CHEMISTRY LETTERS, pp. 1149-1152, 1980.

LASER-PHOTOLYSIS STUDY OF THE EXTERNAL MAGNETIC FIELD EFFECT UPON THE PHOTODECOMPOSITION REACTION OF 1,3-DIPHENYL-2-PROPANONE IN A MICELLE

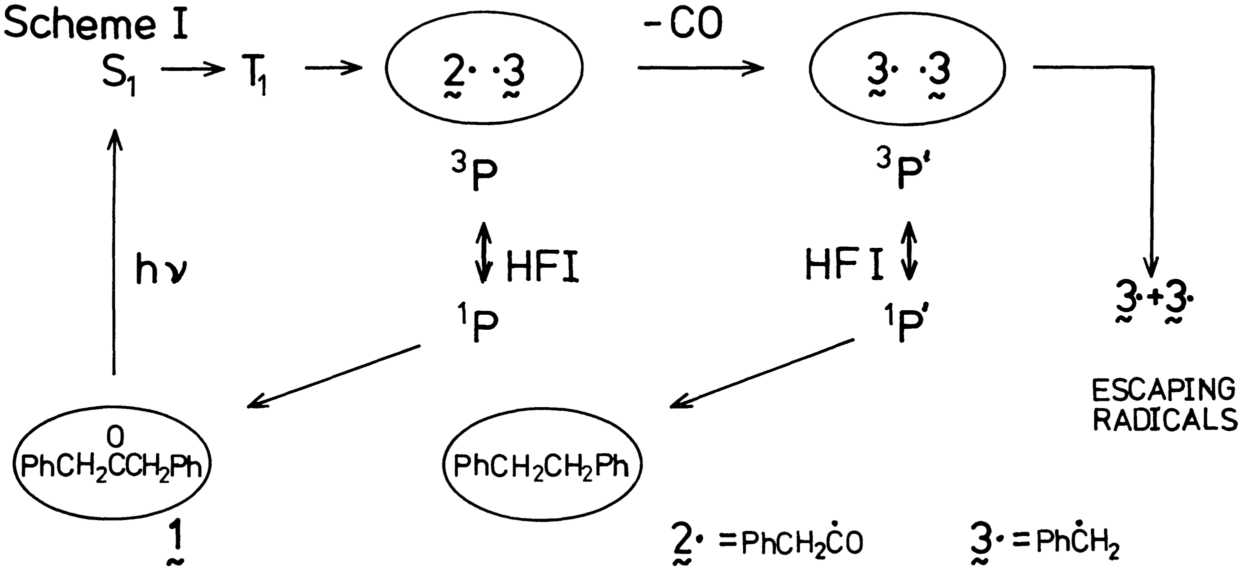
Hisaharu HAYASHI*, Yoshio SAKAGUCHI**, and Saburo NAGAKURA**
*The Institute of Physical and Chemical Research, Wako, Saitama 351
**The Institute for Solid State Physics, The University of Tokyo,
Roppongi, Minato, Tokyo 106

The photodecomposition reaction of 1,3-diphenyl-2-propanone in a micelle was studied with the aid of ns laser-photolysis. The transient absorption due to the benzyl radical was observed and the amount of escaping benzyl radicals from radical pairs was found to be enhanced by 30 % in the presence of a magnetic field of 70 mT.

Magnetic field[1,2] and magnetic isotope[2] effects have been observed for the photodecomposition reactions of dibenzoyl peroxide and 1,3-diphenyl-2-propanone (1) in solutions. These effects were proved to be brought about by the singlet-triplet conversion in the intermediate radical pairs promoted by the electronic Zeeman and hyperfine interactions (HFI) of the component radicals.[3] These effects were found to be enhanced for the reactions in micellar solutions.[4] This is due to the fact that the spin memory of each radical pair can be preserved for a long time because of the confinement of the pair in a micelle.

Recently, we first carried out the laser-photolysis study of the magnetic field effect upon photochemical reactions in micelles and found that the decay of the diphenylmethanone ketyl radical in a sodium 1-dodecanesulfonate (SDS) micelle was slowed down by a low magnetic field (less than 70 mT).[5] In the present paper we

Scheme I



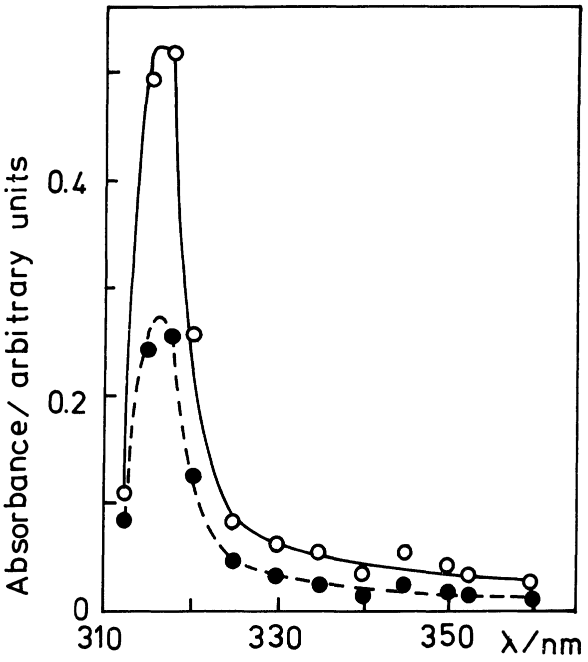


Fig. 1.
Transient absorption spectra observed with the micellar solution of 1 at zero field excited by the fourth harmonic of the Nd:YAG laser:
○ , observed immediately after excitation;
● , observed 500 ns after excitation.

have undertaken to study the primary process of the photodecomposition reaction of 1 in SDS micelles by using the fourth harmonic (266 nm, 5 ns width) of a Q-switched Nd:YAG laser as an excitation light source. The reaction has been proved to occur from the triplet radical pairs (^{3}P and ^{3}P') as is shown in scheme I.4) Here S_1 and T_1 are the lowest excited singlet and triplet states of 1, respectively, and cage recombinations are expected to occur from the singlet pairs (^{1}P and ^{1}P'). Decarbonylation of a $PhCH_2\dot{C}O$ radical was proved to occur on the time scale of tens of nanoseconds.6)

Time-resolved absorption spectra were observed at room temperature with the degassed SDS solutions of 1 (1.15×10^{-2} mol dm^{-3}). The SDS concentration was 8.35×10^{-2} mol dm^{-3}. Strong and very weak transient absorptions were found at zero field in the 310 - 360 nm and 440 - 460 nm regions, respectively. The spectra observed immediately and 500 ns after excitation in the former region are shown in Fig. 1. The spectral shape in this region was independent of time and has a sharp peak at 317 nm. From the position and shape of the observed spectra, the transient absorption was assigned to the benzyl radical.7) The same transient absorption due to the radical was also observed in the presence of a magnetic field of 70 mT.

The time dependence of the transient absorption intensity, I(t), was measured at 317.5 nm with and without the magnetic field. The results are shown in Figs. 2 and 3. The I(t) curves in the ns region (Fig. 2) decrease rapidly at their initial parts and thereafter decay very slowly being almost horizontal about 300 ns after excitation. In the µs region, the curves follow the second order decay (Fig. 3). The initial fast decay in the I(t) curves can safely be assigned to the cage recombination of the benzyl radicals inside the micelle. The nearly constant part may be assigned to the escaping benzyl radicals, the decay of which may be of the second order.

Some external magnetic field effects were found for the I(t) curves shown in Figs. 2 and 3. (I) Although the initial concentration of benzyl radical is insensitive to the magnetic field, the amount of the escaping benzyl radical is increased by the field. The I(400 ns)/I(0 ns) value is expected to represent the concentration ratio of the escaping benzyl radical to the initially prepared

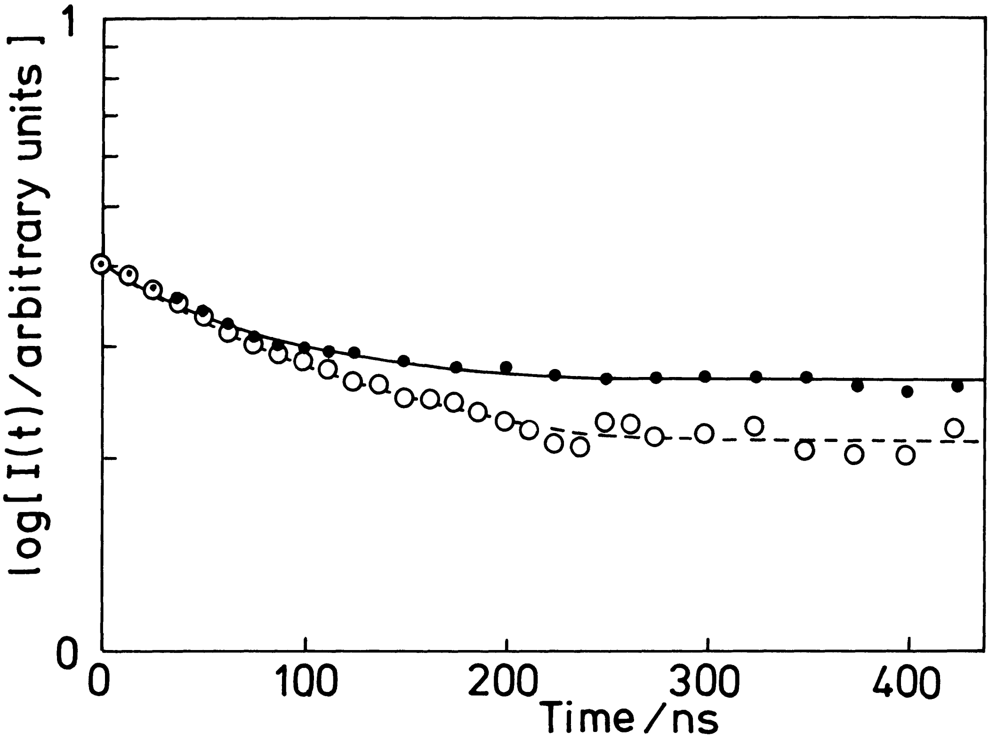


Fig. 2.
Time dependence of the transient absorption intensity (log I(t)) observed in the ns region at 317.5 nm with the micellar solution of 1:
○, at zero field; ●, at 70 mT.

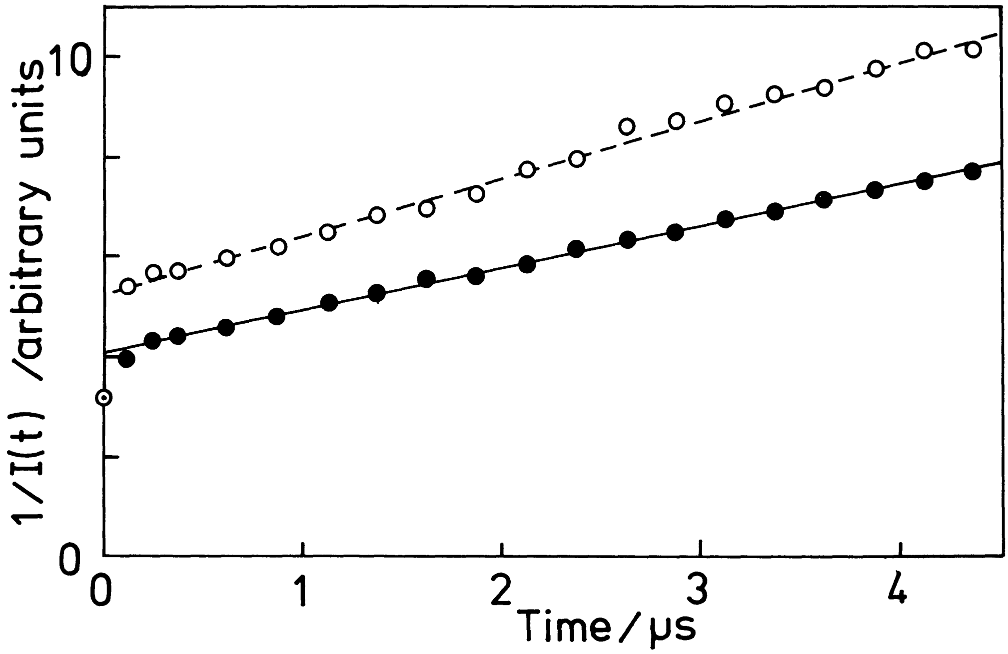


Fig. 3.
Time dependence of the transient absorption intensity (1/I(t)) observed in the μs region at 317.5 nm with the micellar solution of 1:
○, at zero field; ●, at 70 mT.

one. The ratio was determined to be 0.50 ± 0.01 (0 mT), 0.50 ± 0.01 (2.5 mT), 0.52 ± 0.01 (5 mT), 0.58 ± 0.02 (10 mT), 0.62 ± 0.01 (20 mT), 0.64 ± 0.01 (40 mT), 0.65 ± 0.01 (50 mT), and 0.65 ± 0.01 (70 mT), respectively. (II) The slope of the $1/I(t) - t$ line is decreased by 27 % in the presence of a magnetic field of 70 mT.

Effect (I) can be understood qualitatively with the following simple kinetic equations for the sublevel concentrations of the triplet pairs, ^3P and $^3P'$, (x_m, $m = 0, \pm 1$) and the escaping benzyl radical concentration (y):

$$dx_m/dt = -(k_m + k_e)\,x_m \quad (1) \qquad dy/dt = 2\,k_e \sum_m x_m \quad (2)$$

Here k_m and k_e are the averaged rate constant for the triplet-singlet conversion rate of the pairs in the micelle[5)] and that for the escape of benzyl radicals from the radical pairs, respectively. The solutions of Eqs. 1 and 2 are given

$$x = \sum_m x_m = (x_0/3) \sum_m \exp(-(k_m + k_e)t) \qquad (3)$$

$$y = (2x_0/3) \sum_m (k_e/(k_m + k_e))(1 - \exp(-(k_m + k_e)t) \qquad (4)$$

Here x_0 is the initial concentration of the triplet pairs. From the theory of the magnetic field effect upon chemical reactions,[3)] k_1 and k_{-1} are expected to be reduced by a low magnetic field through the HFI mechanism, while k_0 is expected to be unchanged by it. Thus the amount of escaping radicals which is propotional to $\sum_m 2k_e/(k_m + k_e)$ should be increased by the magnetic field. From the observed I(400 ns)/I(0 ns) values, the following relations can be derived when all the k_m values are assumed to be identical with each other at zero field and k_1 is assumed to be equal to k_{-1} at 50 and 70 mT:

$$k_0 = k_1 = k_{-1} = 3\,k_e \qquad \text{(at zero field)} \qquad (5)$$

$$k_0 = 3\,k_e,\ k_1 = k_{-1} = 1.8\,k_e \qquad \text{(at 50 and 70 mT)} \qquad (6)$$

Thus the $k_{\pm 1}$ values are proved to be reduced by about 40 % in the presence of the low magnetic fields.

The decay rate of the escaping benzyl radical was also observed to be influenced by a low magnetic field. But the mechanism is not clear at the present stage of investigation.

References

1) Y. Tanimoto, H. Hayashi, S. Nagakura, H. Sakuragi, and K. Tokumaru, Chem. Phys. Lett., 41, 267 (1976). Y. Sakaguchi, H. Hayashi, and S. Nagakura, Bull. Chem. Soc. Jpn., 53, 39 (1980).

2) A. L. Buchachenko, V. V. Ershov, E. M. Galimov, G. A. Nikiforof, and A. D. Pershin, Dokl. Akad. Nauk SSSR, 228, 379 (1976).

3) H. Hayashi and S. Nagakura, Bull. Chem. Soc. Jpn., 51, 2862 (1978).

4) N. J. Turro, B. Kraeutler, and D. R. Anderson, J. Am. Chem. Soc., 101, 7435 (1979).

5) Y. Sakaguchi, H. Hayashi, and S. Nagakura, Chem. Phys. Lett., 72, 420 (1980).

6) H. Langhals and H. Fischer, Chem. Ber., 111, 543 (1978).

7) H. Hiratsuka, T. Okamura, I. Tanaka, and Y. Tanizaki, J. Phys. Chem., 84, 285 (1980).

(Received July 1, 1980)