

# Magnetic Field and Isotope Effects Induced by Hyperfine Interaction in a Steady State Photochemical Experiment

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**Abstract:** The influence of an external magnetic field on radical reactions is studied in a simple steady-state experiment. This investigates the recombination of a photochemically generated electron donor/acceptor pair (*N,N*-diethylaniline<sup>+</sup>-anthracene<sup>-</sup>) in acetonitrile. As shown by isotopic substitution, the magnetic field dependence of the radical concentrations is due to hyperfine interaction.

## Introduction

It has been known<sup>1</sup> for some years that the pathway of radical reactions may be influenced by small magnetic fields, usually less than 100 G. Such weak fields, though appearing negligibly small when expressed in energy units ( $\leq 0.03$  cal/mol), can nevertheless interfere with changes of the spin orientation of the two unpaired electrons in solvent cage reactions. In this paper, we describe a simple photochemical experiment in the steady state revealing the spin selectivity of radical recombination occurring on the nanosecond time scale.

As a model system, we investigated the recombination of radical ion pairs (Figure 1) in a polar solvent. It is well understood<sup>2</sup> that anthracene in its first excited singlet state (<sup>1</sup>Ac\*) undergoes a diffusion-controlled electron transfer reaction with *N,N*-diethylaniline (DEA) as donor species, thus forming the radical pair, Ac<sup>-</sup> · · D<sup>+</sup>. The back transfer of the electron (with a rate  $k_S$ ) cannot compete with the separation of the radicals by diffusion for two reasons: the repopulation of the singlet ground states is slow owing to the high exothermicity of the reaction<sup>3</sup> and the excited singlet state cannot be reached owing to energy relaxation in the course of ion solvation in the polar environment. However, with the final separation of radicals by diffusion (with the rate  $k_D$ ) another process is competing which is influenced by an external magnetic field *H*. This process is the change of the spin multiplicity in the radical pair, i.e., the transition from the initially formed singlet to a triplet pair state. In a less exothermic, fast reaction such a triplet pair may recombine (with a rate  $k_T$ ) to form an excited triplet state, <sup>3</sup>Ac\*, again in competition with separation by diffusion. Both, triplets and free radicals will finally deactivate to the ground-state species. Thus, continuous excitation of the system yields a steady-state concentration of ions and triplet states.

It is known from the radical pair theory describing the chemically induced dynamic nuclear spin polarization (CIDNP) that the most important mechanism providing singlet-triplet transitions in a radical pair is the hyperfine interaction (HFI).<sup>4</sup> As soon as the two radicals have diffused apart to a distance at which the exchange interaction is negligible, singlet and triplet states of the pair are nearly degenerate.

The spin Hamiltonian governing the spin motion<sup>5</sup>

$$\mathcal{H} = g\beta\mathbf{H}(\mathbf{S}_1 + \mathbf{S}_2) + \sum_i^{(1)} A_i^{(1)} \mathbf{S}_1 \mathbf{I}_i + \sum_j^{(2)} A_j^{(2)} \mathbf{S}_2 \mathbf{I}_j \quad (1)$$

with the isotropic hyperfine coupling constant

$$A = \frac{4\pi}{3} g\beta g_n \beta_n \rho_n$$

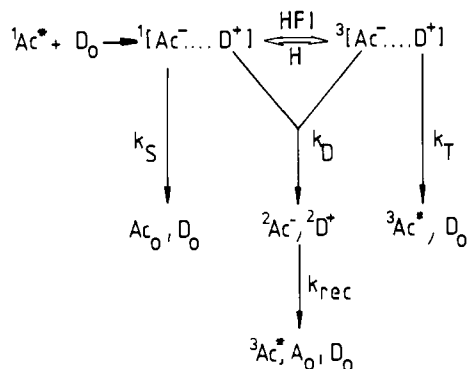
( $\rho_n$  denoting the unpaired electron density at the nucleus) is a sum of the Zeeman interaction of the two unpaired electron

spins,  $\mathbf{S}_1$  and  $\mathbf{S}_2$ , with the external field  $\mathbf{H}$ , and the isotropic hyperfine interaction of  $\mathbf{S}_1$  and  $\mathbf{S}_2$  with the nuclear moments  $\mathbf{I}$  of the radicals 1 and 2, respectively. In zero magnetic field, the hyperfine interaction mixes all three sublevels with the singlet state. In external magnetic fields exceeding the field corresponding to the hyperfine splittings (i.e.,  $H \approx 100$  G for larger organic radicals) the ( $m = 0$ ) triplet level is the only one still interacting with the singlet. Thus, it is qualitatively clear why at zero field strength more triplet product, <sup>3</sup>Ac\*, is formed than in high fields and why the formation rate of free radicals should also be magnetic field dependent. It is this magnetic field dependence of the free-radical concentration which we monitor in a steady-state experiment. For the anthracene triplet states, <sup>3</sup>Ac\*, the situation is more complicated since the decay of triplets by mutual annihilation<sup>6</sup> as well as by interaction with radicals<sup>7</sup> is magnetic field dependent owing to their zero field splitting. Thus, for the interpretation of the magnetic field dependence of the steady-state triplet concentration<sup>8</sup> this superimposed magnetic field should be taken into account.

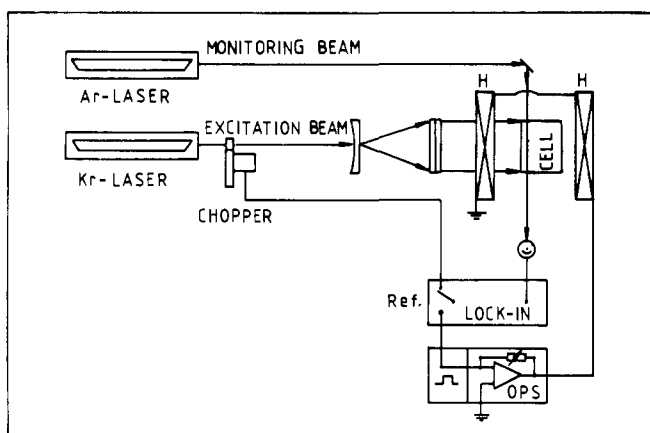
## Experimental Section

**Materials.** Anthracene (PAR grade) was extensively zone refined. Perdeuterioanthracene was kindly put at our disposal by Dr. N. Karl, Kristall-Labor Stuttgart, SFB 67. *N,N*-Diethylaniline (Merck, puriss.) has been redistilled over Zn in the nitrogen stream. The solvent acetonitrile was purified by fractional distillation thoroughly excluding water. The test solutions were carefully freed from oxygen by repetitive thaw and freeze cycles.

**Spectral and Kinetic Data. Apparatus.** Anthracene ( $5 \times 10^{-3}$  M) and *N,N*-diethylaniline ( $5 \times 10^{-1}$  M) were dissolved in acetonitrile. Anthracene has been excited in its long wavelength  $S_0 \rightarrow S_1$  transition by the UV emission of a cw krypton laser (Spectra Physics Model 164) at 351, 364, and 356 nm. At these wavelengths the extinction coefficient of anthracene is approximately  $5 \times 10^3$  mol<sup>-1</sup> cm<sup>-1</sup>.<sup>9</sup> It is assumed that the radical ions are formed in a diffusion-controlled quenching reaction of the singlet excited anthracene with *N,N*-diethylaniline within  $\leq 1$  ns with  $k_q \approx 10^{10}$  mol<sup>-1</sup> s<sup>-1</sup>.<sup>10</sup> Assuming also a diffusion-controlled recombination rate of free ions,<sup>10</sup> the steady-state ion concentration is  $10^{-6}$  M for a photon flux density of  $10^{18}$  photons cm<sup>-2</sup> s<sup>-1</sup>. The absorption monitored with a cw argon laser (Spectra Physics) at 530 nm was 2%, which is in agreement with the extinction coefficient of anthracene anions<sup>11</sup> and their estimated concentration of  $10^{-6}$  M. At 530 nm the absorption coefficient of the anthracene triplet<sup>12</sup> is by a factor of 50 lower than that of the anthracene anion. The total UV output of 30 mW corresponding to  $5 \times 10^{16}$  photons/s was absorbed within the penetration depth of  $\sim 0.5$  mm (Figure 2). The monitor beam was adjusted to guarantee the optimum overlap with the excitation volume. The absorption signal was derived from the lock-in detected relative decrease of the intensity recorded via a photodiode (apparatus, Figure 2). Helmholtz coils with a spatial homogeneity of better than 1% provided the magnetic field  $H$  ( $\leq 300$  Oe). For resolving the small magnetic field modulation of the ion absorption by a phase-sensitive measurement, a bipolar programmable power source (KEPCO BOP 72-5M) supplied the current



**Figure 1.** Reaction scheme for the fluorescence quenching of a singlet excited electron acceptor ( $^1Ac^*$  = anthracene, pyrene) by a donor species in its singlet ground state ( $D_0$  = diethylaniline) in polar solvents. The index 0 denotes neutral molecules in their singlet ground state;  $k_S$ ,  $k_T$ , and  $k_{rec}$  are the rates of geminate recombination to singlet and triplet product states and of the nongeminate recombination of the free ions, while  $k_D$  refers to the production rate of free ions.



**Figure 2.** Experimental setup. The Helmholtz coils H are driven by the operational power supply (OPS).

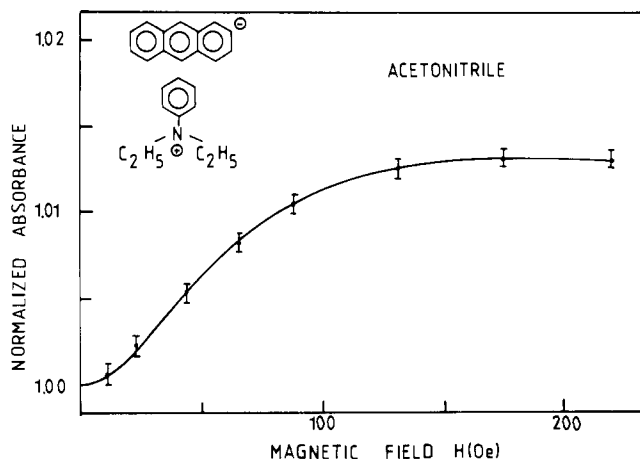
for the Helmholtz coils and the reference signal. The main error in our experiment was due to the ripple of the two lasers.

## Results and Discussion

Measurements on the nanosecond time scale of both the triplet<sup>8,13</sup> and the ion<sup>13</sup> absorption in analogous photochemical electron donor/acceptor systems exhibited a decrease of the triplet absorption with increasing magnetic fields and a concomitant increase of the ion absorption. Figure 3 shows that this enhancement of the radical ion concentration by the magnetic field is also observable in the steady state. The antagonistic dependence of the ion and the triplet absorption on the magnetic field reflects the kinetic condition  $k_S < k_T$ , as will be discussed later. For the electron acceptor species  $C_{14}H_{10}$  the magnetic field dependence shows saturation and a half-width  $H_{1/2} = 75 \pm 3$  Oe. Upon perdeuteration of anthracene the half-width decreases by 17%.

A quantitative theory of these effects<sup>14</sup> has to take into account both the spin motion of the radicals according to the Hamiltonian (eq 1) and the diffusive motion leading to multiple encounters in which spin selective reactions become possible.

A kinetic scheme of these processes, as in Figure 1, is necessarily somewhat oversimplified. In particular, separation of a radical pair by diffusion cannot be described by a first-order reaction. It is well known<sup>15</sup> that the probability of a re-encounter of the pair decays as  $t^{-3/2}$  (where  $t$  is the time after creation of the pair) rather than by an exponential law. Moreover, the transitions between singlet and triplet spin states



**Figure 3.** Magnetic field dependence of the normalized absorbance of anthracene anions measured at 530 nm.

follow a complicated quantum mechanical time evolution which for small radicals is even oscillating. Nevertheless, the kinetic scheme in Figure 1 can serve as a simple recipe to derive the steady-state rates obtained from the exact theory,<sup>14</sup> if the rate constants are interpreted in the following way: (1)  $k_S$  and  $k_T$  denote first-order recombination constants for a radical pair during a collision if the electron spins are in a pure singlet or triplet state, respectively. (2)  $k_D = D/r_0^2$ , where  $D$  is the sum of the diffusion constants of the two radicals and  $r_0$  is the encounter diameter. (3) The magnetic field dependent singlet-triplet transitions are represented by a first-order constant

$$k_{ST}(H) = \frac{1}{N} \sum_{kl} |\langle k | (S_1 + S_2)^2 | l \rangle|^2 \left( \frac{1}{2} |\omega_{kl}| k_D \right)^{1/2} \quad (2)$$

(4) The corresponding rate constant for the backward transition is  $k_{TS}(H) = 1/3 k_{ST}(H)$ . The states  $k, l$  and energy differences  $\omega_{kl} = \omega_k - \omega_l$  refer to the eigenstates and the eigenvalues of the Hamiltonian of eq 1,  $N$  being the total number of these states.

By conventional kinetic analysis of the reaction scheme in Figure 1 we obtain for the probability of free-radical formation

$$\varphi_F = \frac{k_D}{k_D + k_S} + \frac{(k_S - k_T)k_D}{(k_D + k_S)^2(k_D + k_T)} k_{ST}(H) \quad (3)$$

if the rate of formation of singlet radical pairs has been normalized to unity. Furthermore,  $k_D \gg k_{ST}(H)$  was assumed which is always a very good approximation for nonviscous solvents. The evaluation of  $k_{ST}(H)$ , according to eq 2, requires numerical methods which will be discussed elsewhere. Qualitatively,  $k_{ST}(H)$  decreases with increasing magnetic field—owing to the splitting off of the ( $m = \pm 1$ ) triplet sublevels—and saturates at fields  $H$  of the order of the hyperfine splittings  $A$ . This behavior is reflected in Figure 3 showing that—in contrast to the triplets<sup>8,13</sup> in time-resolved experiments—the radical ion concentration increases with the magnetic field. Thus, we conclude from eq 3 that  $k_S < k_T$ , which is also to be expected on theoretical grounds based on exothermicity arguments.<sup>3</sup>

The steady-state free-radical concentration is, of course, determined by both the rate of formation and the rate of depletion of the radicals. The radicals disappear by a bimolecular recombination reaction proceeding again via radical pairs. In this case, however, the initial spin state is a random mixture of singlet and triplet pairs in a 1:3 ratio. Taking this into account an expression analogous to eq 3 is readily obtained which shows that in this case the magnetic field influence on the stationary ion concentration is weak. Moreover, a magnetic

field effect on the recombination of random radicals would again reflect the magnetic field dependence of  $k_{ST}(H)$ , such that the functional dependence shown in Figure 3 is not distorted.

The magnitude of the magnetic field modulation which is  $\approx 2\%$  in Figure 3 can be understood in the following way: if  $k_S \approx 0$ , as for the anthracene/DEA system, the triplet yield is modulated by typically 10–50%.<sup>8,13,14</sup> According to eq 3 (with  $k_S = 0$ ) the probability of free radical formation  $\varphi_F$  is unity minus the triplet yield. Thus, a magnetic field effect on  $\varphi_F$  of several percent is to be expected.

In order to prove directly that the hyperfine interaction between unpaired electrons and nuclei is responsible for the magnetic field effect shown in Figure 3, we have repeated the experiment with perdeuterated anthracene as acceptor. According to eq 1 both, the nuclear spins  $I$  and the nuclear  $g$  factors,  $g_n$ , contributing to the hyperfine splitting  $A$ , enter via eq 2 the magnetic field dependence of the free radical concentration. Both can be quite different for different nuclei, as is shown in the following table for protons and deuterons.

$I$	H	D
$g_n$	5.585	0.857
$H_{1/2}$	$C_{14}H_{10}$ $75 \pm 3$ Oe	$C_{14}D_{10}$ $62 \pm 3$ Oe

As a result, the observed half-width field,  $H_{1/2}$ , was lower for the perdeuterated species. Such an isotope effect, confirming the role of hyperfine interaction in spin-selective radical reactions, can as well be used in a preparative sense for isotope enrichment. Recently an increase of the  $^{13}C/^{12}C$  ratio, based on the difference in hyperfine splitting, has been observed in steady-state photolysis of aromatic ketones and peroxides.<sup>16</sup>

## Conclusions

Owing to the high sensitivity achieved in steady-state experiments using phase-sensitive techniques even small magnetic field effects are easily detected with high accuracy. As shown for the recombination of radical ions formed via electron transfer between anthracene excited in its lowest singlet state and diethylaniline, such experiments can serve as a test for the participation of radical intermediates in the radiationless relaxation of excited states. This seems to be especially interesting for stable photochemical systems and a complex reaction scheme such as the one encountered in the primary steps of photosynthesis.<sup>17</sup>

A steady-state absorption measurement of transient radicals in a magnetic field appears to be also an elegant way to study the mechanism of triplet quenching in polar solvents. When the radical ion pairs is formed from a triplet precursor state, the recombination rate  $k_T$  is assumed to approach zero on energetic grounds and the yield of free radicals is again expected to increase with the external field. The magnetic field effect vanishes in the case of fast spin relaxation as compared to the time constant of the hyperfine interaction. Thus, in a steady-state experiment a low yield of free radicals showing no magnetic field effect indicates the loss of spin correlation after the radical pair has been formed, e.g., due to spin-orbit coupling in one or both components of the pair. This effect has been observed for the radical pair anthracene<sup>+</sup>–erythrosine<sup>-</sup>.<sup>18</sup>

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