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LASER-PHOTOLYSIS STUDY OF THE EXTERNAL MAGNETIC FIELD EFFECT ON THE DYNAMIC BEHAVIOR OF RADICAL PAIRS INVOLVING A GERMYL RADICAL

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The yields of the escaping ketyl radicals from the radical pairs formed through the reactions of triethylgermane with the triplet states of acetophenone and xanthone were found to be increased by a magnetic field. The observed increases at 1 T were 3 and 27% for the ketyl radicals of acetophenone and xanthone, respectively.

During the last decade, chemical reactions through radical pairs have been shown to be influenced by a magnetic field.(1) We first carried out a laser-photolysis study of the magnetic field effect on photochemical reactions in micelles, taking triplet states of ketones (XH) as reaction precursors.(1) Here each of the triplet states ($^3XH^*$) was found to abstract a hydrogen atom from a detergent molecule (RH), forming a radical pair (RP_1) as follows:

$$^3XH^* \quad + \quad RH \quad \rightarrow \quad RP_1 = (H_2X\bullet \quad \bullet R) \qquad (1)$$

The decay of the radicals in RP_1 and their escapes from it occur competitively. We found that the lifetimes of the ketyl radicals in RP_1 and the yields of the escaping ketyl radicals are increased very much in the presence of a magnetic field.(1) These magnetic field effects have been successfully interpreted in terms of the relaxation mechanism,(2) where the triplet-singlet (T-S) conversion rate of RP_1 is shown to be reduced by a magnetic field.

On the other hand, only few pairs the component radicals of which involve heavier atoms than fluorine as radical centers have been so far revealed to show magnetic field effects, where the reactions through such pairs are important in relation to magnetic isotope effects on heavy atoms. Recently, we carried out a laser-photolysis study of hydrogermanes (YGeH)(3) and found that they are good hydrogen donors. In the present paper, we have undertaken to study the magnetic field effects on the abstraction reactions of hydrogen by some triplet ketones from triethylgermane (1) in sodium dodecyl sulfate (SDS) micelles by using the fourth harmonic (266 nm, 5 ns width) of a Q-switched Nd:YAG laser as an excitation light source. Acetophenone (2) and xanthone (3) were chosen as ketones in this study because reaction 1 had been found to scarcely occur for 2 and 3 in SDS micelles.(4)

Time dependence of the absorbance (A(t)) of each of the degassed solutions was measured at room temperature. Their experimental conditions are listed in Table 1 (a - l), where solutions e, f, k, and l were measured in the presence of magnetic fields. Since the transient absorption intensity of triethylgermyl

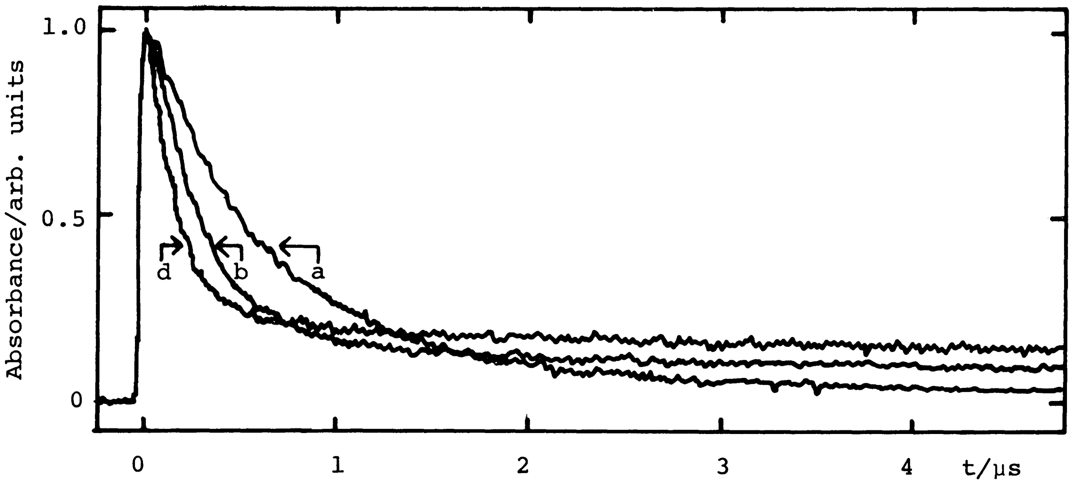

Fig. 1. A(t) curves observed at 350 nm with the SDS micellar solutions (a, b, and d) containing 1 and 2 in the absence of a magnetic field. The experimental conditions of solutions a, b, and d are listed in Table 1.

Table 1. Experimental Conditions and Observed Data[a] of the SDS Micellar Solutions (a - 1).

Solution[b]	Ketone[c]	[1]/mol dm^{-3}	B/T[d]	$k_T/10^6$ s^{-1}	$k_{TK}/10^6$ s^{-1}	C
a	2	0	0	-	1.3[e]	0.02[e]
b	2	0.017	0	-	2.6[e]	0.07[e]
c	2	0.025	0	-	3.3[e]	0.09[e]
d	2	0.037	0	-	4.9[e]	0.124[e]
e	2	0.037	0.1	-	4.9[e]	0.130[e]
f	2	0.037	1.0	-	4.9[e]	0.127[e]
g	3	0	0	0.29[f]	0.29[g]	0.12[g]
h	3	0.007	0	0.63[f]	0.61[g]	0.16[g]
i	3	0.013	0	0.90[f]	0.91[g]	0.17[g]
j	3	0.020	0	1.25[f]	1.23[g]	0.18[g]
k	3	0.020	0.1	1.25[f]	1.24[g]	0.21[g]
l	3	0.020	1.0	1.27[f]	1.13[g]	0.23[g]

a) Experimental errors of k and C are less than 5 and 2% respectively.

b) SDS concentration of the solutions containing 1 and 2 is 0.117 mol dm^{-3} and that of the solutions containig 1 and 3 is 0.08 mol dm^{-3}.

c) Ketone concentrations are (2) 0.007 mol dm^{-3} and (3) 0.001 mol dm^{-3}, respectively.

d) Applied magnetic flux density.

e) Observed at 350 nm.

f) Observed at 610 nm.

g) Observed at 480 nm.

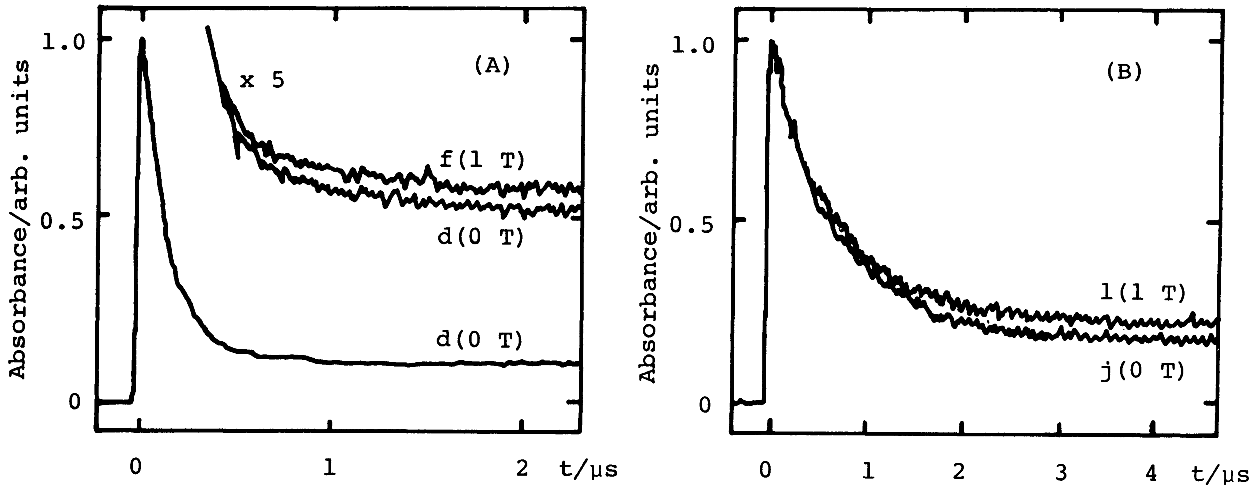

Fig. 2. Observed magnetic field effects on the A(t) curves with the SDS micellar solutions of (A) 1 and 2 at 350 nm and (B) 1 and 3 at 480 nm, respectively.

radical (ε_{max} = 360 nm) was measured to be very small, the A(t) curves were observed at 350 nm for solutions a - f. At this wavelength, $^3\underline{2}^*$ and the ketyl radical of 2 were reported to give strong absorptions.[5)]

The observed A(t) curves with the SDS micellar solutions are shown in Fig. 1. In the measured time range (10 μs) they can be approximately represented by the following equation, A(0) being normalized to one:

$$A(t) = (1 - C)\exp(-kt) + C \qquad (2)$$

The k value probably represents the rate constant (k_{TK}) of a combination of the decay of $^3\underline{2}^*$ and that of the ketyl radical because they could not be obtained separately. The C one represents the relative yield of the escaping ketyl radical. The observed k_{TK} and C values are listed in Table 1 (solutions a - d).

In the absence of 1, the decay of $^3\underline{2}^*$ was shown to be mainly due to its self-quenching process as follows:[4)]

$$^3XH^* + XH \rightarrow RP_2 = (H_2X\bullet \quad \bullet X) \qquad (3)$$

When 1 was added to the SDS micellar solution of 2, the k_{TK} and C values were found to be increased as are shown in Fig. 1 and Table 1. These increases can be considered to be due to the following reaction:

$$^3XH^* + YGeH \rightarrow RP_3 = (H_2X\bullet \quad \bullet GeY) \qquad (4)$$

Since 1 is insoluble in water, this reaction is considered to occur in micelles.

When a magnetic field below 1 T was applied to solutions a and d, their A(t) curves were also represented approximately by Eq. 2 . Although the curve of solution a was insensitive to the field, that of solution d was clearly changed by it as shown in Fig. 2(A). The observed k_{TK} and C values are listed in Table 1 (solutions e and f). The increases in C were about 5 and 3% at 0.1 and 1 T, respectively. Although they were very small, they were clearly beyond the experimental errors (less than 2%) as is shown in Fig. 2(A). Here, the A(t) curves measured by 15 shots of laser pulses were accumulated in this case.

These magnetically induced increases of the yield of the ketyl radical can also be explained by the magnetically induced decrease of the T-S conversion rate in RP$_3$.[1,2] This is the first observation of the magnetic field effect on the reaction of 2. On the other hand, k_{TK} was not changed appreciably by the magnetic fields. This may be due to the fact that the observed k_{TK} values mainly represent the triplet decay, which should be magnetic field independent.[1,2]

Similar transient behavior was also observed with the reaction of $^3\mathrm{3}^*$ and 1 in the SDS micellar solutions as observed with that of $^3\mathrm{2}^*$ and 1. The observed A(t) curves with solutions g - l were also represented approximately by Eq. 2 . At 610 nm, where the absorption coefficient of $^3\mathrm{3}^*$ is much larger than that of the ketyl radical of 3,[6] the decay rate constants (k_T) were obtained as listed in Table 1. They can be safely assigned to that of $^3\mathrm{3}^*$. By the addition of 1 to the SDS micellar solution of 3, the k_T value was found to be increased as shown in Table 1. This increase is also due to reaction 4. As expected, the k_T values observed with and without 1 were insensitive to a magnetic field below 1 T.

In the next place, the A(t) curve was measured at 480 nm. At this wavelength the ketyl radical gives an absorption peak,[6] but its intensity is probably smaller than that of $^3\mathrm{3}^*$ at 480 nm. Therefore, the observed k value probably gives the rate constant (k_{TK}) of a combination of the decay of $^3\mathrm{3}^*$ and that of the ketyl radical. The C value also gives the relative yield of the escaping ketyl radical. When a magnetic field below 1 T was applied to solutions g and j, the A(t) curve of the former solution was independent of it but that of the latter was changed by it as is shown in Fig. 2(B). The k_{TK} and C values observed at 0.1 and 1 T are listed in Table 1 (k and l). From the C values, the increases of the yield of the escaping radical were obtained to be 17 and 27% at 0.1 and 1 T, respectively. The decrease in k_{TK} observed at 1 T can be considered to be due to the decrease of the decay rate of the ketyl radical in RP$_3$,[1] although its rate constant could not be obtained separetely from k_T. These magnetic field effects were larger than those observed in the reaction of 2, and can also be interpreted in terms of the magnetically induced decrease of the T-S conversion rate of RP$_3$.[1,2]

The observed magnetic field effects in the present study were much smaller than those observed in the reactions through RP$_1$.[1] This may be due to the increase in the relaxation rate of RP$_3$ through the heavy atom effect of Ge and also those in the recombination and escape rates of the component radicals in RP$_3$. However, it is noteworthy that the radical pairs involving a germyl radical still gave some magnetic field effects in their reactions. This seems to suggest the possibility of separating isotopes of such heavy atoms as Ge by using the magnetic isotope effect as a new technique.

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