

THE EFFECT OF EXTERNAL MAGNETIC FIELD ON PHOTOCHEMICAL FREE RADICAL REACTIONS.
THE SINGLET AND TRIPLET SENSITIZED PHOTOLYSIS OF DIBENZOYL PEROXIDE

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Application of external magnetic field (0-14 kG) on the singlet and triplet sensitized photolysis of dibenzoyl peroxide scarcely affects the yield of phenyl benzoate resulting from cage recombination between benzoyl and phenyl radicals, suggesting that only a slight fraction of the geminate product arises from radical pairs which can suffer the effect of magnetic field.

The effect of external magnetic field on photochemical reactions has recently been examined for several reactions. Gupta and Hammond reported the magnetic field effect on photosensitized isomerization of stilbene and 1,3-pentadiene,²⁾ and Atkins postulated that a triplet sensitizer molecule would act on an olefinic molecule to give a triplet exciplex and its intersystem crossing to a singlet state would be affected by the magnetic field.³⁾ Matsuzaki and Nagakura reported that magnetic field quenches the fluorescence of carbon disulphide vapour probably through the enhancement of the intersystem crossing of its excited singlet state to its triplet state.⁴⁾ Further attention seems increasingly paid to the effect of magnetic field upon chemical reactions.⁵⁾

Recently chemically induced dynamic nuclear polarization (CIDNP) has been actively investigated. According to radical pair model in CIDNP theory, when two radicals are born in a singlet pair, their electron spins, through their Zeeman interaction with magnetic field and their hyperfine interaction with nuclear spins, will be dephased to develop triplet pair character during the lifetime of the pair within a solvent cage; the dephasing will cause nuclear magnetic polarization of the radicals which subsequently result in CIDNP of products, and the rate for the geminate reaction is proportional to the singlet character of the radical pair.⁶⁾ As the development of the triplet pair character is expected, in a magnetic field over a few thousands gauss,⁷⁾ to increase with the increase of both the field strength and the difference of g-values of the radicals, one could guess that the application of the higher magnetic field would reduce the yield of the geminate product from the radical pair born in the singlet state. The CIDNP signals have actually been shown to be dependent on the strength of magnetic field through

the change of the extent of mixing between singlet and triplet pair character.⁸⁾ However, to our knowledge, it has never been reported whether the external magnetic field, which can affect CIDNP, does or does not affect the actual yield of products from radical pairs.⁹⁾ The present communication concerns with this task.

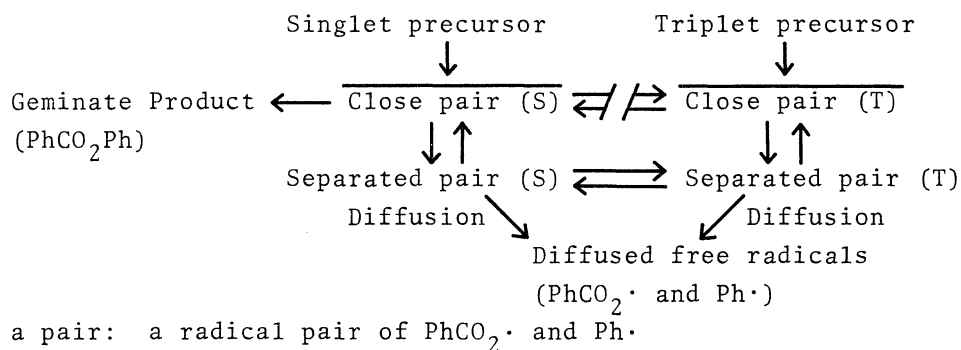
Previously we have found that in the photolysis of dibenzoyl peroxide the sensitization with excited singlet aromatic hydrocarbons gives moderate yield of phenyl benzoate through recombination of a benzoyl radical and a phenyl radical within a solvent cage whereas the sensitization with triplet aromatic ketones gives only a negligible amount of the benzoate.¹⁰⁾ For example, the yields of phenyl benzoate are 17 and 3% from chrysene and 3-methoxyacetophenone sensitization, respectively. This finding together with relatively large difference in g-values between benzoyl and phenyl radicals has led us to examine the effect of magnetic field on this free radical cage reaction.

A solution of dibenzoyl peroxide (0.04 M) either with chrysene (0.002 M) as a singlet sensitizer or with 3-methoxyacetophenone (0.10 M) as a triplet sensitizer in benzene or in toluene in a Pyrex tube was deaerated by an argon or nitrogen atmosphere. The tube was immersed in a water bath with a Pyrex window kept at 20°C and placed in a JEOL electro-magnet JM-210 with varying field strengths (0-14 kG) and irradiated with a 450 W high pressure mercury lamp until the peroxide completely disappeared; its decrease was monitored by iodometric titration of an aliquot. The resulting phenyl benzoate was determined by vpc with the use of an internal standard.¹¹⁾ In order to get reproducible results as far as possible, a batch solution was divided into several tubes and successively irradiated under varying field strengths and the vpc determinations were carried out in duplicate or triplicate ways for each run.

The typical results for chrysene-sensitized photolysis in benzene and in toluene and 3-methoxyacetophenone-sensitized photolysis in benzene are depicted in Figures 1, 2 and 3, respectively, in which the yields of phenyl benzoate relative to that in the absence of applied magnetic field are plotted against the field strength. These figures indicate that the yield of phenyl benzoate was scarcely varied by the application of external magnetic field. The variation seems not to exceed appreciably the experimental error.¹²⁾

The present results could be understood as described below. Decomposition of dibenzoyl peroxide molecule sensitized by the excited singlet hydrocarbon molecule will give a singlet pair of a benzoyl radical and a phenyl radical in a close distance separated by a carbon dioxide molecule within a solvent cage, and the electron spins of these two radicals will considerably interact through exchange interaction. This close pair, as shown in the scheme, would undergo recombination into the geminate product or displacement of the constituent radicals into a considerably separated pair in very weak or negligible exchange interaction. The separated pair would diffuse or revert into the close pair. On the application of an external magnetic field, the singlet separated pair would more facily invert into the corresponding triplet pair than the close pair, because the separated pair is in less exchange interaction and would have longer lifetime before the

Scheme



recombination than the close pair.¹³⁾ When a benzoyl and a phenyl radical with their g -values of 2.010 ¹⁴⁾ and 2.002 ¹⁵⁾, respectively, constitute a singlet pair in negligible exchange interaction, their electron spins are estimated to be dephased into a triplet pair with an angular frequency amounting to 10^9 radians sec^{-1} at 13 kG.¹⁶⁾ This estimation suggests that the dephasing process would compete with the diffusion of the free radicals out of the cage; the lifetime of a solvent cage of benzene is estimated to be 10^{-9} - 10^{-10} sec at ambient temperature. The resulting triplet separated pair would diffuse.

It would be possible that if most fractions of the close pairs born from the singlet sensitization displace into singlet separated pairs to suffer the spin-inversion effect of the magnetic field and subsequently revert into close pairs to give the geminate product, its yield would be decreased with the increase of the strength of the applied magnetic field. In the triplet sensitization, on the other hand, the yield of the geminate product would be increased with the increase of the field strength through the enhancement of the intersystem crossing of the separated triplet pair by magnetic field. However, the present results rule out the above possibility and suggest that radical pairs sufficiently separated to suffer magnetic field effect do not effectively revert into the close pairs subsequently to recombine.¹⁷⁾ It seems therefore reasonable to conclude that the geminate product would mostly result from the radical pairs with considerable exchange interaction born immediately after the bond cleavage of the precursor molecules and only a slight fraction of the geminate product would result from the radical pairs once displaced in separated distance susceptible to magnetic field which are the most responsible for the nuclear magnetic polarization of reaction products.

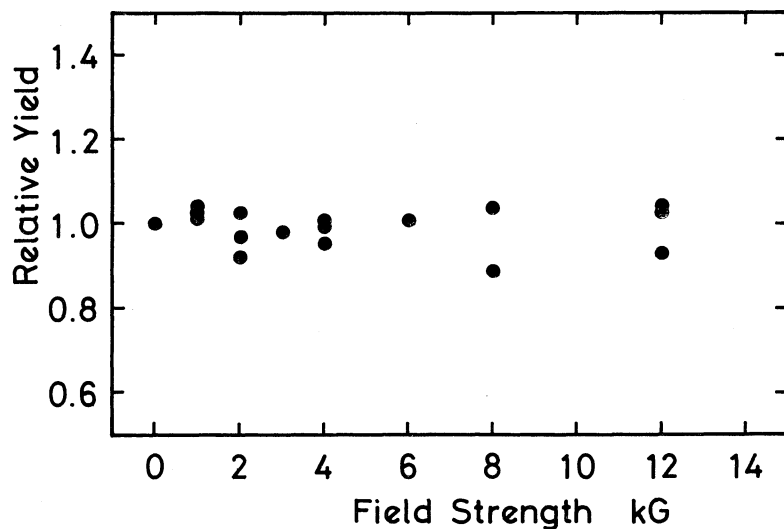


Figure 1. The Effect of Magnetic Field on the Yield of Phenyl Benzoate(Relative to Yield in the Absence of the Applied Field) in Chrysene(0.002 M)-sensitized Decomposition of Dibenzoyl Peroxide(0.04 M) in Benzene.

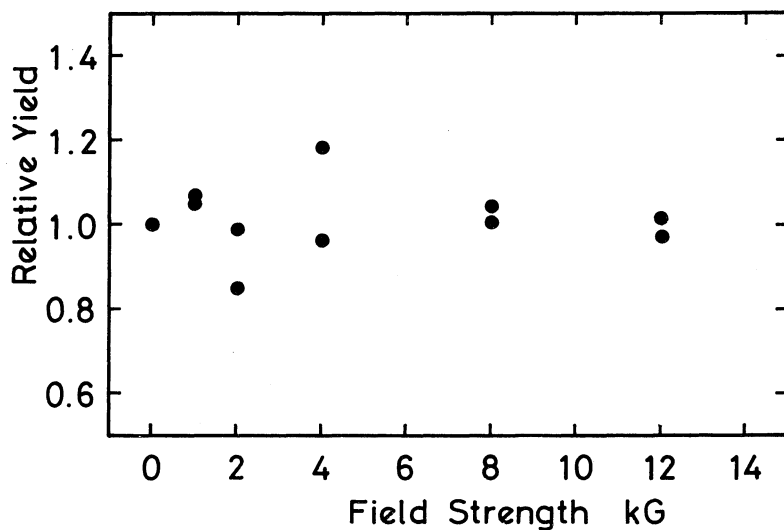


Figure 2. The Effect of Magnetic Field on the Yield of Phenyl Benzoate(Relative to Yield in the Absence of the Applied Field) in Chrysene(0.002 M)-sensitized Decomposition of Dibenzoyl Peroxide(0.04 M) in Toluene.

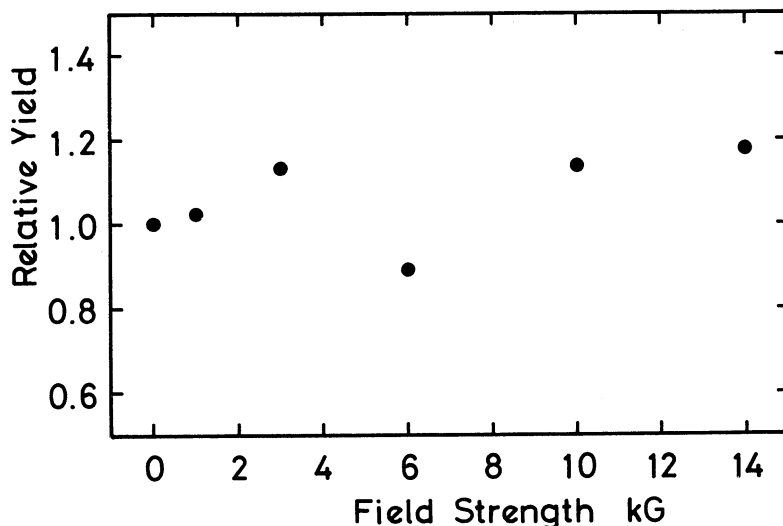


Figure 3. The Effect of Magnetic Field on the Yield of Phenyl Benzoate (Relative to Yield in the Absence of the Applied Field) in 3-Methoxyacetophenone (0.10 M) -sensitized Decomposition of Dibenzoyl Peroxide (0.04 M) in Benzene.

References and Notes

- 1) To whom correspondence should be addressed. Special visiting fellow of Research Institute for Polymers and Textiles in 1973-1974.
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- 7) At magnetic field less than a few thousand gauss, S_0 state of a radical pair would mix with T_{-1} state leading to the development of the triplet pair character (see Reference 8).
- 8) M. Lehnig and H. Fischer, *Z. Naturforsch.*, **24a**, 1771 (1969); H. Fischer and M. Lehnig, *J. Phys. Chem.*, **75**, 3410 (1971) and literatures cited by H. Fischer in Reference 4, p. 211; R. Kaptein and J. A. Hollander, *J. Amer. Chem. Soc.*, **94**, 6269 (1972); G. L. Closs and C. E. Doubleday, *ibid.*, **95**, 2736 (1973); P. W. Atkins, *Chem. Phys. Lett.*, **24**, 45 (1974).

- 9) During the course of the present work, Russian workers published a communication for the determination of the products from reactions of benzylic chlorides with n-butyl lithium carried out at 15 or 25 kG and in the absence of applied magnetic field. (R. Z. Sagdeev, Yu. N. Molin, K. M. Salikhov, T. V. Leshina, M. A. Kamha, and S. M. Shein, *Org. Magn. Resonance*, 5, 603 (1973).)
- 10) K. Tokumaru, A. Ohshima, T. Nakata, H. Sakuragi, and T. Mishima, *Chem. Lett.*, 571 (1974).
- 11) 4-Methylbiphenyl or phenyl 4-chlorobenzoate was employed as an internal standard. In small scale runs, dibenzoyl peroxide, sensitizer and vpc internal standard were dissolved in benzene or in hexadeuterobenzene in a Pyrex nmr tube and irradiated in a JEOL JES-ME 1X ESR cavity (0-6.5 kG) with a 400 W high pressure mercury lamp and the proceeding of the reaction was monitored by nmr of hexadeuterobenzene solution.
- 12) Particular care was taken in the determination of the benzoate from the triplet sensitization because of the low yield of phenyl benzoate produced.
- 13) F. J. Adrian, *J. Chem. Phys.*, 53, 3374 (1970), 54, 3912 (1971).
- 14) The g-value for the benzoyl radical has not yet been determined, but it can be estimated as nearly 2.01 on the reasonable assumption that this radical has nearly the same value as related radicals, $\text{DO}_2\text{CCH=CHCO}_2\cdot$ ($g = 2.0119^{\text{a}}$) and $\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\cdot$ ($g = 2.0093^{\text{b}}$). (a) B. Eda and M. Iwasaki, *J. Chem. Phys.*, 55, 3442 (1971); b) H. C. Box, H. G. Freund, K. T. Lilga, and E. E. Budzinski, *J. Phys. Chem.*, 74, 40 (1970).)
- 15) P. H. Kasai, P. A. Clarke, and E. B. Whipple, *J. Amer. Chem. Soc.*, 92, 2640 (1970).
- 16) The difference of the angular frequencies of the two free radicals ($\Delta\omega$) with a difference of their g-values (Δg) in a magnetic field, H_0 , is calculated as follows:
- $$\Delta\omega(\text{radian sec}^{-1}) = 2\pi\beta h^{-1}\Delta g H_0 = 8.79 \times 10^6 \Delta g H_0 (\text{gauss})$$
- 17) The referee suggested that the interaction of radicals with solvent molecules might play an important role in the magnetic field effect on radical pairs.

(Received November 30, 1974)