Influence of Micelles and Magnetic Isotopes on Magnetic Field Dependence of Lifetimes of Benzophenone Ketyl-Alkyl Radical Pairs

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Influence of micelles and magnetic isotopes on magnetic field dependence of lifetimes of benzophenone ketyl-alkyl radical pairs in micellar solutions was studied below 14 T. The lifetimes were dependent on micelles and independent of isotopes. The lifetimes of radical pairs are controlled by the electron dipole interaction of the radical pairs in < 2 T and by the competition of the *anisotropic* Zeeman interaction and the escape from the micelles in > 4 T.

In high magnetic fields, *anisotropic* hyperfine (δhf) and *anisotropic* Zeeman (δg) interactions and an electron dipole-dipole (dd) interaction modulating spin-lattice relaxation (SLR) of radical intermediates are responsible for magnetic field effects (MFEs) on the lifetimes of radical intermediates.[1] Studies of magnetic isotope effects (MIEs) on MFEs give important information for the interpretation of the MFEs. (1) In benzophenone (BP) ketyl-alkyl radical pairs in micellar solutions, Sakaguchi et al. reported MIEs on MFEs on the decay rates below 0.07 T upon ^{13}C and ^{2}H substitutions in the BP moiety.[2] They used an *isotropic* hyperfine (hf) mechanism for the interpretation. (2) In triplet biradicals formed from BP-CO$_2$-(CH$_2$)$_{12}$-O-diphenylmethane (DPM), Nakagaki et al. have shown large MIEs on MFEs on the biradical lifetimes even above 0.1 T,[1b,3] where not the *isotropic* hf interaction but the δhf, δg, and dd interactions are responsible for the MFEs. At 1.5 T the lifetimes were 9.9 and 7.7 μs in naturally-abundant and ^{13}C-substituted DPMs, respectively, which shows a decrement of 22%. Since the MIEs were observed even at 4 T, they have proved importance of the SLR due to the δhf interaction below 4 T.

In a triplet BP ketyl (BPH)-alkyl radical pair in an aqueous sodium dodecyl sulfate (SDS) solution, Fujiwara et al. demonstrated an enormous increase in lifetimes below 2 T followed by no detectable change in 2-14 T.[4] In comparison with a theoretically-obtained local magnetic field (H_{loc}) modulating the SLR, the δhf interaction due to the BPH and alkyl radicals was tentatively recognized to be responsible for the MFE in 0.1-2 T. In this study, therefore, influence of micelles and magnetic isotopes on the magnetic field dependence (MFD) of the lifetimes in 0-14 T was investigated, and the main deactivation process in each high magnetic field was explored. Especially in 0.1-2 T, which is in main operation, the SLR due to the δhf interaction or that due to the dd one ? If the SLR of the radical pair is controlled predominantly by the δhf interaction due to the BPH radical, an effect of isotope-substituted BPs could be observed.

The radical pairs were produced at room temperature by 355 nm laser irradiation of aqueous micellar solutions of naturally-abundant and ^{13}C-substituted (^{12}C- and ^{13}C-) BPs in their benzylic positions. The micellar solutions were 0.4 mol dm^{-3} SDS, 0.4 mol dm^{-3} hexadecyl trimethylammonium chloride (HDTCl), and 0.1 mol dm^{-3} polyoxyethylene(23) lauryl ether (Brij35). All sample solutions were degassed by several freeze-pump-thaw cycles to remove oxygen.

The reaction scheme in SDS is explained as follows:

$^1\mathrm{BP}^* \xrightarrow{\mathrm{ISC}} {}^3\mathrm{BP}^* \xrightarrow{\mathrm{SDS}} {}^3[\mathrm{BPH}\cdot\cdot\mathrm{SDS}] \longrightarrow \mathrm{BPH}\cdot + \cdot\mathrm{SDS}$
↑ 355 nm ISC ↑ ↓ ←Magnetic Field Effect
BP $^1[\mathrm{BPH}\cdot\cdot\mathrm{SDS}] \longrightarrow \mathrm{BPH\text{-}SDS}$

Upon photoexcitation, the excited triplet state (^{3}BP*) of BP abstracts a hydrogen atom from SDS to generate a triplet radical pair composed of a BP ketyl radical (BPH·) and an alkyl radical (·SDS) formed from SDS. The abbreviation for the alkyl radical in HDTCl is ·HDTCl. The triplet pair ^{3}[BPH··SDS] undergoes intersystem crossing (ISC) to the singlet one ^{1}[BPH··SDS]. A free BPH· is yielded from the triplet pair as a result of escaping from a micellar core. The magnetic field influences the ISC in the radical pair to modulate the rate. Therefore, the radical pair lifetime varies along with the magnetic field intensity.

The MFD of radical pair lifetimes below 14 T was obtained by using a pulse magnet-laser flash photolysis apparatus.[4] The MFD was estimated by analyzing the transient absorption decay profiles of BPH· at 525 nm. All the decay profiles consist of a single-

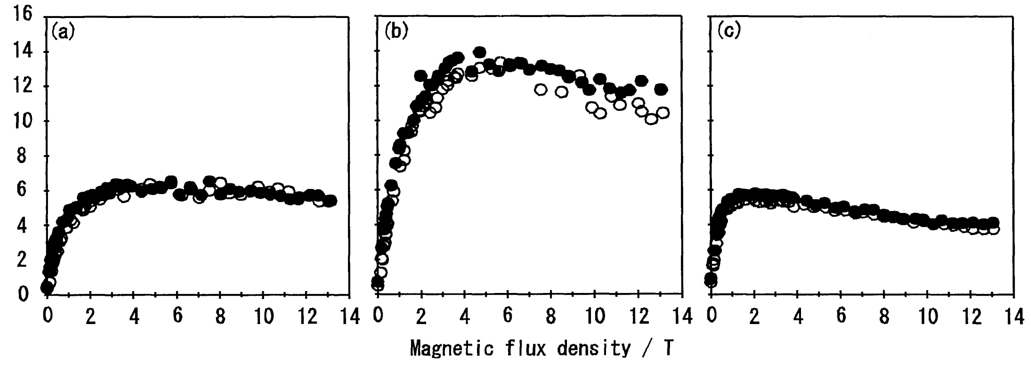

Figure 1. Micelle and magnetic isotope effects on MFDs of radical pair lifetimes derived from ^{12}C- (●) and ^{13}C- (○) BPs in micellar solutions. Surfactants are (a) SDS, (b) HDTCl, and (c) Brij 35, respectively.

exponential decay due to the radical pair and a long-lived component due to the free BPH·. Effects of micelles and isotopes on the MFD of the lifetimes are depicted in Figure 1.

First, let us consider the micellar dependence. The lifetime in SDS increased with increasing the magnetic field to attain to a maximum value of 6.6 μs at 4 T. The value was almost constant in 4-14 T. In HDTCl which has a pure alkyl methylene chain similar to that in SDS, the lifetime also increased up to 14 μs at 4.5 T followed by a slight but definitely detectable decrease at 5-14 T. In Brij35 which has twenty-three CH_2CH_2O units in the chain, the lifetime increased below 2 T and decreased above 2 T. The decrease was more drastic than that in HDTCl. The monotonous decrease extended to *ca.* 70% of the maximum value (5.8 μs). The MFD of a yield of the free BPH· was identical with that of the lifetime in each micelle. These results indicate that the radical pair lifetime is strongly dependent on the micelles.

Secondly, let us consider isotope dependence of the lifetime on ^{12}C- and ^{13}C-BPs. In all the micelles no significant difference between the isotope-substituted BPs was observed, which is contrastive with the large MIE of 22% decrement in the biradical lifetimes, as mentioned above.[1b] These observations apparently demonstrate that the radical pair lifetimes in the micellar solutions are dependent on the micelles, not BPH·.

In 0.1-4 T in SDS and HDTCl and in 0.1-2 T in Brij35 where the radical pair lifetime is increasing, the lifetime is considered to be determined mainly by the SLR due to the δhf and/or dd interactions. The results may suggest that (i) if the δhf interaction is predominant, an H_{loc} value for BPH· can be neglected compared with the value for the alkyl radical and/or (ii) the dd interaction, which is independent of the isotopes, between the component radicals is more effective than the δhf interaction. Based on the theoretical H_{loc} values for ^{12}C-BPH· (0.15 mT),[4,5] ^{13}C-BPH· (0.94 mT),[5] and ·SDS (0.83 mT),[4] the value for ^{13}C-BPH· comparable to that for ·SDS shows that the case (ii) may be tenable in contrast with the biradical cases.[1b,3]

Above 4 T in SDS and HDTCl and above 2 T in Brij35 where the lifetimes are decreasing or unchanging, the lifetimes are almost determined by the SLR due to the δg interaction and the escape of the component radical from a micelle. The SLR due to the δg interaction and the escape are independent of the isotopes so that the MIE should not be observed. ① Since in HDTCl there is a little decrease in lifetimes, the lifetimes are considered to be determined by the SLR mostly due to the δg interaction. ② Although the δg interaction due to ·SDS probably has an identical magnitude with that due to ·HDTCl, no detectable decrease was observed in SDS, and neither attained the lifetime to 14 μs. This result indicates that the rate-determining step in SDS is the escape, not the SLR due to the δg interaction.[1c,4] ③ In Brij35 the lifetimes are decided by the SLR due to the δg interaction judging from an appearance of the decrease in lifetimes. The lifetimes would not show the decrease if those are controlled by the escape.

The drastic reversal in lifetimes in Brij35 may be due to an oxygen atom which is next to the radical center on a carbon in the chain. Because an oxygen atom has a large spin-orbit coupling constant compared with a carbon, the δg interaction may be more operative than those in SDS and HDTCl which have pure methylene chains. Although the *isotropic* Δg mechanism is also enhanced, the decrease (7.4×10^4 s^{-1}) in the SLR rate at 14 T could not be explained by the too large radical pair ISC rate (10^8 s^{-1}) estimated by g=2.00298 (BPH·)[6] and g=2.0031 (MeC·HOEt).[7] Further detailed discussion is now in progress.

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