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REVIEW COMMENTARY

MAGNETIC FIELD EFFECTS UPON PHOTOCHEMISTRY OF BIFUNCTIONAL CHAIN MOLECULES

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External magnetic field effects are discussed for three typical examples of photoreactions involving biradical intermediates: photo-induced intramolecular electron transfer in chain molecules D—$(CH_2)_n$—A consisting of an electron donor (D) and an acceptor (A), intramolecular hydrogen abstraction in bifunctional species :X—$(CH_2)_n$—YH containing a hydrogen donor (YH) and an acceptor (:X in the excited triplet state) and photochemical homolytic ring opening of a cyclic ketone which yields a biradical consisting of an acyl and an alkyl group. There has been progress in the elucidation of reaction mechanisms through the analysis of magnetic field effects on lifetimes of reaction intermediates and product yields in radical reactions involving biradicals. Extremely small interactions such as the Zeeman energy and hyperfine interaction may give rise to a large change in the distribution of photo-products derived from bifunctional chain molecules.

INTRODUCTION

Although there have been a number of reports on magnetic field effects (MFE) on chemical reactions, clear experimental evidence of MFE was not obtained until recently.[1] Photosensitized decomposition of dibenzoyl peroxide is one of the earliest observations of photochemical MFE in the liquid phase.[2]

Nagakura and co-workers[3,4] have presented the general theory for the radical pair model (RPM) in interpreting anomalous ESR spectra observed for irradiated organic single crystals. It was shown that the singlet–triplet mixing can be induced by hyperfine coupling and the Zeeman mechanism. This RP model has been playing a central role in explaining nuclear and electronic spin polarization induced by chemical reactions (CIDNP and CIDEP).[1a,5] This model also provides a theoretical basis for MFE on reaction rates and product yields of chemical reactions through radical pairs. For example, MFE on reaction yields were analytically formulated for various cases according to the RP model.[6] Sakaguchi *et al.*[7] proposed a classification of the external magnetic field effects by taking account of the relative importance of the hyperfine coupling and the electronic Zeeman terms. Hayashi and Nagakura[8] studied the external magnetic field effects by including explicitly the relaxation of electronic spins.

The purpose of this review is to show that MFE on chemical reactions can provide a useful method for elucidating reaction mechanisms and techniques for controlling reaction rates and product yields, and also that studies on MFE in the condensed phase are at present approaching maturity.

This paper is concerned with MFE on the dynamic behaviour of biradicals produced in photochemical reactions of bifunctional chain molecules. The emphasis is put on the most recent studies mainly by Japanese workers in the late 1980s and 1990s.

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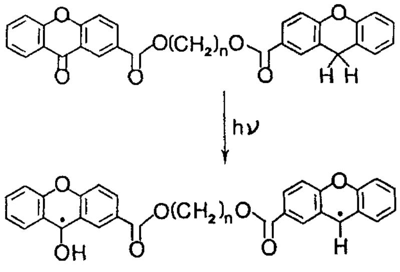
Pioneering work by Weller and co-workers[9–11] was concerned with external magnetic field effects on the yield of the molecular triplet state of pyrene through an exciplex in the singlet state derived from excited pyrene and *N,N*-dimethylaniline. They extended their studies to intramolecular exciplex formation by synthesizing bichromophoric chain molecules containing 1-pyrenyl and 4-*N,N*-dimethylaminophenyl groups.[12–14] It is also possible to identify another type of modification from an intermolecular hydrogen abstraction between an aromatic carbonyl compound and a hydrogen donor in micellar media.[15] Tanimoto and co-workers[16,17] employed polymethylene-linked systems consisting of a hydrogen donor and acceptor, e.g. bifunctional chain molecules containing xanthone and xanthene moieties, which on photolysis can yield a biradical as shown in Scheme 1.



Scheme 1

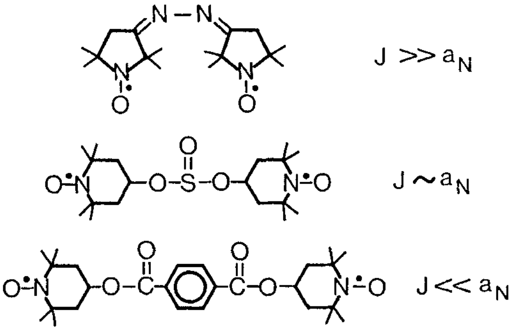
Hence the photochemistry of bichromophoric chain molecules bridges the gap between photochemistry in homogeneous and inhomogeneous solutions.

Since spin correlation effects in radiolysis has been reviewed by Brocklehurst[18] and magnetic field effects in chemical kinetics and related phenomena have been extensively discussed by Steiner and Ulrich,[1a] basic concepts and theory will not be repeated here in detail.

CHAIN LENGTH EFFECTS

Magnetic properties of biradicals

Consider a hypothetical biradical $^{\bullet}X{-}(CH_2)_n{-}Y^{\bullet}$ which has two spin states, namely singlet and triplet. The separation of these states, $2J$, depends on the chain length, n, because the exchange interaction (J) between two unpaired electrons within radical sites X and Y decreases approximately exponentially with respect to the inter-radical distance. On the other hand, the hyperfine interaction between the electronic spin and nuclear magnetic moments in the two fragments, X and Y, is independent of the chain length n. For example, the properties of nitroxide biradicals have been investigated by means of ESR spectroscopy.[19,20] Three different situations have been observed, $J \gg a$, $J \approx a$ and $J \ll a$, as shown in Scheme 2.



Scheme 2

A spin-motion expression for a radical pair with one magnetic nucleus of general spin I [hyperfine coupling (hfc) constant a] was obtained in the zero-field by Salikov:[21]

$$^{S}p_{T}(t) = I(I+1)(a^2/R^2)\sin^2(Rt/2)$$

where

$$R = I(I+1)a^2 + (2J + a/2)^2$$

(The left superscript of the conditional probability $^{S}p_{T}(t)$ denotes the multiplicity in which the radical pair was formed at $t = 0$ and the right subscript denotes the multiplicity that is probed at time t.) From this equation it is concluded that singlet–triplet transitions are suppressed owing to the factor a^2/R^2 when the magnitude of the exchange interaction exceeds that of hyperfine coupling. Therefore, one of the necessary conditions for observing MFE is that the separation between the singlet and the triplet states ($2J$) must be negligibly small in comparison with the hyperfine interaction between the electronic spin and nuclear magnetic moments, i.e. $2J \ll a$. Whereas $2J$ is dependent on the inter-radical distance, the magnitude of a is almost insensitive to the chain length. The relationship $2J \ll a$ may be satisfied at longer chain lengths.

Appearance of large magnetic field effects with $n \geq 10$. An empirical rule

An intramolecular excimer formation is highly efficient at the particular chain length of 3 for a series of bifunctional chain molecules, $Ar{-}(CH_2)_n{-}Ar$, where Ar represents an aromatic chromophore.[22] In a similar manner, we have systematically studied the influence of the chain length on MFE for several series of biradicals produced on photolysis.[23–28] We can conclude that relatively large magnetic field effects appear for long chain biradicals with $n \geq 10$. When the linking chain contains heteroatoms, the total number of atoms connecting the two radical sites is considered to be the chain length. The following are typical examples of the chain length dependence of MFE.

Nakagaki and co-workers[23–26] measured magnetic field effects on photo-redox reaction yields of chain molecules, A—$(CH_2)_n$—D, where A = 4-nitrophenoxyl or 4-nitro-1-naphthoxyl and D = anilino. The escape process is identified as a bimolecular reaction, while the cage process is characterized as an intramolecular photo-redox reaction. In both cases, oxidative dealkylation takes place on photolysis, which yields unsubstituted aniline (see later, Switching of reaction pathways due to magnetic field effects). Large magnetic field effects are observed for longer chain species with $n \geqslant 8$. The results obtained for the nitronaphthoxyl series are shown in Figure 1. Since the ether oxygen and the anilino nitrogen can be regarded as a part of the linking chain, the total number of connecting atoms is $\geqslant 10$.

Tanimoto *et al.*[16] studied photo-induced intramolecular hydrogen abstraction for a series of chain species containing xanthene and xanthone moieties. They found a sharp rise in the chain length dependence of MFE at $n = 6$ (see Figure 2). Because their chain compounds contain two ester bonds, the total number of linking atoms is ten at $n = 6$. It should be noted that all the species shown in Figure 2 have an average distance of $\geqslant 1{\cdot}2$ nm. Another chain molecule studied by Tanimoto and co-workers[29,30] consists of phenanthryl (Phen) and *N*,*N*-dimethylaminophenyl (DMA) chromophores. They observed a conspicuous intensity enhancement of exciplex fluorescence for Phen—$(CH_2)_n$—DMA at $n = 10$ in the presence of a magnetic field (see Figure 3).

Staerk *et al.*[13] reported similar phenomena for pyrenyl—$(CH_2)_n$—DMA. In their case, ten is also a 'magic number' where the exciplex emission is enhanced.

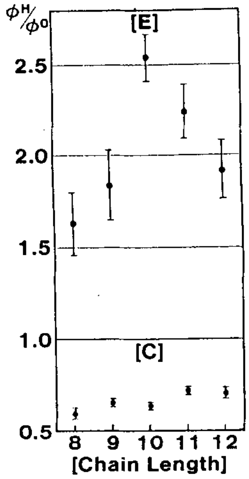


Figure 1. Dependence of the relative yield, Φ^H/Φ^0, on the chain length (n) observed for the photoreactions of 4-$O_2NC_{10}H_6$-1-$O(CH_2)_nNHC_6H_5$. The escape product ([E]) was identified as 4-$O_2NC_{10}H_6$-1-$O(CH_2)_{n-1}CHO$, which is formed by the bimolecular photo-redox reaction of 4-$O_2NC_{10}H_6$-1-$O(CH_2)_nNHC_6H_5$. On the other hand, the cage product ([C]) was characterized as 4-$ONC_{10}H_6$-1-$O(CH_2)_{n-1}CHO$, which is produced by the intramolecular photo-redox reaction. The error bar represents the standard deviation

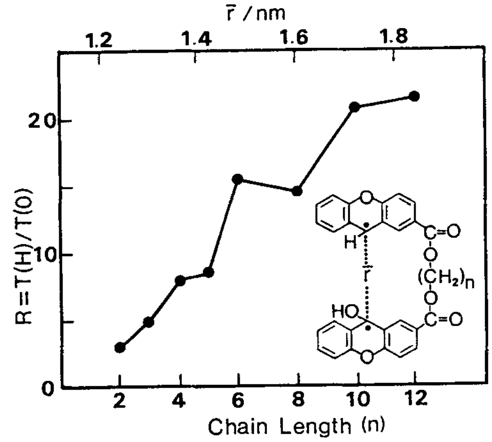


Figure 2. Dependence of magnetic field effect parameter R [$=\tau(0{\cdot}8\ \mathrm{T})/\tau(0\ \mathrm{T})$] on chain length for photochemistry of XO-(n)-XH in acetonitrile. The mean inter-radical distance is also shown at the top. See also Table 2

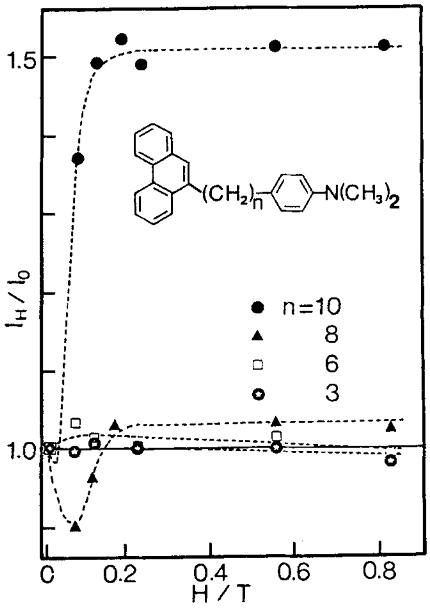


Figure 3. Magnetic field effects on photo-stationary fluorescence intensity at 540 nm of Phen—$(CH_2)_n$—DMA ($n = 3, 6, 8, 10$) obtained by photo-excitation at 308 nm. I_0 and I_H denote the fluorescence intensity in the absence and presence of a magnetic field, H

Schulten and Bittl[31,32] calculated the magnetic field dependence of the triplet yield of charge-separated biradicals derived from pyrenyl—$(CH_2)_n$—DMA ($n = 8$–10) by taking account of a stochastic folding motion of the methylene chain. A simpler explanation will be given below and can be applied to the observation of large magnetic field effects when $n \geqslant 10$. The dependence of the exchange interaction J on the inter-radical distance r and the distribution of the end-to-end distance are calculated according to the equations quoted by Bittl and Schulten.[32] The following equation is used for evaluating the exchange interaction J:

$$J(r) = J_0 \exp(-\alpha r) \qquad (1)$$

$J_0 = 9{\cdot}46 \times 10^8$ mT and $\alpha = 21{\cdot}36\ \mathrm{nm}^{-1}$; r is the inter-radical distance. A small variation in r may make a great difference to the magnitude of $2J$, e.g. $2J$ ($r = 1{\cdot}0$ nm) $= 1{\cdot}0$ mT, $2J$ ($r = 1{\cdot}1$ nm) $= 0{\cdot}12$ mT and $2J$ ($r = 1{\cdot}2$ nm) $= 0{\cdot}014$ mT. Since the magnitude of the hyperfine interaction a is typically of the order of 1–10 mT, $2J \ll a$ can be satisfied in conformational isomers with $r \geqslant 1{\cdot}1$ nm. The distributions of the end-to-end distance (r) for chain species with $n = 9$ and 10 are obtained by using the following equation:

$$p_0(r) = r^2(r - r_{\max})^2 \exp\{-[(r - r_1)/r_2]^2\} \qquad (2)$$

This equation was proposed by Bittl and Schulten[32] for a smooth fit to the actual distribution of end-to-end distance, in which the hydrogen atoms were not explicitly described but only included through an increase in the van der Waals radii of the carbon atoms. The results obtained for $n = 9$ and 10 are shown in Figure 4. It can be seen that the distribution of nine methylene conformers with $r \geqslant 1{\cdot}1$ nm is very small in comparison with the rest of the conformer distribution. On the other hand, the abundance of conformers with $r \geqslant 1{\cdot}1$ nm is fairly high in the case of species with $n = 10$. This difference in the end-to-end distance distribution can readily account for the appearance of large MFE when $n \geqslant 10$.

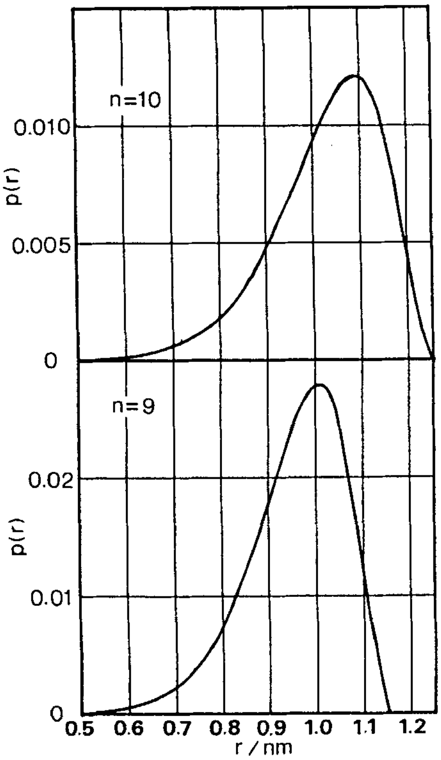


Figure 4. Distribution of end-to-end distances simulated by using equation (2) (top, $n = 10$; bottom, $n = 9$). Parameters given in ref. 32 were used: $r_{\max} = 11{\cdot}5$, $r_1 = 25$, $r_2 = 5$ at $n = 9$ and $r_{\max} = 12{\cdot}5$, $r_1 = 30$, $r_2 = 6$ at $n = 10$

Tanimoto *et al.*[16] suggested that the exponential approximation of the $2J$ function is inadequate, because the $2J$ values, calculated by averaging all the $2J(r)$ values for the distribution, do not reproduce the observed tendency. The exchange interaction J may not be a simple function of the inter-radical distance. In other words, the influence of the relative orientation of two radical sites on J must be explicitly taken into consideration for a detailed explanation of the dependence of MFE on chain length.

MAGNETIC FIELD EFFECTS ON REACTION RATES AND PRODUCT YIELDS

Cage and escape processes in radical reactions

A radical pair produced on photolysis in solution is surrounded by solvent molecules and still retains the spin multiplicity of its precursor at the nascent stage. While the singlet radical pair in a solvent cage can readily undergo recombination to yield a so-called cage product, the triplet radical pair may not easily recombine to produce a stable species with the singlet spin multiplicity. Therefore, the triplet radical pair undergoes a so-called escape process to form an escape product. Cage and escape processes are depicted in Figure 5. We can generally expect that an appreciable change in the intersystem crossing rate between the singlet and the triplet radical pairs $k_{\mathrm{isc}}(\mathrm{ST})$ can affect the decay kinetics of radical pairs and product distributions.

Since the MFE described in this paper is mainly due to the hyperfine coupling (hfc) mechanism, $k_{\mathrm{isc}}(\mathrm{ST})$ decreases in the presence of magnetic fields. When the hfc mechanism is of dominant importance, the reaction yields of cage products derived from the triplet radical pair decrease, whereas those derived from the singlet pair increase on application of an external magnetic field. The opposite relationship is expected for the reaction yields of escape products. The yields of escape

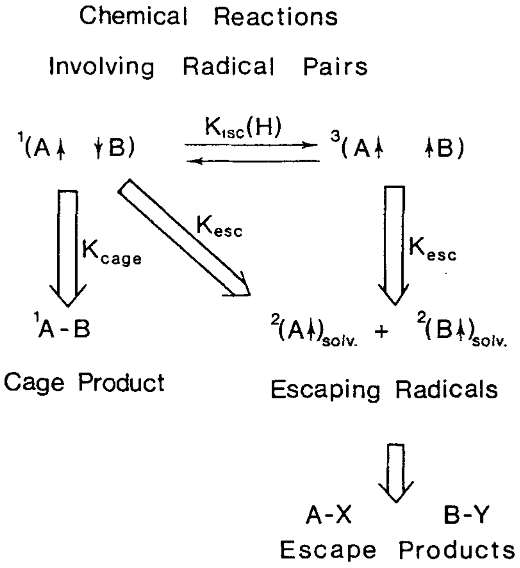


Figure 5. Simplified kinetic scheme for a reaction involving radical pairs

products of triplet pair origin increase, whereas those of singlet pair origin decrease in the presence of magnetic fields.

Magnetic field effects on reaction rates or product yields are observed when k_{isc}(ST) is of the same order of magnitude as that of the escape process. If k_{isc}(ST) is negligibly small in comparison with the escape rate, k_{esc}, detection of MFE on rates or yields may be difficult. Some photochemical reactions in micellar media have been selected for the study of MFE. The role of micellar media is to slow the escape process. A methylene chain can act both as a spacer and as a linker which prevents the complete diffusion of two radical sites, X and Y.

If k_{isc}(ST) is negligibly small compared with the rate for cage product formation, k_{cage}, magnetic field effects on the cage product may be small in the reaction of singlet pair origin. When the triplet pair is initially generated, the cage product cannot be formed directly from the triplet pair. Therefore, the cage product is formed after intersystem crossing from the triplet to the singlet radical pair. Since k_{isc} is greatly dependent on the field strength, H, the magnetic field effects on cage product yields in triplet pair reactions may be larger than those in singlet pair reactions. In fact, most MFE studies are concerned with photochemical reactions of initially prepared triplet pairs. It is interesting that Weller and co-workers[12-14] observed magnetic field effects on the dynamic behaviour of singlet radical pairs, whereas Tanimoto and co-workers[15-17] studied triplet radical pairs.

Switching of reaction pathways due to magnetic field effects

We have observed that the product distribution of photo-redox reactions for a homologous series of bichromophoric species containing nitronaphthoxyl and anilino moieties, $4\text{-}O_2NC_{10}H_6\text{-}1\text{-}O(CH_2)_nNHC_6H_5$, depends on the chain length.[25-26] Figure 6 shows that several photo-products are formed through cage and escape processes. The cage process is an intramolecular photo-redox reaction, which yields $4\text{-}ONC_{10}H_6\text{-}1\text{-}O(CH_2)_{n-1}CHO$ and aniline. The escape process is a bimolecular redox reaction which gives $4\text{-}ONC_{10}H_6\text{-}1\text{-}O(CH_2)_nNHC_6H_5$, $4\text{-}O_2NC_{10}H_6\text{-}1\text{-}O(CH_2)_{n-1}CHO$ and aniline.

The product distribution of the nitronaphthoxyl series was recorded as a function of chain length in the absence and presence of an external magnetic field (see Table 1). The branching ratio between the cage and escape processes, R_b is critically dependent on the chain length, n, and the magnetic field strength, H. When $n = 8$, the major process in zero field is the intramolecular photo-redox reaction, whereas the intermolecular escape reaction becomes dominant in the presence of a high field, 0·64 T (see Figure 7). For longer chain species ($n \geqslant 9$), the intramolecular cage process always predominates in the absence or presence of the magnetic field.

A prototype of reaction switching due to MFE has been reported for the nitronaphthoxyl species with $n = 12$.[25] The escape/cage branching ratio depends on the time of irradiation when acetonitrile was used as a solvent. Addition of γ-cyclodextrin also enhances the escape product yield (see Table 1). This suggests that the inclusion complexation of the donor (D) or the acceptor (A) moiety plays an important role in suppressing the intramolecular cage product formation.

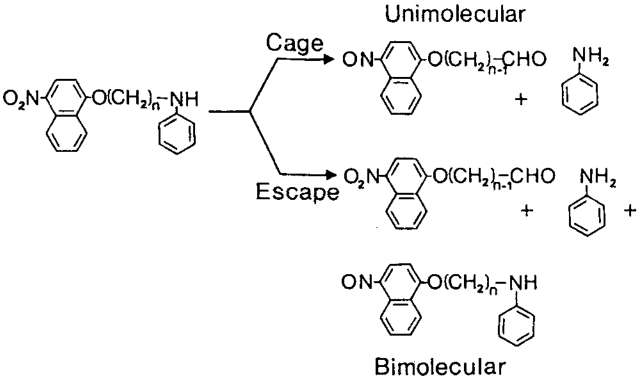


Figure 6. Cage and escape processes in photochemistry of $4\text{-}O_2NC_{10}H_6\text{-}1\text{-}O(CH_2)_{12}NHC_6H_5$. The cage process is identified as a unimolecular reaction and the escape process is a bimolecular redox reaction

It should be noted that such a small perturbation caused by an external magnetic field (0·64 T) can give rise to appreciable changes in product distributions.

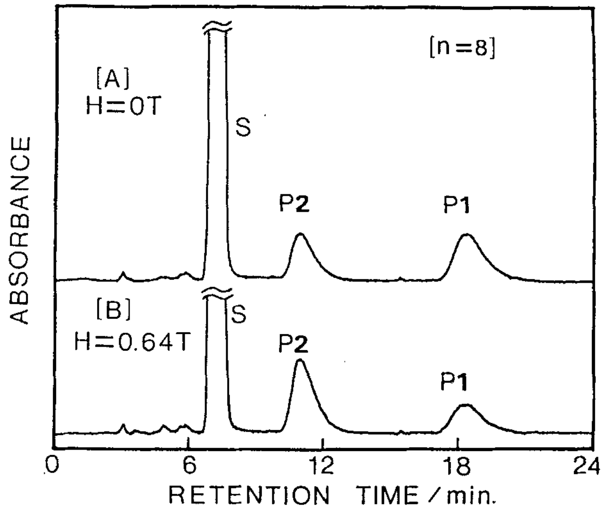


Figure 7. Chromatograms recorded after photolysis of chain species $4\text{-}O_2NC_{10}H_6\text{-}1\text{-}O(CH_2)_8NHC_6H_5$ in (A) the absence and (B) the presence of an external magnetic field (0·64 T). S = starting species; P1 = cage product with a nitroso-naphthoxyl chromophore; P2 = escape product with a nitronaphthoxyl chromophore. Concentration, $1 \cdot 2 \times 10^{-4}$ M in benzene solution. Absorbance at 370 nm was monitored. Normal-phase column, Cica-Merck LiChrosorb Si 60 (10 μm)

Table 1. Magnetic field effects on branching ratio in competitive photoreactions of 4-nitro-1-naphthoxyl—$(CH_2)_n$—NHC_6H_5 in benzene

n[a]	$R_b(0)$[b]	$R_b(H)$[c]
8	0·62	1·74
9	0·34	0·95
10	0·18	0·77
11	0·18	0·56
12	0·18	0·60
12	0·51[d]	1·06[d]
12	0·62[e]	1·49[e]

[a] n = chain length.

[b] $R_b(0)$ = Φ(escape product)/Φ(cage product) in the absence of an external magnetic field.

[c] $R_b(H)$ = Φ(escape product)/Φ(cage product) in the presence of an external magnetic field H (0·64 T).

[d] Data obtained in DMF–water mixed solvent (80 : 20, v/v).

[e] Data obtained in DMF–water mixed solvent (80 : 20, v/v) containing $6 \cdot 9 \times 10^{-3}$ M γ-cyclodextrin.

MFE ON PHOTOCHEMICAL REACTIONS VIA BIRADICALS

Mechanistic classification of photochemical biradical formation

Figure 8 illustrates three typical examples of biradical photochemistry, i.e. photo-induced homolytic ring cleavage, hydrogen abstraction and electron transfer. The three kinds of photoreactions are described in the following sub-sections.

Photo-induced electron transfer

A paper by Weller *et al.*[12] on intramolecular exciplex formation for pyrenyl—$(CH_2)_n$—DMA is one of the earliest studies of MFE on bichromophoric photochemistry. The chain length was varied from 6 to 16. The higher homologues ($n \geqslant 10$) exhibit an exciplex fluorescence, the intensity of which is appreciably enhanced on application of external magnetic fields.[13]

Tanimoto and co-workers[29,30] studied the MFE on the exciplex fluorescence of bichromophoric chain molecules containing phenanthryl (Phen) and *N,N*-dimethylaminophenyl (DMA) moieties in acetonitrile. The methylene chain length was varied from 3 to 10. These compounds were investigated by different spectroscopic methods, i.e. time-resolved absorption and emission measurements. A singlet biradical formed after photo-excitation of the Phen chromophore at 300 nm is involved in exciplex formation. Since the $k_{isc}(H)$ decreases on application of external magnetic fields, the fluorescence intensity of the exciplex derived from the singlet biradical is enhanced by a factor of 1·5 for the species with $n = 10$.

Tanimoto and co-workers also detected another kind of fluorescence due to the excited state of an electron donor–acceptor complex, which is formed on UV excitation of the ground-state complex at 330 nm. Two kinds of fluorescence could be distinguished by measuring emission lifetimes and fluorescence excitation spectra. The MFE was observed only for the

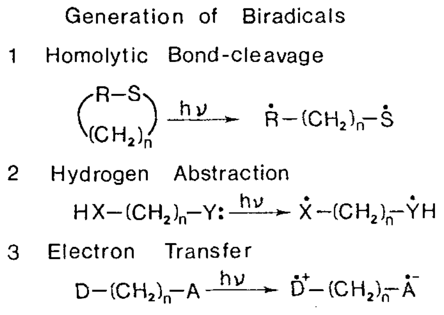


Figure 8. A general scheme for photochemical generation of biradical intermediate

exciplex dynamically generated after excitation of an extended conformer of the methylene-linked species.

MFE studies on photoelectron transfer in porphyrin derivatives containing viologen acceptors have been reported by Matsuo's and Mataga's groups.[33–37] Nakamura *et al.*[33] elucidated MFE on the back electron transfer of tetraphenylporphyrins ($ZnPC_nV$, where *n* denotes the number of linking methylene groups) by means of laser flash photolysis. The reverse electron transfer rate was substantially suppressed by a factor of ten for $ZnPC_8V$ in the presence of magnetic fields $\geqslant 0{\cdot}1$ T. The total number of atoms connecting two chromophores in $ZnPC_8V$ is 13, because a phenoxyl moiety can be regarded as part of a linker.

Saito *et al.*[34] examined MFE on the lifetime of the charge-separated biradical for porphyrin–methylviologen linked systems, $PnMV^{2+}$ (*n* refers to the number of methylene groups), in polar media by using nanosecond laser photolysis. A drastic increase in the lifetime was observed on application of magnetic fields. For example, the biradical lifetime was almost three times longer than the zero-field value in the case of $P11MV^{2+}$ under a magnetic field of 50 mT. They showed that the long-lived biradical is formed through an intramolecular electron transfer from the porphyrin triplet state. Fourteen atoms are involved in the spacer part of $P11MV^{2+}$. Matsuo and co-workers[35–37] studied the influence of the media and additives on MFE. They investigated the photochemical electron transfer of bichromophoric chain molecules $D—(CH_2)_n—A$, where the donor D is zinc porphinate (ZnP) or phenothiazine and the acceptor A is a viologen moiety (V).

Usui *et al.*[35] reported photo-induced electron transfer from amphiphilic ZnP in bilayer membranes to various V derivatives in the presence of external magnetic fields. Application of magnetic fields appreciably retarded the reverse electron transfer when the photoreduced viologen moiety was tightly bound to the oxidized counterpart (ZnP cation radical) by either coulombic or amphiphilic interactions.

Yonemura *et al.*[36] observed MFE on photochemical electron transfer for phenothiazine–viologen linked compounds in the presence of cyclodextrins in aqueous solutions. Laser irradiation at 351 nm generated a charge-separated biradical. The decay rate of the biradical was decreased by an order of magnitude on going from 0 to 0·3 T. They suggested that an escape process is a bimolecular reaction involving the starting species and the charge-separated biradical.

Zinc tetraporphinate–viologen methylene-linked pairs have been studied in reversed micelles (AOT–isooctane or *n*-hexane) by laser photolysis at 351 nm.[37] The radical decay rate of the porphyrin–viologen linked compounds was decreased by an order of magnitude to reach a plateau region above 0·3 T. The large external magnetic field effects were explained on the basis of Zeeman splitting of the triplet in combination with electron spin relaxation from the sublevels. Supporting evidence for this was obtained by the use of paramagnetic lanthanide ions.

Hiramatsu *et al.*[38] observed MFE on photo-induced absorbance change for $4\text{-}O_2NC_6H_4O(CH_2)_{12}\text{-}4\text{-}OC_6H_4P(C_6H_5)_2$ (4NP-TPP). The photo-redox reaction of 4NP-TPP is characterized as an intramolecular oxygen transfer from the NO_2 group to triarylphosphine, which yields the nitrosophenoxyl and phosphine oxide moieties. They suggested that the primary photochemical process is a photo-induced electron transfer from triarylphosphine moiety to the nitrophenoxy acceptor in the excited triplet state.

Bichromophoric species containing a 4-(4-phenylamino)phenoxyl group and benzophenone chromophore[39] have been studied by laser photolysis in the presence of external magnetic field. Both electron transfer and hydrogen abstraction reactions are involved in the primary process. Biradical lifetimes are lengthened by a factor of 15 in the presence of an external magnetic field (0·56 T).

It should be noted that the most commonly employed chain length is 8–12 methylene groups, which corresponds to more than ten atoms connecting the two radical sites.

Photo-induced hydrogen abstraction

Photochemical hydrogen (H) abstraction reactions have been extensively studied for aromatic carbonyl compounds. *n*-Alkyl anthraquinone-2-carboxylate (AQC) is a prototype of chain molecules which undergo an intramolecular hydrogen abstraction reaction.[40] Whereas one of the two carbonyl groups in the anthraquinone moiety acts as a hydrogen acceptor, the hydrogen donor site in the alkyl chain of AQC esters is not well established.

Since a xanthene moiety is known as a good hydrogen donor, Tanimoto and co-workers[17] studied photochemical H abstraction by a xanthone moiety from the xanthyl hydrogen in α-(xanthone-2-carbonyloxy)-ω-(xanthene-2-carbonyloxy) alkanes [hereafter abbreviated as XO-(*n*)-XH, $n = 2–12$, and the structure described in Scheme 1]. The sites involved in an intramolecular photoreaction were identified by means of laser flash photolysis.

Tanimoto *et al.*[17a] extended their study by replacing the xanthone moiety in XO-(*n*)-XH with anthraquinone, benzophenone and acetophenone chromophores and keeping the xanthene as an H donor. They reported MFE on lifetimes of biradicals formed by intramolecular hydrogen abstraction reactions. The results are summarized in Table 2. They also examined the effects of trivalent lanthanide ions on the lifetimes of the methylene-chain-linked triplet biradical shown in Scheme 1 on application of external magnetic fields.[17b]

Table 2. Magnetic field effects on lifetimes of biradicals derived from Ar—$(CH_2)_{12}$—XH[a]

Ar	XO[b]		XO	
Solvent	Acetonitrile		Benzene	
Wavelength[c] (nm)	345	380	345	490
τ (0 T) (μs)	0·14	0·18	0·13	0·20
τ (0·8 T) (μs)	3·0	4·0	4·2	4·8
R[d]	21·4	22·2	32·3	24·0
Ar	AQ[e]		BP[f]	
Solvent	Benzene		Acetonitrile	
Wavelength (nm)	345	490	345	545
τ (0 T) (μs)	0·14	0·17	0·38	0·23
τ (0·8 T) (μs)	3·0	3·4	5·1	5·7
R	21·4	20·0	13·4[g]	24·8[g]
Ar	AP[h]			
Solvent	Acetonitrile			
Wavelength (nm)	345			
τ (0 T) (μs)	8			
τ (0·8 T) (μs)	10			
R	1·25[g]			

[a] XH = xanthene-2-carbonyloxy.
[b] XO = xanthone-2-carbonyloxy.
[c] Wavelength at which transient decay curves were observed.
[d] R = ratio of lifetimes observed in the presence and absence of 0·8 T = τ(0·8 T)/τ(0 T).
[e] AQ = anthraquinone-2-carbonyloxy.
[f] BP = 4-benzoylphenoxy.
[g] These values are less reliable owing to interference from T–T transitions.
[h] AP = 4-acetylphenoxy.

Dipole–dipole interactions seem responsible for the quenching of the triplet biradical by the lanthanide complexes, while the Heisenberg exchange interaction is dominant in the quenching by the copper complex.

The lifetime of the triplet biradical derived from XO-(n)-XH decreases to a minimum (140–170 ns) at 270–340 K, and then increases slightly (200–210 ns) at 350 K.[17c] This anomaly may result from the difference in the temperature dependence of the rate processes of chain motion and end-to-end recombination reaction. Thus, kinetic analysis revealed that the biradical lifetime is determined by a combination of rate constants: k_c for the collision of two terminal groups, k_0 for the dissociation of terminal groups, k_{isc} for the intersystem crossing of the biradical and k_r for the end-to-end recombination.[17c]

Although H abstraction reactions by nitroaromatic species have been investigated by many workers, the photochemical primary process has not been fully understood in comparison with that of aromatic carbonyl compounds. Nakagaki *et al.*[27] studied intramolecular photo-redox reactions of A—$(CH_2)_n$—D in benzene, where A = 4-nitrophenoxyl, D = *N*-benzylanilino and n = 12. They observed magnetic field effects on reaction yields for the cage and escape processes. Two different cage and two different escape processes were identified through MFE on the photo-redox reaction yield. The major process is hydrogen abstraction at the benzylic position of the *N*-benzylanilino chromophore. Another process is H abstraction at the methylene group adjacent to the anilino nitrogen. Two different biradicals were formed in the intramolecular reaction, and therefore two kinds of magnetic field effects are observed for the redox yields. The branching process is shown in Figure 9. Magnetic field effects on the cage product formation via BR-1 biradical were enhanced on substitution of carbon-13 for a normal carbon at the α-position in the benzylic radical.[27]

When the anilino derivatives are irradiated instead of the *N*-benzylanilino compounds, the hydrogen abstraction takes place exclusively at the CH_2 group adjacent to the aniline nitrogen. One of the most extensively studied species is 4-nitro-1-naphthoxyl—$(CH_2)_n$—NHC_6H_5.[25,26] Since the cage and the escape processes are competitive, the branching ratio of the two different reaction pathways is dependent on the applied field strength, chain length and solvent properties (see Table 1).

The magnetic field (H) dependence of the relative yields Φ^H/Φ^0 for the species with n = 12 is shown in Figure 10. Figure 11 illustrates the reaction scheme and kinetic parameters for analysing the observed results. The dependence of cage and escape product formation on H is described by the following equations:

$$(\Phi^H/\Phi^0)_{\text{cage}} = k_{isc}(H)\,[k_{isc}(0)+k_{esc}]/k_{isc}(0)\,[k_{isc}(H)+k_{esc}] \quad (3)$$

$$(\Phi^H/\Phi^0)_{\text{escape}} = [k_{isc}(0)+k_{esc}]/[k_{isc}(H)+k_{esc}] \quad (4)$$

These equations were derived from the following three assumptions:

(1) photo-stationary conditions are satisfied, i.e. $d[^3BR]/dt = d[^1BR]/dt = 0$;
(2) the cage product formation is much more rapid than other processes occurring from ^{1}BR, eg. $k_{isc} \ll k_{cage}$; and
(3) the external magnetic field has no effect on k_{esc} or k_{cage}.

The second assumption has been usually employed for the analysis of radical pair reactions involving triplet precursors.[15a,41]

From the relative yield values for the cage and escape

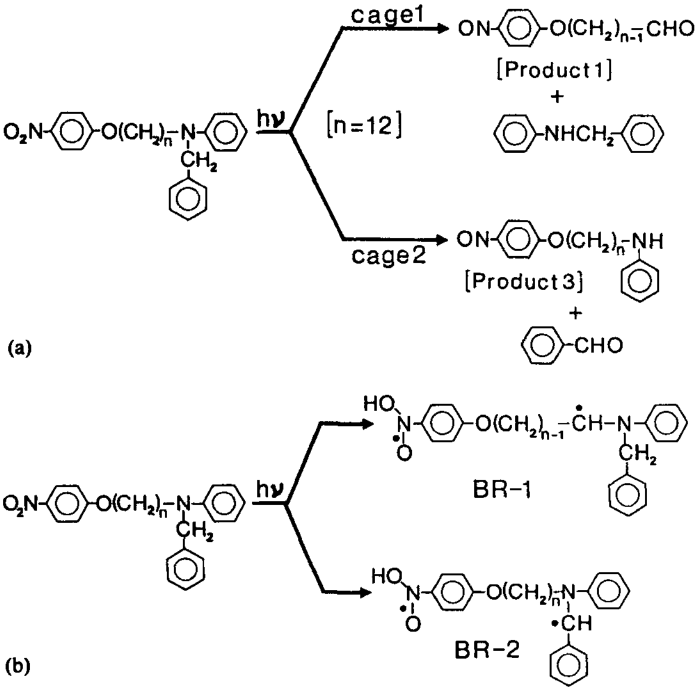


Figure 9. (a) Two independent reaction pathways in the photo-redox reaction via hydrogen abstraction for 4-$O_2NC_6H_4O(CH_2)_{12}N(C_6H_5)CH_2C_6H_5$. (b) Formation of two different biradicals, BR-1 and BR-2

products plotted in Figure 10, $Q(H) = (\Phi^H/\Phi^0)_{cage}/(\Phi^H/\Phi^0)_{escape} = k_{isc}(H)/k_{isc}(0)$ was evaluated and is given in Figure 12 as a function of the magnetic field strength, H. It should be noted that the relative intersystem crossing (ISC) rate $k_{isc}(H)/k_{isc}(0)$ may change from 1 to ca. 1/3 in the presence of high fields (>0·6 T) for the 12-methylene compound. The dependence of the ISC rate on the magnetic field strength shows saturation in the relatively high field region (>0·5 T). This suggests that the relaxation among the triplet manifold may play some role in determining the ISC rate. In addition, the reduction factor of the intersystem crossing rate for the 10-methylene compound is about 1/4, which can be easily evaluated from Figure 1. This finding cannot be accounted for by the equal population among the triplet sublevels at the initial stage of photoreaction.

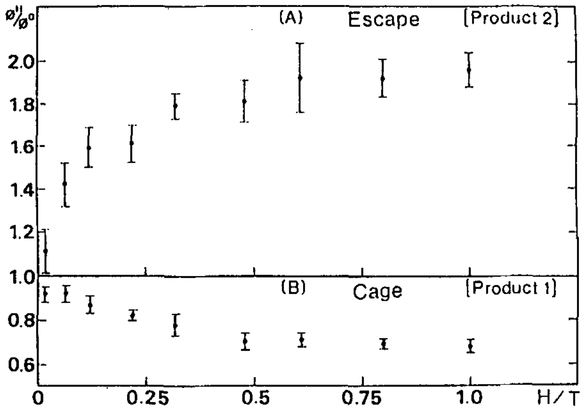


Figure 10. Dependence of magnetic field effect parameter, Φ^H/Φ^0, on magnetic field strength for photochemistry of 4-$O_2NC_{10}H_6$-1-$O(CH_2)_{12}NHC_6H_5$. (A) Escape product 4-$O_2NC_{10}H_6$-1-$O(CH_2)_{11}CHO$ and (B) cage product 4-$ONC_{10}H_6$-1-$O(CH_2)_{11}CHO$. The error bar represents the standard deviation

Photochemical ring opening

Photochemical ring cleavage of cycloalkanones has been extensively studied by a variety of methods including magnetic resonance and magnetic field effects.[42-49] The reaction intermediate formed by the Norrish type I cleavage is a biradical consisting of acyl and alkyl radicals. Cyclic ketones containing two

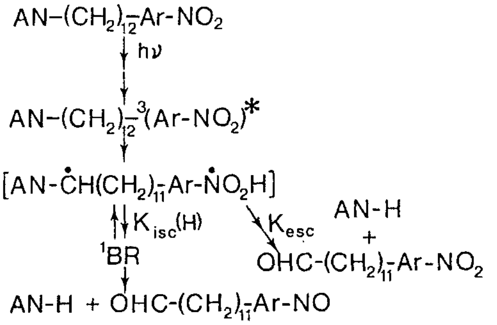


Figure 11. Reaction scheme for photo-redox process. BR represents a biradical reaction intermediate. Superscripts 1 and 3 indicate the spin multiplicity

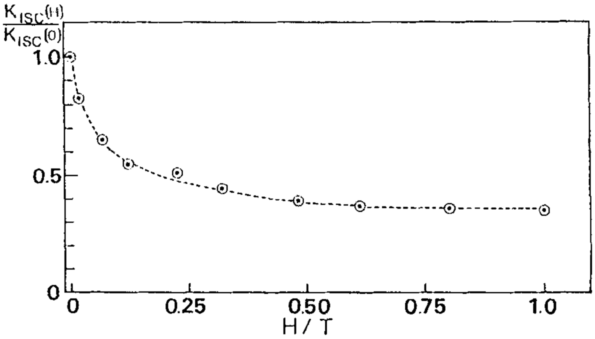


Figure 12. Dependence of $Q(H) = k_{\rm isc}(H)/k_{\rm isc}(0)$ on the field strength, H

phenyl groups at the 2-position undergo ring opening in the $^{3}n\pi^{*}$ state.[43,44] The lifetime of the biradical intermediate derived from the 13-membered ketone $O{=}C{-}(CH_2)_n{-}C(C_6H_5)_2$ depends on the magnetic field strength, i.e. the lifetime decreases in the presence of low fields and then increases on application of high fields. The magnetic field effects on biradical lifetimes were much smaller for shorter biradicals derived from ketones with a small ring size. It is noteworthy that the 13-membered cycloalkanone yields a biradical with 11 methylene groups and that an empirical rule of $n \geqslant 10$ holds in this case. Sakuragi and co-workers[43] observed no magnetic field effects on disappearance of the starting cycloalkanone by steady-state photolysis. This suggests that the triplet biradical intermediate does not undergo a product-forming process without intersystem crossing into the singlet biradical.

Doubleday and co-workers[45] described the dynamics of flexible triplet biradicals produced from α-alkylated and α-phenylated cyclic ketones. They analysed the magnetic field effects on biradical lifetimes and the dependence of the intersystem crossing rate on temperature and concluded that there are two independent mechanisms for intersystem crossing, namely hyperfine coupling and spin–orbit coupling.[45c–f]

Turro *et al.*[46b] reported ^{13}C enrichment studies of 2-phenylcyclododecanone in the presence and absence of radical scavengers at 20 °C in the earth's field (0·5 G). The competition between cage and escape processes was successfully utilized for the separation of magnetic ^{13}C isotopes from non-magnetic ^{12}C isotopes.

BIRADICALS STUDIED BY CIDEP AND CIDNP

The time-resolved ESR, CIDEP and CIDNP techniques have been applied to the study of biradicals produced photochemically in liquid solution. These methods are closely related to the magnetic field effects on chemical reactions. Biradicals derived from cyclic ketones have been extensively studied by means of CIDNP and CIDEP.[47–49] Acylalkyl and bisalkyl biradicals have been well characterized by numerical simulations of observed magnetic resonance spectra.[48,49]

The biradical depicted in Scheme 1 is one of the most thoroughly examined reaction intermediates by the use of CIDEP and CIDNP.[50–52] Maeda *et al.*[51] evaluated the upper and lower limits of $|J|$ by simulating the observed CIDEP spectra obtained for XO-(n)-XH ($n = 3$, 6, 8 and 12). They also detected CIDNP spectra for XO-(n)-XH and found that the effective $|J|$ value measured by the low-field CIDNP method is larger than that of spin-correlated CIDEP.[52] This means that the biradicals which have shorter inter-radical distances are observed by means of CIDNP in comparison with CIDEP. The effective $|J|$ values measured by both methods increase with increasing temperature and with decreasing methylene chain length.[51,52] This tendency is in agreement with the results obtained by magnetic field effects.[17] It can be concluded that the shortening of the inter-radical distance takes place at higher temperature, which may cause a temperature effect on $|J_{\rm eff}|$.

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