

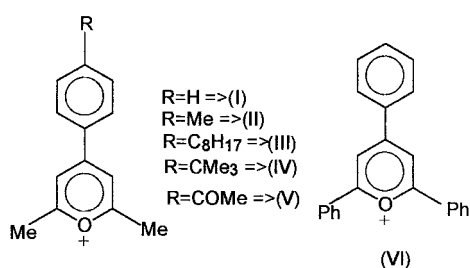
# Micellar confinement of charged donor-acceptor system: A case of large MFE

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Magnetic field effect (MFE) on the radical pairs (RP) generated by photoexcitation of derivatives of phenyl pyrylium ion (PP<sup>+</sup>) in the presence of an electron donor, biphenyl or skatole, has been observed. In these systems the observed MFEs are large and vary interestingly amongst derivatives.

## Introduction

It is well established that the magnetic field effect on the geminate recombination of radical pairs depend not only on the relative spin evolution of the two interacting radicals, but also on the spatial evolution.<sup>1-4</sup> Empirically it is found that micellar confinement, which reduces the escape rate from a cage of appropriate dimension and which increases the probability of repeated collisions at proper time intervals, leads to an increase of MFE. The amplification of the MFE by micellar confinement has been particularly successful for neutral radical pairs produced by H-abstraction or bond dissociation of an uncharged molecule. For ionic confinement of donor-acceptor systems, problems arise due to the greater solubility of ions in water. A partial confinement is still possible by taking ionic (anionic or cationic) micelles. However, if the donor and the acceptor are oppositely charged species; then only one of the two may be confined by the charged head-group of the micelle. The natural solution to the problem, therefore, is to have only one of the two partners charged, and the other neutral but highly soluble in the micellar core. Primarily from this point of view we chose several phenyl pyrylium ions PP<sup>+</sup> (I-VI)<sup>5-7</sup> and coupled them with charge-neutral donors, such as biphenyl and skatole, and investigated the MFE on the radical pairs generated by photo-excitation. A large MFE on the yields of free radicals and the lifetimes of <sup>3</sup>RP was observed.<sup>8,9</sup>



Scheme 1.

## Results and discussion

The salient points of our work may be briefly summarized as follows:

(1) Biphenyl quenches the excited <sup>1,3</sup>PP<sup>+</sup> producing singlet and triplet RPs.<sup>5-7</sup> The <sup>1</sup>RP recombines fast and there is hardly any spin evolution during the lifetime of the <sup>1</sup>RP. Thus, the MFE is negligible for <sup>1</sup>RP. We have measured the field effect on the fluorescence, but could only detect minor changes. It has also been reported that singlet exciplexes are formed with naphthalene, pyrene etc. as donor.<sup>7</sup> However, our efforts in this case to observe any significant MFE on exciplex emission failed.

(2) The triplet (RP) decay has been followed by laser flash photolysis (LFP). A pulsed magnetic field has been synchronized with LFP to measure the yields and the lifetimes of RP as a function of fields upto 5T.<sup>10</sup> Some typical decay curves of the donor-acceptor system BP/PP<sup>+</sup> are shown (Figs. 1-3). It may be noticed that there is large change in yields with magnetic field, the rate of change being maximum at low fields. The lifetimes of the RP was estimated from the curves following the prescription of Nagakura and Hayashi.<sup>1,11</sup> The lifetime vs. field curve exhibits the same qualitative features as the yield vs. field curve. There occurs near-saturation twice, at low fields as well as at high fields. The low-field MFE can be explained by the Hyperfine Coupling Mechanism.<sup>2</sup> The slopes of the MFE curves depend on the average hyperfine coupling field of the two component radicals, which has been estimated from the expression  $B_{1/2} = 2(B_1^2 + B_2^2)/(B_1 + B_2)$  where  $B_i$  = isotropic hyperfine field of  $i$ -th radical. The semi-empirical UHF INDO method was followed to estimate the  $B_{1/2}$ .<sup>12</sup> The calculated values do not change significantly from I to IV and are of the order of 53 gauss. This roughly agrees with the experimental  $B_{1/2}$  (50 gauss).

(3) The MFE due to the isotropic hyperfine coupling, however, saturates out at low fields and therefore, can not be the explanation for variation at high fields. The mechanism appropriate for high fields is the Relaxation Mechanism proposed by Nagakura and Hayashi.<sup>1,13</sup> At zero field the relaxation rate  $T_{\pm} \rightarrow S$  is large but as the field increases the relaxation rate decreases, eventually leading to the escape of spin-trapped triplet radicals thus causing an increase in the free radical yield. The accepted mechanism of spin relaxation

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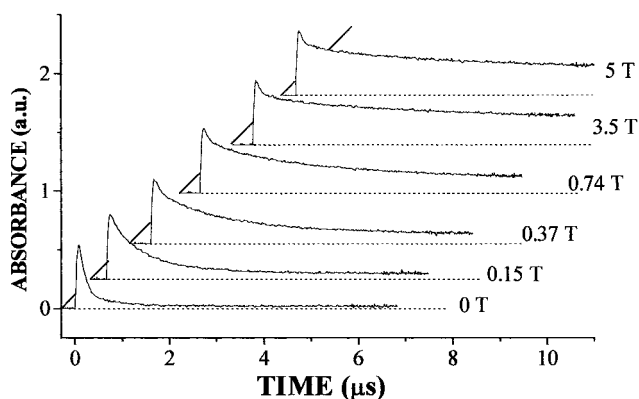


Fig. 1. Decays of the transient absorption observed at 680 nm for (I) ( $1 \times 10^{-4}$  M)/BP ( $1 \times 10^{-3}$  M) system in SDS micelle (0.1 M) in presence of various external high fields.

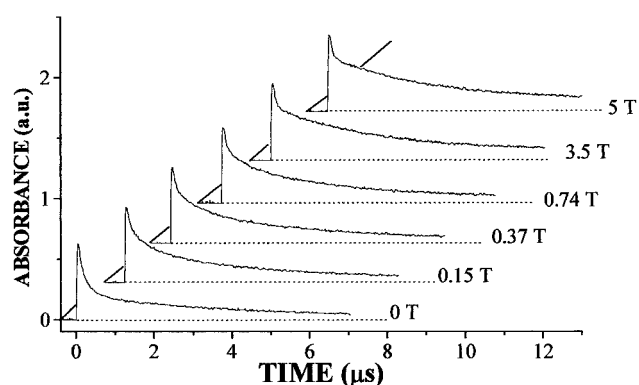


Fig. 2. Decays of the transient absorption observed at 680 nm for (II) ( $1 \times 10^{-4}$  M)/BP ( $1 \times 10^{-3}$  M) system in SDS micelle (0.1 M) in presence of various external high fields.

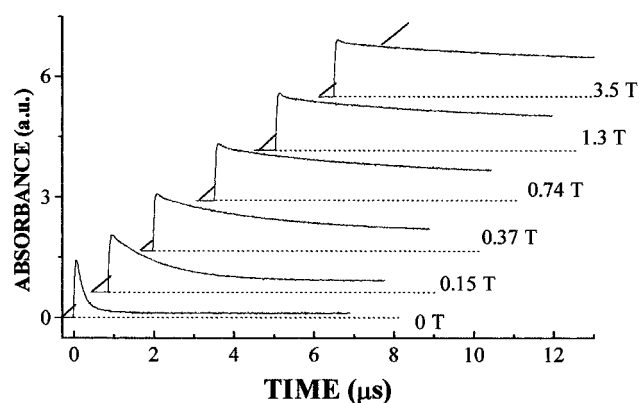


Fig. 3. Decays of the transient absorption observed at 680 nm for (V) ( $1 \times 10^{-4}$  M)/BP ( $1 \times 10^{-3}$  M) system in SDS micelle (0.1 M) in presence of various external high fields.

is that the molecules with anisotropic  $g$  value or anisotropic  $HFC$  tumble leading to spin relaxation. Additionally, the  $\Delta g$  mechanism proposes an increase in the  $S \leftrightarrow T_0$  rate with field, which should, in principle, cause a decrease of lifetime and eventually a saturation. However, in the case of the radical

pair under discussion, the observed yield and the lifetime increase and not decrease with field, indicating the irrelevance of the  $\Delta g$  mechanism. The residual MFE in the presence of  $Gd^{3+}$ , which has been ascribed to the  $\Delta g$ -Mechanism by Hayashi,<sup>11</sup> has been found to be negligibly small, from which we conclude that the  $\Delta g$ -mechanism is not relevant for explanation of high-field variation. The anisotropic  $\partial g$  and  $\partial_{HFC}$  contribution however, need to be considered. For the set of acceptors investigated, we notice that the low-field-induced change and the high-field induced change roughly bear a constant proportion. This correlation goes in support of the contention that  $\partial_{HFC}$  is the main contributor. The shape of the lifetime vs. field curve is indicative of a small  $\partial g$  parameter and a large  $\tau_C$  (correlation time).<sup>1,13</sup>

(4) The MFE is distinctly larger for the acceptor I compared to the acceptor II. One may try to understand this roughly in terms of the unpaired  $\pi$ -electron density at the carbon atom near the H-atom at the para position of the phenyl ring. In the radical II, the separation between the ring C atom and the H atom has increased; that should make the  $HFC$  weaker. However, our calculation of  $HFC$  shows there is hardly any difference between the hyperfine fields of the two molecules, I and II. This has led us to suppose that in addition to other mechanisms the field-insensitive  $-CH_3$  rotation in II is contributing to the spin relaxation rate. Unlike the  $\partial_{HFC}$ -induced spin relaxation, this methyl-rotation-induced relaxation is field independent and hence, just like the S.O coupling, the  $-CH_3$  rotation reduces the MFE in II. The  $CH_3$ -rotation may be represented by an Angular Momentum vector ( $R_z$ ) which is capable of interacting with the component of spin-vector parallel to the  $R_z$ . Since the C-H bond has a bond moment of 0.4 Debye, its rotation produces a circular current and hence, a local magnetic field is generated. This magnetic field may interact with spin-vector leading to a change in the latter.

(5) The acceptor V can produce two types of  $^3RP$  – one by H-abstraction from the SDS molecule ( $^3RP-1$ ) and the other by electron acceptance from the donor hydrocarbon, biphenyl ( $^3RP-2$ ). The MFE on the  $^3RP-2$  is much larger than that on  $^3RP-1$ . At intermediate concentrations of biphenyl, both  $^3RP-1$  and  $^3RP-2$  are formed and the observed MFE is an average of the two MFEs. Since both  $^3RP-1$  and  $^3RP-2$  are surface located but the MFE is small for one and large for another, we conclude that 2D-geminate recombination is not the cause of high MFE in  $^3RP-2$ .<sup>2,14,15</sup>

(6) In order to explain the increase of the peak height (at  $t = 0$ ) with increase of field in the case of TPP<sup>+</sup>/skatole system,<sup>16</sup>) we had to assume two channels for the formation of  $^3RP$  by electron transfer – one fast, and the other slow. The static quenching of the acceptor by the donor leads to a prompt growth of the  $^3RP$ , while the dynamic quenching of the acceptor located at the outer periphery leads to a comparatively slow growth of the  $^3RP$ .

## Conclusion

MFE is found to be very large in the case of all acceptors, specially I and V. The radical yield increases nearly 20 times the zero-field value if a 5T field is applied. This large MFE may be exploited to control magnetically reactions photosensitized by pyrylium ions. The reasons for the observed large MFE are not immediately obvious. The nature of the dynam-

ics in the confined region could be an important factor. In this case the two component radicals of the RP are placed in two different regions of the micelles, one in the hydrocarbon core and the other at the interface. This might allow sufficient time for a RP to spin-evolve prior to recombination, leading to a large MFE.

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