

Radio Frequency Magnetic Field Effects on a Radical Recombination Reaction: A Diagnostic Test for the Radical Pair Mechanism

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The influence of applied magnetic fields on the yields and rates of free radical reactions is well described by the radical pair mechanism (RPM) and has proved to be a rich source of information on the chemical, magnetic, and motional properties of the radicals involved.¹ The RPM has been discussed in relation to the putative effects of extremely low frequency (ELF) electromagnetic fields on biological systems,² an area in which there is a plethora of contradictory observations, few successful replication studies, and a great deal of uncertainty concerning plausible mechanisms.³ In complex systems, especially when the identities of the radicals may be completely unknown, it is very difficult to prove conclusively the existence of a radical pair process because the response to an applied magnetic field is very sensitive to the detailed properties and behavior of the radicals. Here we demonstrate a diagnostic test for the operation of the RPM, based on the expectation⁴ that chemical reactions that are sensitive to weak (<1 mT) static or ELF (e.g., 50 or 60 Hz) magnetic fields should also respond to radio frequency fields (RF) of comparable intensity.⁵

The RPM explains a variety of magnetic effects on radical reactions.^{1,6,7} The sensitivity of radical recombination to relatively weak magnetic interactions (typically 4–6 orders of magnitude smaller than the thermal energy, $k_B T$) arises from competing spin-allowed reactions of the singlet (S) and triplet (T) electronic states of radical pairs in which the electron spins are correlated. The relative yields of the products of the two reactions are controlled by the facile interconversion of the S and T radical pair states by intramolecular electron–nuclear hyperfine interactions, a process that can be influenced by an applied magnetic field via the electron Zeeman interaction.⁸ An RF field, either alone⁹ or in conjunction with a strong (>10 mT) static field,¹⁰ can alter the relative product yields if it is in resonance with the energy-level splittings arising from the hyperfine and Zeeman interactions and hence is able to modulate the $S \leftrightarrow T$ interconversion. The modification of a biological response to an applied static or ELF field by the application of a RF field would provide strong support for a RPM hypothesis, give clues to the identity of the radicals, and militate against other possible mechanisms that would be unlikely to show comparable sensitivity to ELF and RF fields.

Magnetic field effects on the photochemical reaction of chrysene (Chr) with isomers of dicyanobenzene (DCB) were detected via the fluorescence of the exciplex formed exclusively from the singlet state of the radical ion pair created by photoinduced intermolecular electron transfer.¹¹ The influence of a 300 μ T RF field on the recombination of perdeuterated chrysene and 1,4-DCB radicals as a function of the strength of the applied static field is shown in Figure 1 for four radio frequencies, for both parallel and perpendicular arrangements of the two fields. Several features are apparent: (a) the effect of the RF field depends strongly on its frequency, (b) the parallel and perpendicular responses differ but have comparable amplitudes, (c) the signals are weak for static fields

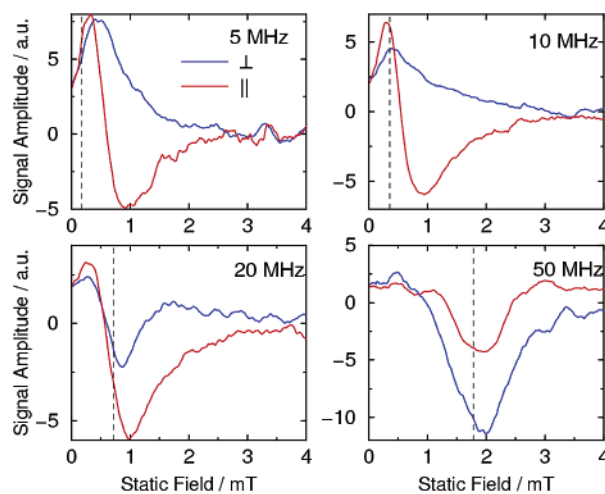


Figure 1. Effect of a $\sim 300 \mu$ T RF field on the recombination of the photoinduced chrysene- $d_{12}^{*+}/1,4$ -dicyanobenzene $^{*-}$ radical pair as a function of the strength of the applied static magnetic field. Red and blue lines are for parallel (||) and perpendicular (\perp) fields, respectively. The frequencies of the RF field are as indicated. The vertical dashed line indicates the static field at which the RF radiation is in resonance with the electron Zeeman interaction.

above 3 mT where the RF is off-resonance with respect to both hyperfine and Zeeman interactions, and (d) at the higher radio frequencies, a dominant peak emerges close to the high-field electron paramagnetic resonance condition ($\sim 0.036 \text{ mT MHz}^{-1}$).¹²

To some extent, these observations can be understood in terms of the behavior of radical pairs in a static magnetic field that greatly exceeds the hyperfine interactions, an experiment known as reaction yield detected magnetic resonance (RYDMR).¹⁰ Under these conditions, a resonant effect on the radical recombination is found provided the RF field is parallel to the static field and when its frequency matches the electron Zeeman splitting.¹² However, for comparable Zeeman and hyperfine interactions, as is the case for Figure 1, a more complex response can be anticipated in which the number and position of the resonances and the selection rules for RF-induced transitions are determined by the combined effects of the two interactions.¹³

To probe the influence of the hyperfine interactions, measurements were made at a radio frequency of 5 MHz for four radical pairs comprising Chr- h_{12}^{*+} or Chr- d_{12}^{*+} paired with one of the three isomers of DCB $^{*-}$, chosen to give a range of effective hyperfine coupling constants $\langle a \rangle$. As shown in Figure 2, the parallel and perpendicular signals differ and their width increases with $\langle a \rangle$, but their basic shapes remain unchanged.

The RPM offers scope for computer simulation of chemical magnetic field effects by combining spin-dependent kinetics with a quantum mechanical description of the spin evolution. Although a simple approach using a rotating frame transformation to remove

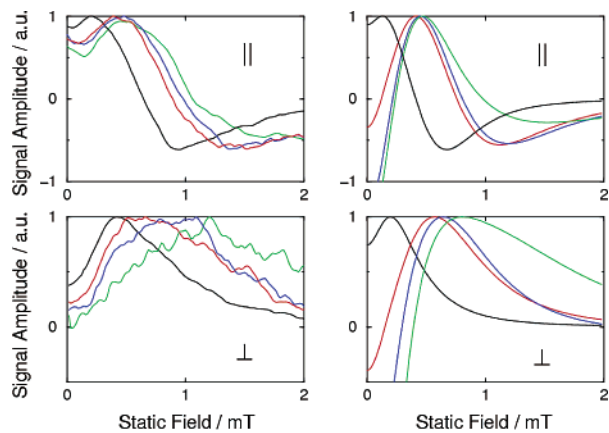


Figure 2. Effect of a $\sim 300 \mu\text{T}$, 5 MHz RF field on the recombination of photoinduced chrysenes $^{+}$ /dicyanobenzene * radical pairs as a function of the strength of the applied static magnetic field. The experimental measurements are on the left, and the corresponding simulations are on the right. The two magnetic fields are parallel (\parallel) in the top two panels and perpendicular (\perp) in the bottom two. All spectra have been scaled to the same maximum intensity because the different exciplexes have very different fluorescence intensities. Black: Chr- $d_{12}^{+}/1,4\text{-DCB}^{*-}$. Red: Chr- $h_{12}^{+}/1,4\text{-DCB}^{*-}$. Blue: Chr- $h_{12}^{+}/1,2\text{-DCB}^{*-}$. Green: Chr- $h_{12}^{+}/1,3\text{-DCB}^{*-}$.¹⁴

the time dependence of the RF field is successful for high-field RYDMR,¹⁵ this method fails when the static field is neither much stronger than the linearly polarized RF field nor perpendicular to it. We have therefore used a modified form of the γ -COMPUTE algorithm, devised for the simulation of magic angle spinning NMR spectra of powdered samples.¹⁶ The results for a 5 MHz RF field are also shown in Figure 2: for each of the four radical pairs, the four nuclear spins with the largest hyperfine interactions are included.¹⁴ Despite this approximation, necessary to limit the size of the calculation, the agreement with the experimental data is striking. The value of the recombination rate constant used ($k = 5.6 \times 10^7 \text{ s}^{-1}$) is not crucial; similar spectra are found for k in the range $3.0\text{--}7.0 \times 10^7 \text{ s}^{-1}$. Not only do the simulations correctly predict the general shape of the parallel and perpendicular spectra, they also reproduce the shift of the extrema to higher fields with increasing $\langle a \rangle$. The large negative signals for magnetic fields ≤ 0.5 mT are an artifact of the exponential model, which is likely to be absent in a more realistic treatment of the distribution of radical encounter times.

Effects of this kind could form the basis of a general diagnostic test for the operation of the RPM that does not require prior knowledge of the nature and properties of the radical reaction. As shown here, radical pair reactions that respond to an applied static field should (a) also be sensitive to the frequency and direction of an additional RF field of comparable intensity and (b) exhibit a Zeeman resonance at a frequency that is not strongly dependent on the hyperfine interactions provided they are weaker than the applied static field.

Sensitivity to RF fields has been proposed as a test for the involvement of photoinduced radical pairs in the mechanism of avian magnetoreception—the process by which birds sense the Earth's magnetic field as a source of compass information—and to discriminate against a mechanism based on ferromagnetic particles. Ritz et al.¹⁷ have very recently shown that the magnetic orientation of migratory birds can be disrupted by weak RF fields. For a 470 nT, 7 MHz field, the birds were disoriented when the oscillating

field was at an angle of 24° or 48° to the geomagnetic field (46 μT) but were unaffected when the two fields were parallel. Disorientation was also found for 85 nT broadband (0.1–10 MHz) fields. These remarkable observations provide the clearest evidence thus far for the participation of a radical pair reaction in magneto-reception, and indeed in an intact biological system of any kind. They also reveal some curiosities, which investigations of the sort reported here may be able to resolve: why is no effect found for parallel fields in a situation where the static field is weak compared to hyperfine interactions, and how can such extraordinarily weak oscillating fields have a sufficient effect on a radical pair reaction.

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Supporting Information Available: Apparatus and hyperfine coupling data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) Radical pairs were produced in a spin-correlated singlet state by UV continuous illumination. The linearly polarized RF field was 100% audio frequency amplitude-modulated, and the exciplex fluorescence was detected by a photomultiplier and lock-in amplifier. To this apparatus, described in detail elsewhere (Timmel, C. R.; Woodward, J. R.; Hore, P. J.; McLauchlan, K. A.; Stass, D. V. *Meas. Sci. Technol.* **2001**, *12*, 635–643), was added a pair of water-cooled Helmholtz coils to provide a static magnetic field of up to 4 mT, mounted to allow different relative orientations of the two fields. The strength of the static field was swept, maintaining a fixed frequency and strength for the RF field. The experiment measures the integral of the modulated fluorescence over a cycle of the audio frequency modulation. All experiments were performed at room temperature. The samples comprised 0.5 mM Chr and 10 mM DCB in a 9:1 cyclohexanol/acetonitrile mixture (by volume).
- (12) The radio frequency, ν_{RF} , is related to the static field strength, B_0 , by $\nu_{\text{RF}} = \gamma B_0 / 2\pi$, where γ is the gyromagnetic ratio of the electron.
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