

Reexamination of the Photochemical Primary Process of Photo-Fries Rearrangement Reaction as Studied by MFE Probe

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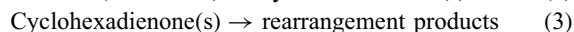
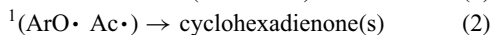
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A photo-Fries rearrangement reaction of 1-naphthyl acetate in *n*-hexane was studied by a nanosecond laser flash photolysis technique under magnetic fields of 0 to 1.65 T. The escaped yield of 1-naphthoxyl radical decreased with increasing magnetic field (*B*) at $0 < B \leq 0.005$ T, but inversely increased with increasing *B* at much higher fields of $0.005 \text{ T} < B \leq 1.65 \text{ T}$. Such inverted magnetic field effects (MFEs) can be interpreted with the hyperfine coupling and the Δg mechanisms through the singlet radical pair. The fact that MFEs are observed for the present photo-Fries rearrangement reaction suggests a singlet radical pair intermediacy with a lifetime as long as several ns.

Magnetic field effects (MFEs) on photochemical reactions through radical pairs (RPs) and biradicals have received considerable attention during the past three decades and the mechanism of MFEs has been well clarified experimentally and theoretically.^{1–3} In RPs generated by photochemical reactions, the unpaired electron spins on each radical are coupled, giving two different spin states: singlet (S) and triplet (T). Magnetic fields interact with these spins and affect the reaction of the RPs without changing other parameters such as the reaction rate of singlet RPs, activation barrier, and diffusion motion of the radicals. Since the interaction between magnetic fields and spins can be described by quantum chemistry, MFE studies on RPs provide valuable information on their kinetics and dynamics, and in particular on aspects of the reaction mechanism such as reaction precursor, and intermediacy. Thus, we call this technique *magnetic field effect probe (MFE probe)*. Recently, using the *MFE probe*, we have reported the microviscosity of alcoholic solutions⁴ and nanoscale heterogeneous structure of ionic liquids.^{5–7} In this Letter, we reexamined the reaction mechanism of a photo-Fries rearrangement reaction by using the *MFE probe*.

The photo-Fries rearrangement reaction has been believed to occur via geminate RPs formed by C–O bond cleavage in $\pi\sigma^*$ or $\pi\pi^*$ state aryl esters (ArOAc).^{8,9}



Here, $^1\text{ArOAc}^*$, $\text{ArO}\cdot$, $\text{Ac}\cdot$, and $^1(\text{ArO}\cdot \text{Ac}\cdot)$ denote the singlet excited state of ArOAc, aryloxy radical, acetyl radical, and the singlet radical pair, respectively. For example, recently, Lochbrunner et al. measured broad and weak femtosecond transient absorption spectra of a photo-Fries reaction of 4-*t*-butylphenyl acetate in cyclohexane and reported the cyclohexadienone formation time of 13 ps.¹⁰ This result indicates that the lifetime of the geminate RPs is as short as 13 ps. On the other hand, Nakagaki et al. reported that magnetic isotope effects

(MIEs) were observed for a photo-Fries reaction of ^{13}C -labeled 1-naphthyl acetate (NA) in acetonitrile with a magnetic field of 0.64 T.¹¹ Assuming a rate constant of spin conversion of 10^9 – 10^8 s^{-1} , if the lifetime of geminate RPs is 13 ps, the MIEs cannot be expected to be observed for the reaction of NA. It is therefore worthwhile to reexamine the photochemical primary process of the photo-Fries rearrangement of NA in nonviscous homogeneous solvent by the *MFE probe*.

A ns-laser flash photolysis of NA (Cica, SP grade) in *n*-hexane was performed at 296 K. Sample solution was deoxygenated by pure nitrogen bubbling and was pumped through a quartz flow cell. The concentration of NA in *n*-hexane was $0.50 \times 10^{-3} \text{ mol dm}^{-3}$. The excitation light source was the 4th harmonic of a Nd:YAG laser (6 – 7 mJ cm^{-2}).

Time profiles of the transient absorption, $A(t)$, were measured at 410 nm, because 1-naphthoxyl radical shows a transient absorption around 380–410 nm.¹¹ The $A(t)$ curves typically observed at 0 and 1.65 T are shown in Figure 1. The $A(t)$ curve observed at 410 nm shows exponential and second-order decay components due to the T–T absorption of NA and 1-naphthoxyl radical, respectively. We can see from this figure that an appreciable MFE on the second-order decay component of 1-naphthoxyl radical is observed. The fact that MFEs were observed for the present reaction in *n*-hexane strongly indicates that the lifetimes of the RPs of 1-naphthoxyl and acetyl radicals are as long as several ns, because the spin conversion should

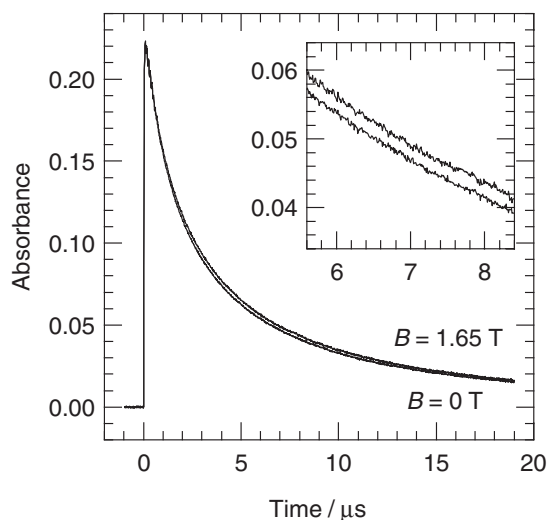


Figure 1. Time profiles of transient absorption observed for 1-naphthoxyl radical at 410 nm in the absence and presence of a magnetic field of 1.65 T. Inset: Plots in the time range of 5.6–8.4 μs .

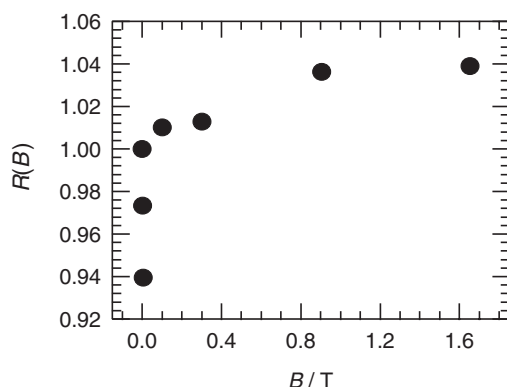


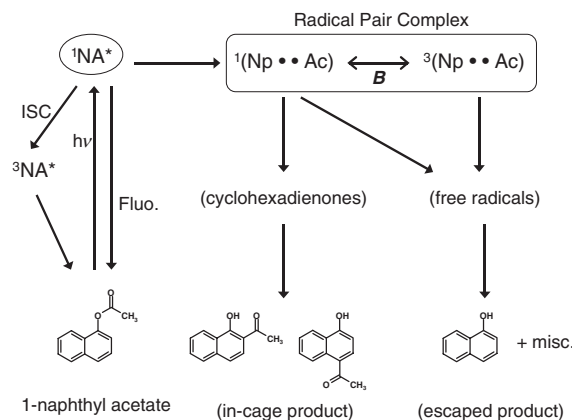
Figure 2. Magnetic field dependence of the relative radical yield of 1-naphthoxyl radical observed at 410 nm.

compete with the disappearance of the RPs. These results are consistent with a report of MIE by Nakagaki et al.¹¹ Although the present MFEs are not so large, it is concluded that the observed MFEs are believed owing to the main reaction path from the following reasons: (1) the transient absorption is strong and its intensity shows linear dependence for excitation energy in the range of 3–9 mJ cm⁻², (2) the decay kinetics is very simple, and (3) the small MFEs observed is reasonable for the small Δg value of 0.0038.

Next, we measured the magnetic field dependence of the MFEs under magnetic fields up to 1.65 T. Since the lifetime of T–T absorption of NA (³NA*) was estimated to be 7.1 μ s, using the escaped radical yield, $Y(B)$ at a delay time of 7 μ s after laser excitation, the relative radical yield $R(B)$ was calculated by $R(B) = Y(B)/Y(0\text{ T}) = A(B)/A(0\text{ T})$. The obtained $R(B)$ values are plotted against B in Figure 2. The magnetic field dependence on the $R(B)$ values shows inversion. The $R(B)$ value decreases steeply with increasing B from 0 to 0.005 T attaining the minimum value of $R(0.005\text{ T}) = 0.94 \pm 0.02$. Subsequently $R(B)$ gradually increases with increasing B . Finally, $R(1.65\text{ T})$ is 1.04 ± 0.02 . The cross field of $R(B) = 1$ was observed at 0.1 T. Similar MFEs were observed in acetonitrile, cyclohexane, and decahydronaphthalene. Thus the same reaction mechanism should be proposed to both present and previous¹¹ studies.

From the magnetic field dependence of $R(B)$, the observed MFEs can be interpreted by the hyperfine coupling mechanism (HFCM) associated with the Δg mechanism (Δg M). The spin conversion by the HFCM and the Δg M compete with escape. We therefore considered the rate of escape. The escaping rate from the solvent cage depends on the solvent viscosity. Using the Stokes–Einstein relation with $\eta = 0.2942 \times 10^{-3}$ Pa s, the escape rate constant (k_{esc}) was estimated to be 2.9×10^9 s⁻¹ at 298 K.^{12,13} Comparing with this value and the S–T conversion rate of 3.1×10^8 s⁻¹ at 1.65 T,^{1–3} the escape rate is much larger than the S–T conversion rate. Thus these estimations with normal diffusion failed to interpret the observed MFEs. At this stage, we consider a much slower diffusion process due to the formation of radical pair complexes of 1-naphthoxyl and acetyl radicals.

The key species of the photo-Fries rearrangement reaction is believed to be the cyclohexadienone.¹⁴ However, as reported by Lochbrunner et al., if the formation time of cyclohexadienone is several tens of ps,¹⁰ there is no reason for observation of the



Scheme 1. Mechanism of the photo-Fries rearrangement reaction of 1-naphthyl acetate in *n*-hexane.¹⁵

MFEs. The present study by the *MFE probe* suggests that a long lifetime RP such as a radical pair complex shown in the Scheme 1 should be considered as the primary intermediate.

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- ^{1,3}NA*, Np•, Ac•, ^{1,3}(Np •• Ac) denote the singlet or triplet excited state of NA, 1-naphthoxyl radical, acetyl radical, and the singlet or triplet radical pair, respectively.