiquinone (eq 8). The concentration of the protonated semiquinone of MD in the micelle phase, which disproportionates faster than the semiquinone anion,<sup>21</sup> is larger than that of semiquinone of NQ due to the solubility difference. Therefore, recycling of the parent quinone from the escaped semiquinone for MD may be much larger than that for naphthose miquinone, and thus the final concentration of spin adduct is larger in the case of MD than that in the case of NQ.

(B) Dependence on Spin Trap. The fact that a larger magnetic-field dependence in the spin adduct yield is detected with DMNS than with PBN (Figure 2) can be explained (1) with the difference in the solubilities of these two spin traps in water, and (2) with the assumption that the SDS radical escapes from the micelle, where the radical pair was located, to the aqueous phase. This assumption does not mean that the escaped SDS radical stays in the aqueous phase, but means that (1) the radical pair collapses by either the disruption of the micelle or the escaping of one (or both) of the component radicals, which are then cast into the aqueous bulk phase; (2) the escaped radicals may be captured again in other micelles separately (in most cases) while losing the coherence between the two spins; (3) the escaped radicals may repeat going out from a micelle and being recaptured into another micelle during their lifetime. DMNS which has a sulfonate group is freely soluble in water (and insoluble even in a polar solvent such as isopropyl alcohol), and should be mainly in the aqueous phase where it may capture only the escaped SDS radical. On the other hand, PBN is less soluble in water, and a large part of PBN molecule may be in the micelle phase. Thus, it may trap the SDS radical in both the micelle and the aqueous phases. Because the formation rate of the radical pair is independent of the magnetic field as shown with Figure 3, the formation rate of the SDS radical (which is in the micelle phase at its birth) is also independent of the magnetic field. Therefore, the yield of the spin adduct of the SDS radical captured in the micelle may not be dependent very much on the magnetic field. Thus it is reasonable that the yield of the spin adduct with DMNS, which captures the SDS radical in the aqueous phase, is dependent on the magnetic field to a greater extent than that with PBN.

(C) Qualitative Analysis of the Magnetic-Field-Dependent Yield. Because the  $T_0$ - $S_0$  mixing rate is not very much dependent on the extenal magnetic field if the difference between the g values of the component radicals of radical pair is small as in the present case, the magnetic-field-dependent spin adduct yield can be described qualitatively with the magnetic-field dependence of  $T_{\pm 1}$ - $S_0$ and  $T_{\pm 1}$ - $T_0$  mixings (i.e. those two rates mainly modify the intersystem crossing rate ( $k_{ISC}$ ) with a change of the external magnetic field). The magnetic field dependent part of these mixing rates ( $G(B_0)$ ) has the form (see Appendix):

$$G(B_0) = 1/(\mp 2\delta J + g\beta B_0 + a)^2$$
(14)

where  $a = \sum_{j} (A_j M_j)/2$  ( $M_j$  is the nuclear spin quantum number for the z coordinate of the j'th nucleus) and  $\delta$  is zero or 1 for the  $T_{\pm 1}-T_0$  transition or  $T_{\pm 1}-S_0$  transition, respectively. g and  $\beta$ represent the averaged g factor of the radicals and the Bohr magneton of the electron, respectively. Since this function rapidly falls to zero when  $B_0$  become larger than  $(a \pm 2J)$ ,  $k_{\rm ISC}$  also has



Figure 6. Magnetic field dependence of the spin adduct yield in the photoreduction of MD in SDS micellar solution in the presence of DMNS (1.0 mM) as the spin trap. The concentration of MD were (A) 0.10, (B) 0.33, (C) 0.75, and (D) 1.5 mM. Three independent and random ordered observations were made at each magnetic field  $(B_0)$ , under which the UV irradiation was made. Averaged values and standard errors are shown.

nearly a constant value when  $B_0$  is much larger than  $(a \pm 2J)$ . Because J is nearly zero<sup>19</sup> and the averaged a is about 1.5 mT, the magnetic field modulation of the spin adduct yield at the magnetic fields up to 500 mT (shown in Figure 2) cannot be explained with this model only.

It has been noticed that another mechanism, spin-lattice relaxation, exists for the mixing between those levels.<sup>23</sup> Spin-lattice relaxation has the dependence on the magnetic field as shown in the following equation:

$$G(B_0) = 1 / \{ (1/\tau_r \gamma)^2 + B_0^2 \}$$
(15)

where  $\gamma$  represents the gyromagnetic ratio of the electron spin and  $\tau_r$  is the rotational correlation time of the component radicals of the radical pair, which may be in the range  $10^{-10}-10^{-9}$  s.<sup>24</sup> The correlation time of  $10^{-10}$  s corresponds to 60 mT  $(1/\tau_r\gamma)$  in the above discussion. Thus, the spin adduct yield continue to increase over several hundred gauss if this mechanism really works and if the rotational correlation time of the radicals in the micelle is as short as  $10^{-10}$  s.<sup>24</sup> Although it is difficult to obtain a rotational correlation time of a molecule exactly,<sup>25</sup> using an approximate equation (eq 1 of ref 21) we obtain about  $6 \times 10^{-10}$  s for both cases in Figure 1.  $\tau_r$  for the smaller molecule (semiquinone or SDS radical) may be considerably smaller than this value and the above-mentioned mechanism is quite possible.

Sakaguchi and Hayashi<sup>18</sup> suggested the spin-lattice relaxation of the components of the radical pair may contribute to the  $T_{\pm}-T_0$ and  $T_{\pm}-S_0$  transitions, because the yield of semiquinone of the present system increases steadily even at a field of 1.4 T. We confirmed the same kind of increase in the spin adduct yield as shown in Figure 2.

V. Concentration Dependence. Figure 6 shows the dependence of the spin adduct yield on the magnetic field at various con-

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Figure 7. Lifetimes as a function of magnetic field  $(B_0)$  for various stable nitroxide radicals during the photoreduction of NQ in a SDS micellar solution. The concentration of NQ was 0.33 mM and those of the stable nitroxide radicals were  $3.0 \times 10^{-5}$  M. The intensity of the UV light for the photoirradiation in the system containing TEMPOL or TEMPO was reduced to 1/6 of that in the system containing 5-SAL or 12-SAL. The decay curves could be approximately expressed as  $S = S_0 \exp(t/T)$  (this approximation was good in the initial stage of the reaction), where  $S_0$  and S are the signal intensity at time 0 and time t. Lifetimes were obtained with above equation and S and  $S_0$ .

centrations of MD. At low concentrations (curves A and B), the yield increases steadily with increasing magnetic field. At higher concentration of MD (curve C) the yield initially increases then decreases with increasing magnetic field. When the concentration of MD is increased further, as shown with curve D, the yield decreases monotonously with increasing magnetic field.

This curious dependence of the yield on the magnetic field can be interpreted with the assumption that the spin adduct is quenched by the transient species, e.g. SDS radical and semiquinone radical, during the photoreduction of MD. In fact, when the concentration of MD is low, the concentration of the spin adduct increases approximately in proportion to the concentration of MD (especially at low magnetic field). This fact indicates that at higher magnetic field the concentration of escaped radicals increase and they quench the spin adduct. Essentially the same phenomenon was observed in the photoreduction of NQ in the SDS micellar solution.

VI. Quenching of Stable Nitroxides during the Photoreduction of Naphthoquinone. To know the dynamics of the transient radicals in the photoreduction of naphthoquinones, a stable nitroxide radical was mixed in the reaction system instead of a spin trap. As stable nitroxides, lipid soluble nitroxides (5-SAL and 12-SAL), a water-soluble nitroxide (TEMPOL), and a nitroxide a little soluble in water (TEMPO) were employed. Before this experiment we made certain that the nitroxide radicals are relatively stable against photoirradiation under our experimental conditions. For TEMPO radical, for example, photoirradiation by the same UV source with the same filter for 1 min reduced the radical concentration by only about 0.9%. This decomposition rate is negligible compared with the decomposition rate due to the intermediates of the photoreduction of naphthoquinones (Figure 7).

Figure 7 shows the lifetime (T) of various nitroxides during the photoreduction of NQ in a SDS micellar solution as a function of the magnetic field. For a small nitroxide radical the decay was so rapid that the light intensity was reduced to 1/6 of the original intensity. Interestingly, T is dependent on the magnetic field, and the dependence is larger for water-soluble nitroxides. It is also noteworthy that the concentration of 5-SAL decreases faster than that of 12-SAL.

These results are explained as follows based on the same hypothesis mentioned above: (1) the concentration of the escaped radical is modified by the magnetic field; (2) the component radicals of the radical pair escape into water phase upon decay of the radical pair; (3) then these radicals migrate between the two phases. The rapid decay of the small stable nitroxide radicals may be due to (1) the relatively large solubility in water of these small nitroxides compared with those of fatty acid labels; (2) the large translational diffusion rates of the former radicals than those of the latter; (3) the fact that the radical in the micelle may be protected from the attack of the reactive species.

The faster decay rate for 5-SAL than that for 12-SAL can be explained with the averaged position of the quinone molecule in the micelle; i.e., if the quinone molecule diffuses freely in the micelle (radius r), the averaged radial coordinate is 3r/4 when it abstract a hydrogen from a SDS molecule, thus the coordinate of the radical center of the SDS radical may be also near this value of 3r/4. Because the radical center of 5-SAL is closer to this averaged coordinate of the SDS radical, the life span of 5-SAL may be shorter than that of 12-SAL whose radical center is located near the center of the micelle.

The lifetime of TEMPOL was shorter than that of TEMPO as shown in Figure 7. Because the former is more soluble in the aqueous phase than the latter, this phenomenon also supports our hypothesis that the component radicals of the radical pair go out of the micelle (to the aqueous phase) upon escaping from the radical pair. When PBN is added at a concentration of 20 mM to the above systems, the half-life of the stable nitroxide radicals increased by more than 40% but did not increase further when PBN solution (20 mM, 1.0-cm light path) was used as the filter. This fact indicates that the PBN molecule may trap the SDS radical prior to its reaction with the stable nitroxide, and that the semiquinone radical also quenches the stable nitroxides.<sup>26</sup>

Acknowledgment. Valuable discussions with Prof. E. G. Janzen, Dr. Y. Kotake (University of Guelph), and Dr. H. Taniguchi (Yamaguchi University) are gratefully acknowledged. Sincere thanks also should go to Professor K. Ishizu (Ehime University) for supplying the purified TEMPO. This work was supported in part by a grant from the Ministry of Education, Science, and Culture of Japan.

### Appendix

From the reaction scheme, we obtain differential equations for the chemical species in the system:

$$d[^{3}RP]/dt = y[NQ] - (k_{E} + k_{ISC})[^{3}RP] + k_{REV}[^{1}RP]$$
(A1)

$$d[{}^{1}RP]/dt = k_{ISC}[{}^{3}RP] - (k_{P} + k_{rec} + k_{REV})[{}^{1}RP]$$
(A2)

Under steady-state conditions, those differentials for the transient species, triplet ( ${}^{3}RP$ ) and singlet ( ${}^{1}RP$ ) radical pair, naphthosemiquinone ( ${}^{\bullet}NQH$ ), and SDS radical ( ${}^{\bullet}SDS$ ), with time are negligible compared with the concentrations or the differentials for the other stable species. Thus

$$[{}^{3}RP] = p[NQ]; [{}^{1}RP] = q[NQ]$$
 (A3)

where p and q are given by

 $p = (k_{\rm p} + k_{\rm rec} + k_{\rm REV})y / \{(k_{\rm E} + k_{\rm ISC}) \times (k_{\rm p} + k_{\rm rec} + k_{\rm DEV}) - k_{\rm ISC} k_{\rm DEV}\}$ (A4)

$$q = k_{\rm ISC} y / \{ (k_{\rm E} + k_{\rm ISC}) (k_{\rm p} + k_{\rm rec} + k_{\rm REV}) - k_{\rm ISC} k_{\rm REV} \}$$
(A5)

It is usually assumed that  $k_p$ , the rate for cage-product formation, is much larger than the other rates.<sup>5a,e,fj</sup> Since both  $k_{ISC}$  and  $k_{REV}$ 

<sup>(26)</sup> Hydroquinone also quenches the stable nitroxide radical. However, the rate was slower by more than one order (at a concentration of 0.1 mM) and was neglected here.

decrease with increasing magnetic field, p increases but q decreases at high magnetic fields. From the differential equation for NQH\*, the following equation is derived:

$$[NQH^{\bullet}]^{2} = k_{E}[^{3}RP]/2k_{D}$$
 (A6)

The decrease of NQ is thus described by using eq A3 and A4:

$$d[NQ]/dt = -y[NQ] + k_{rec}[^{1}RP] + k_{D}[NQH^{*}]^{2}$$

$$= -\{y - k_{\rm rec}q - k_{\rm E}p/2\}[{\rm NQ}]$$
(A7)

We propose the following reaction rate for the decay of the SDS radical.

$$d[SDS^{\bullet}]/dt = k_{E}[^{3}RP] - \{W + k_{T}[TNO]\}[SDS^{\bullet}]$$
 (A8)

where W is the decay constant of the SDS radical with other reactions. Using the steady-state conditions for the concentration of the SDS radical and refering the reaction 5, we obtain the differential equation for the spin adduct concentration. Thus

$$d[TRNO^{\bullet}]/dt = k_{E}p[NQ]\{k_{T}[TNO]/(W + k_{T}[TNO])\}$$
$$= k_{E}\Phi p[NQ]$$
(A9)

where  $\Phi$  represents the ratio of the SDS radical trapped by the spin trap.

From the standard perturbation method, the adiabatic transition between the two levels (j - i) is given as follows:<sup>2b</sup>

$$k_{ij} = 1/N \sum_{M'} f\{\sum_{M} H_{ij}^2 / (H_{ii} - H_{jj})^2\}$$
(A10)

Here, f is a function which depends on the dynamical properties of the radical pair and  $H_{ii}$  and  $H_{ij}$  are the matrix elements of the spin Hamiltonian with the usual basis set of  $\{T_1, T_0, T_{-1}, \text{ and } S\}$ , and M, M' represent sets of nuclear state for i and j electron spin state, respectively. N is the number of different nuclear state,  $\Pi^{a}(2I_{i}+1)\Pi^{b}(2I_{i}+1)$ , here  $I_{i}$  and  $I_{i}$  represent quantum numbers of nuclear spins on radical a and b, respectively. Since we do not have the function f for the RP in the micelle phase, we use following equation to obtain qualitative features of the magnetic-field dependence of cage product formation.

$$k_{ij} \propto 1/N \sum_{M'M} \{H_{ij}^2/(H_{ii} - H_{jj})^2\}$$
(A11)

Because in the present system the hfc's (hyperfine coupling constant) are much larger than the difference in the Zeeman energy, we take into account only the hfc's. Because the matrix elements<sup>2b</sup> for the  $T_{\pm}-T_0$  and  $T_{\pm}-S_0$  transitions differ only in their sign, those transition rates are the same except for a small difference in the denominator of (A7), which is given as follows:

$$1/(H_{ii} - H_{jj})^2 = 1/(\mp 2\delta J + g\beta_{\rm e}B_0 + \sum_l A_l M_l/2)^2$$
(A12)

where  $H_{ii}$  represents the energy of the T<sub>±</sub> state and  $H_{ii}$  represents the energy of the  $T_0$  state ( $\delta = 0$ ) or S state ( $\delta = 1$ ).

Registry No. NQ, 130-15-4; SDS, 151-21-3; SDS<sup>•</sup>, 106163-40-0; SDS-DMNS spin adduct, 106163-41-1; SDS-PBN spin adduct, 106191-53-1; MD, 58-27-5; PBN, 3376-24-7; TEMPOL, 2226-96-2; TEMPO, 2564-83-2; 5-SAL, 29545-48-0; 12-SAL, 29545-47-9; DMNS, 106163-42-2.

# Interfacial Tensions and Phase Behavior of Alcohol–Hydrocarbon–Water–Sodium Chloride Systems

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The phase behavior and interfacial tensions of mixtures of alcohol, alkane, water, and sodium chloride that split into two or three liquid phases at 25 °C are reported as a function of type of alcohol and alkane and sodium chloride concentration. The patterns of phase and tension behavior are similar to those observed with surfactant-based microemulsion systems but in a higher tension regime. The qualitative patterns of phase and tension behavior in the alcohol systems appear to be characteristic of all amphiphile-oil-brine systems, although the magnitudes of the interfacial tensions of microemulsion against oil-rich or water-rich phases can be some hundredfold smaller than the corresponding tensions of the alcohol-rich phase against oil-rich or water-rich phases. This difference appears to be a distinguishing feature of microemulsions and presumably arises from the relatively large scale of microemulsion microstructure. Microemulsions in multiphase equilibria incorporate tenfold or more water or oil than do corresponding alcohol solutions, and this argues for the topology and persistence of that microstructure.

### Introduction

Alcohols can solubilize substantial amounts of water and oil together into isotropic solutions.<sup>1-4</sup> Although some such solutions have been referred to as "detergentless microemulsions", 2,5,6 evidence is lacking<sup>1,7,8</sup> that they are, in fact, microemulsions, i.e., isotropic, thermodynamically stable, microstructured fluid phases that contain substantial amounts of two ordinarily immiscible liquids (i.e., water and oil) and surfactants.<sup>9</sup> Microemulsions are association colloids being at low oil to water concentration a swollen micellar solution and at low water to oil concentrations a swollen inverted micellar solution. At comparable oil to water ratios, there is now considerable evidence $^{10-15}$  that some microemulsions are bicontinuous in oil-rich and water-rich regions, as

postulated a decade ago,<sup>16</sup> and that others are concentrated swollen micellar or inverted micellar solutions.<sup>17-19</sup> Monohydric alcohols,

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