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Classification of the External Magnetic Field Effects on the Photodecomposition Reaction of Dibenzoyl Peroxide

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The external magnetic field effects upon product yields in the singlet sensitized photolysis of dibenzoyl peroxide in toluene were studied. The observed field dependencies were classified into four types, and were interpreted in terms of the electronic Zeeman and hyperfine interactions in the intermediate radical pair. Especially large magnetic field effects were observed for the yields of dimethylbiphenyls, new products in this reaction.

Studies of external magnetic field effects upon intramolecular and intermolecular dynamical processes, have recently made much progress. New phenomena have been observed concerning intramolecular and intermolecular energy transfer[1] and also concerning chemical reactions[2–9] and their mechanisms have been clarified for some cases. Many problems, however, are still left unsolved in this field. The external magnetic field effect upon chemical reactions may be expected to be fruitful research field to be developed in future.

In a previous paper,[6] we first observed an external magnetic field effect upon the product yield of a photochemical reaction in solution, taking as an example the singlet sensitized photodecomposition reaction of dibenzoyl peroxide in the presence of magnetic field range, 1.0—4.3 T. We found the effect upon the yield of phenyl benzoate and interpreted the result in terms of the electronic Zeeman interaction in an intermediate radical pair. On the other hand, product yields and reaction intermediates for some other reactions through radical pairs have been found to be influenced by hyperfine interactions in low magnetic fields below 0.1 T.[7,8] Recently, we have published the theoretical study of external magnetic field effects on chemical reaction in solutions which occurs through radical pair formation,[10] and have classified them into three types.

In the present study, we have studied the photodecomposition reaction of dibenzoyl peroxide in the presence not only of high fields (4.3 and 6 T) but also of low fields below 78 mT. In the course of this study, we have found some new products and have succeeded in observing several different types of magnetic field effects on the product yields.[11]

Experimental

Toluene solutions (0.5 ml) of dibenzoyl peroxide (0.04 M) containing chrysene (0.002 M) as a singlet sensitizer[12] in Pyrex glass cells were degassed with the freeze-thaw technique, and were sealed under a nitrogen atmosphere. In the low magnetic field experiment below 78 mT the cells were placed in a hand-made coil which was cooled in a water bath, the temperature being kept 16.5±0.3 °C. The solution was irradiated with a 1 kW high pressure mercury lamp through a water filter and Pyrex glass. The decrease of dibenzoyl peroxide was monitored by iodometric titration of an aliquot and the half life under our experimental conditions was determined to be 11 min. Therefore the irradiation time was set to be 80 min in such a way that the dibenzoyl peroxide decomposed almost completely. In the high magnetic-field experiment, ternary solutions containing dibenzoyl peroxide and chrysene in toluene were irradiated in the presence of a magnetic field of 4.3 or 6 T induced by a superconducting magnet, and the details of the experiment were the same as described before.[6] The products were identified by GC-MS and VPC by comparing their retention times with those of the corresponding authentic samples. The yield, $P(H)$, of each product in the presence of an external magnetic field, H, was determined by VPC using 1,4-dicyanobenzene as an internal standard.

The viscosity dependence of the magnetic field effect upon the yield of phenyl benzoate was examined by changing the solvent viscosity. The viscosity was increased by the addition of polystyrene to the solvent. Polystyrene (Wako Pure Chemical Industries Ltd. polymerization degree 1600—1800) was purified by repeating twice precipitation from its toluene solution by methanol. The viscosity was measured by Ostwald's viscometer.

Results and Discussion

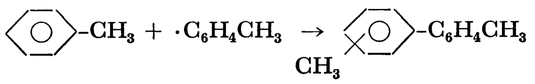
The singlet sensitized photolysis of dibenzoyl peroxide proceeds as follows:

$$
\begin{array}{l}
PhCO_2OCOPh^* \longrightarrow \\
\qquad \overline{PhCO_2\cdot + Ph\cdot} + CO_2 \longrightarrow \\
\qquad \quad \downarrow \qquad PhCO_2Ph \text{ (cage product)} + CO_2 \\
\qquad PhCO_2\cdot + Ph\cdot \text{(escaping radicals)} + CO_2 \qquad (1) \\
\qquad \qquad \qquad \downarrow \\
\qquad \qquad \text{escape products}
\end{array}
$$

For this reaction in toluene, we identified 14 products the molecular weights of which are less than 212.[13] They are listed in Table 1 together with their yields. Among them *m,n′*-dimethylbiphenyls (**6**'s) were found in this study for the first time, although the others had already been detected.[14]

Phenyl benzoate (**2**) and biphenyl (**1**) are cage products[15] and the others in Table 1 are considered to be escape ones. From Table 1 we can see the following characteristic features of the yields of dimethylbiphenyls (**6**). Firstly, the dimethylbiphenyls with a methyl group on the 4-position are not observed. Secondly, the yield is larger for 3,3′-**6** than for 2,2′-**6** and 2,3′-**6**.

The simplest possible mechanism for the formation of dimethylbiphenyls in the present system is the tolylation of toluene which proceeds as follows;



$$-CH_3 + \cdot C_6H_4CH_3 \rightarrow \underset{CH_3}{-}C_6H_4CH_3 \qquad (2)$$

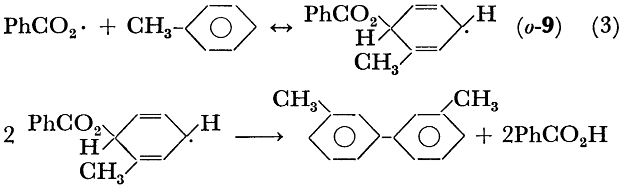
Table 1. Identified products and their yields in the presence of 0.3 mT

	Products	Yield[a]
Cage products	biphenyl (**1**)	0.9
	phenyl benzoate (**2**)	11.6
Escape products	benzoic acid (**3**)	---[b]
	o-methylbiphenyl (*o*-**4**)	6.4
	m-methylbiphenyl (*m*-**4**)	18.9[c]
	p-methylbiphenyl (*p*-**4**)	
	1,2-diphenylethane (1,2-**5**)	
	2,2′-dimethylbiphenyl (2,2′-**6**)	0.1
	2,3′-dimethylbiphenyl (2,3′-**6**)	0.8
	3,3′-dimethylbiphenyl (3,3′-**6**)	1.4
	o-tolyl benzoate (*o*-**7**)	2.6
	m-tolyl benzoate (*m*-**7**)	---[b]
	p-tolyl benzoate (*p*-**7**)	---[b]
	benzyl benzoate (**8**)	---[b]

a) In mol% of dibenzoyl peroxide. b) --- indicates that their yields were not measured because of the incomplete separation between these compounds under our VPC conditions. c) Only the sum of the yields of these compounds was measured because they were not resolved from one another under our VPC conditions.

However, the partial rate factors (F_i) for this reaction determined by Ito *et al.*[16] (F_o:F_m:F_p=3.3:1.0:1.3) are completely different from the present results in Table 1. Thus the tolylation mechanism is disregarded.

Another possible mechanism for the formation of **6**'s is an assisted reaction[17] by $PhCO_2\cdot$ radicals. For example, 3,3′-**6** can be formed through (*o*-benzoyloxy)-methylcyclohexadienyl radical (*o*-**9**):



The benzoyloxylation of toluene may preferably occur on the *o*-position through the hyperconjugation of the methyl group. The steric hindrance of the benzoyloxyl group is considered to disturb formation of the dimethylbiphenyls with a methyl group on the 4-position (2,4′-, 3,4′-, and 4,4′-dimethylbiphenyls). Thus, the assisted reaction scheme explains the observed yields of the dimethylbiphenyls. According to this mechanism, dimethylbiphenyls are escape products. This conclusion is also supported by the changes of the yields of dimethylbiphenyls due to dissolved oxygen and due to the excitation light intensity.[18]

From the magnetic field dependence of the measured $P(H)$ values listed in Table 1, the products can be classified into four groups.

[1] phenyl benzoate (**2**)

[2] 1,2-diphenylethane (1,2-**5**), *o*-, *m*-, and *p*-methylbiphenyls (*o*-, *m*-, and *p*-**4**'s) and biphenyl (**1**)

[3a] 2,2′-, 2,3′-, and 3,3′-dimethylbiphenyls (**6**'s)

[3b] *o*-tolyl benzoate (*o*-**7**)[19]

The observed relative change, $R(H)$, of the yield of the typical product in each group is plotted against log H in Fig. 1. Here $R(H)$ is defined

$$R(H) = [P(H)-P(0)]/P(0)$$

Here, $P(0)$ is the yield without an external magnetic field (in actuality, under the residual field (0.3 mT) of the magnets).

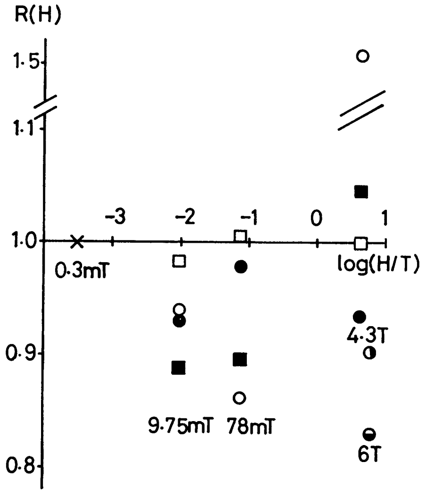


Fig. 1. $R(H)$-H plots in toluene and the viscosity dependence of R_2 (6 T): ● $R(H)$ for **2** (type 1); □ $R(H)$ for mixture of 1,2-**5**, *m*-**4**, and *p*-**4** (type 2); ○ $R(H)$ for 3,3′-**6** (type 3a); ■ $R(H)$ for *o*-**7** (type 3b); ◑ R_2 (6 T) for η_r=3.6; ◒ R_2 (6 T) for η_r= 8.8. Here, $\eta_r=\eta_{solvent}/\eta_{toluene}$.

According to the theory of the external magnetic field effect on chemical reactions through a radical pair,[10] the field dependence of $P(H)$ for cage or escape products from Γ-precursors (Γ is singlet, triplet, or free radical) can be represented qualitatively as shown in Fig. 2.[20]

Case (a) in Fig. 2. can be applied to reactions in which the energy separation, $|2J|$, between the singlet, S, and triplet, T_m (m=0, ±1), states of the intermediate radical pair is smaller than or comparable to the largest

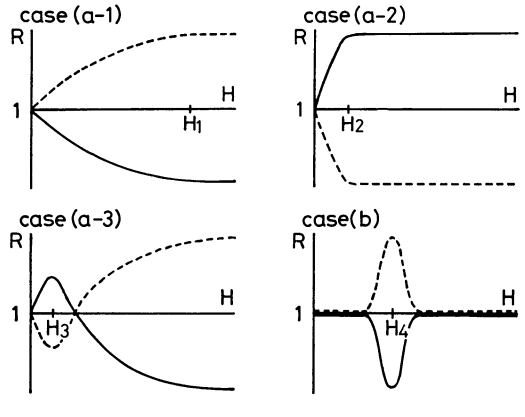


Fig. 2. Theoretical classifications of the magnetic field dependences on the product yields. The full curves indicate the magnetic field dependence of the cage (escape) product from a singlet (triplet or free radical) precursor; the broken curves indicate the magnetic field dependence of the escape (cage) product from a singlet (triplet or free radical) precursor. See text for H_1, H_2, H_3, and H_4.

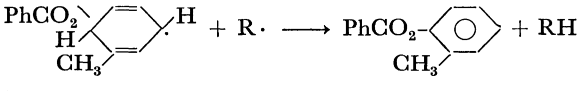
off-diagonal matrix element between S and T_m. Case (a) is further divided into three sub-groups according to the effective off-diagonal matrix elements: (a-1) electronic Zeeman interaction between S and T_0 (the first term in Eq. 2 of the previous paper[10]) is effective; (a-2) hyperfine interactions between S and T_m (the second and third terms in Eq. 2 and Eqs. 3 and 4 of the previous paper[10]) are effective; (a-3) both interactions are effective. Here we added a new situation (case (b)) which is applicable to reactions where $|2J|$ is larger than the largest off-diagonal matrix element.

Let us summarise the field dependence of $P(H)$ for the cage (escape) product from a singlet (triplet or free radical) precursor (full curves in Fig. 2). In case (a-1), $P(H)$ decreases with increasing magnetic field by the S-T_0 conversion through the electronic Zeeman term[10] and converges into a constant at a high magnetic field H_1. In case (a-2), $P(H)$ increases suddenly at a low field, H_2, and remains almost constant above H_2. In case (a-3), $P(H)$ first increases with the increasing magnetic field but begins to decrease from a fairly low magnetic field, H_3. In case (b), $P(H)$ suddenly decreases at a level-crossing field, $H_4 = |2J|/(g\beta)$, through a sudden increase of the S-T_m ($m=1$ or -1) conversion in the radical pair.[2] Here g is the mean value of the isotropic g-factors of the component radicals. $P(H)$ for the cage (escape) product from a triplet or free radical (singlet) precursor can be represented as shown by the broken curves in Fig. 2.

Let us consider the $R(H)$ values observed in this study (Fig. 1) on the basis of the above-mentioned theoretical classification. We can see from Fig. 1 that $R(H)$ of **2** (group [1]) decreases with increasing magnetic field, and those of the products in group [2] are nearly constant independent of the applied field within the limits of experimental error. **2** is a cage product from the singlet radical pair containing Ph· and $PhCO_2$·, and the products in group [2] except for **1** are the escape products from the radical pairs shown in Eq. 1. The $R(H)$ values of **2**, *o*-**4**, *p*-**4**, and 1,2-**5** at the high field region, 1—4.3 T, were measured and analysed theoretically in the previous paper,[6] being classified to case (a-1). According to the present results at the low field region below 78 mT, no appreciable hyperfine effect (case (a-2)) could be detected for the products in groups [1] and [2]. Thus $R(H)$'s of **2** in the whole magnetic field region under the measurements are well explained in terms of the electronic Zeeman effect and **2** is regarded as one of the typical examples belonging to case (a-1).

1 is a cage product as **2**, but its $R(H)$ is independent of the applied field within the limits of experimental error. Thus **1** belongs to group [2]. The electronic Zeeman effect may be disregarded for this case because Δg is equal to zero for the radical pair containing the two phenyl radicals.

The $R(H)$ values of the products in groups [3a] and [3b] are smaller than 1.0 in the low field region and larger than 1.0 at the field of 4.3 T (Fig. 1). Actually $R_{3,3'\text{-}6}$ (78 mT) was determined to be as small as 0.86 and $R_{3,3'\text{-}6}$ (4.3 T) as large as 1.51. The latter is one of the largest external magnetic field effects upon the reaction yields observed so far. The above-mentioned field dependence of the $R(H)$ for the products of groups [3a] and [3b] clearly corresponds to the broken curve of case (a-3) in Fig. 2. Therefore they are regarded as escape products, since the present photodecomposition reaction occurs from the singlet precursor. This conclusion is supported by the following facts: (1) **6**'s are considered to be produced through dimerization of the **9** radical as is shown in Eq. 3. (2) According to Nakata *et al.*,[14] **7**'s are formed by the reaction between the **9** radical and the escaping (R·) radical. For example, *o*-**7** can be formed through the following reaction.



(4)

(3) The **9** radical is formed from the escaping benzoyloxyl radical as is shown in Eq. 3.

Thus, the magnetic field dependence of $R(H)$ for the products of groups [3a] and [3b] is explained in terms of the mixed effects of the electronic Zeeman and hyperfine interaction. Precisely speaking, the $R(H)$ value at 4.3 T is much smaller for *o*-**7** than for **6**'s, while in the low field region the values are similar to each other for *o*-**7** and **6**'s (see Fig. 1). This might be due to the fact that the yields of each **7** is proportional to the concentration of the corresponding(benzoyloxy)-methylcyclohexadienyl radical but that of *m,n'*-**6** is proportional to the product of the concentrations of *m''*- and *n''*-**9**.

We measured the viscosity dependence of $R(H)$ for **2**. The viscosity was increased by addition of polystyrene to the solvent (toluene). We can see from Fig. 1 that R(6 T) for **2** at $\eta_r = 8.8$ was determined to be as small as 0.83, and the decrease in the yield of the cage product due to a magnetic field was proved to be enhanced by solvent viscosity.

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19) *m*-and *p*-**7**'s may belong to this group. Since these compounds were not resolved from **8** under our VPC conditions, their $P(H)$ could not be measured.

20) In Fig. 2, we show the yields of the products which are given only from singlet states. Those of other reactions can similarly be analysed.