Communication

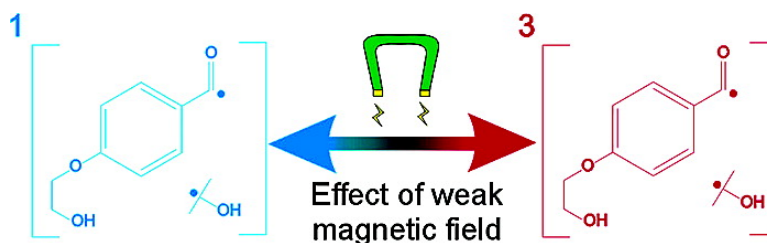# Effect of a Weak Magnetic Field on the Reaction between Neutral Free Radicals in Isotropic Solution

Claire B. Vink, and Jonathan R. Woodward

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 2 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

Effect of a Weak Magnetic Field on the Reaction between Neutral Free Radicals in Isotropic Solution

Claire B. Vink and Jonathan R. Woodward*

Department of Chemistry, University of Leicester, University Road, Leicester, LE1 7RH, U.K.

Received October 5, 2004; E-mail: jrw16@le.ac.uk

In this paper, we describe the first observation of the effects of a weak magnetic field on the recombination reaction of neutral free radicals in isotropic solution. This work also represents the first use of time-resolved mid-infrared spectroscopy in the measurement of magnetic field effects (MFEs).

There has been recent and rapidly increasing interest in the effects of magnetic fields, particularly very weak ones, on the recombination reactions of free radicals through the radical pair mechanism (RPM).[1] This has been fuelled by both the concerns over the potential effects of electromagnetic fields (EMFs) on human health[2] and the proposals that the RPM may be the mechanism responsible for the magnetic compass in birds and some other animals.[3] While the literature contains many examples of the effects of magnetic fields of magnitude sufficient to retard singlet−triplet-state mixing in the radical pair (RP) by energetically separating the $T_{\pm 1}$ sublevels through the Zeeman interaction[4] (typically involving fields of a few millitesla or greater), there have been very few reports of the effects of very weak magnetic fields (typically less than 1 mT) that can enhance singlet−triplet-state mixing in the RP through a removal of hyperfine spin-state degeneracies and unlocking of coherences between states with different degrees of singlet−triplet character.[5] In those few studies, careful steps are taken to extend the lifetime of the RP sufficiently that effects of the very weak field have time to develop. This involves using radical ion pairs in solutions where the RP lifetime is extended due to electrostatic interactions or by encapsulating RPs in micelles, which keeps the RP in contact for a sufficient length of time. Here, we report the first low-field effect (LFE) obtained for a neutral radical pair in isotropic solution. We also describe, for the first time, the observation of a magnetic field effect detected using time-resolved infrared spectroscopy. The full details of our experimental apparatus will be described in a future publication.

The reaction investigated is the radical recombination reaction occurring after the photodecomposition of 2-hydroxy-4′-(2-hy-droxyethoxy)-2-methylpropiophenone (α-HP) and is described in Scheme 1. α-HP is photoexcited using the fourth harmonic of an Nd:YAG laser. It undergoes intersystem crossing, and the resultant triplet-state molecule cleaves α to the carbonyl group to generate an RP consisting of radicals A and B. The generation and subsequent decay of these radicals is monitored via the absorption of infrared light (from a lead salt diode laser) into the carbonyl-stretching mode of radical A. The maximum absorption for this mode occurs at 1805 cm^{-1}. The detection is selective for this radical as the IR frequency varies significantly from that of the parent molecule (1663 cm^{-1}, FTIR spectrum of solid sample). Figure 1 shows the decay curve obtained from the photolysis of a 1 mM solution of α-HP in cyclohexanol at room temperature and indicates the excellent signal-to-noise ratio obtainable.

The IR absorption technique used means that no reaction products are detected at the IR frequency employed, in contrast to the majority of studies in the UV−vis region where product spectral

Scheme 1. Photochemical Reaction Scheme for 2-Hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone in Solution
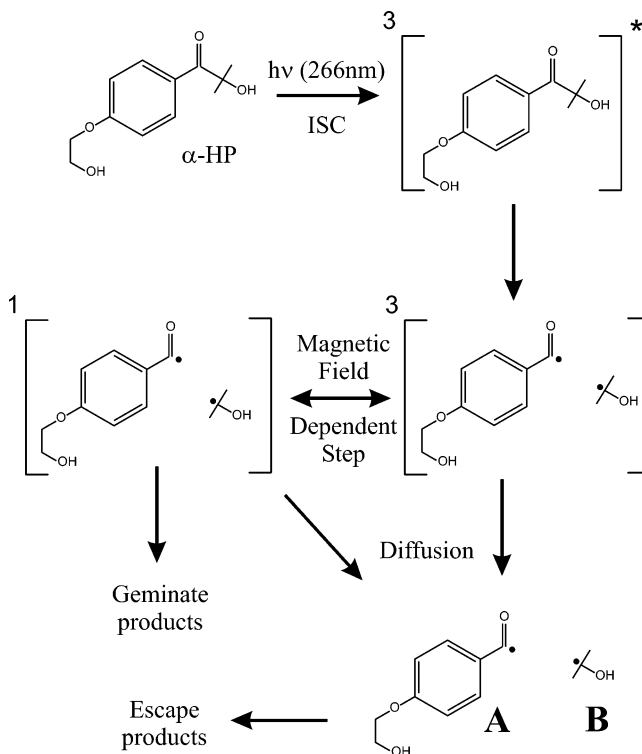
overlap is significant.[6] Thus, the curve represents the true decay curve due to removal of the radical intermediates. To study the effect of magnetic field on the radical decay kinetics, a pulsed current source was constructed which, when used to supply a pair of Helmholtz coils, produces a static magnetic field of up to 21 mT for a duration of approximately 2 ms. The experiment involves recording consecutive decay curves in the presence and absence of this magnetic field and repeating the process for a user-defined
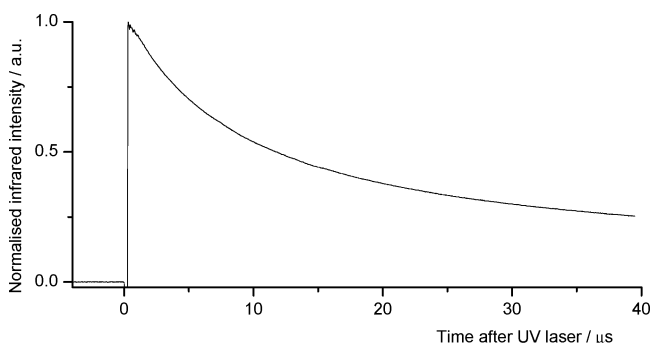
Figure 1. Transient decay curve recorded at 1805 cm^{-1} and corresponding to the absorbance of radical A in cyclohexanol.
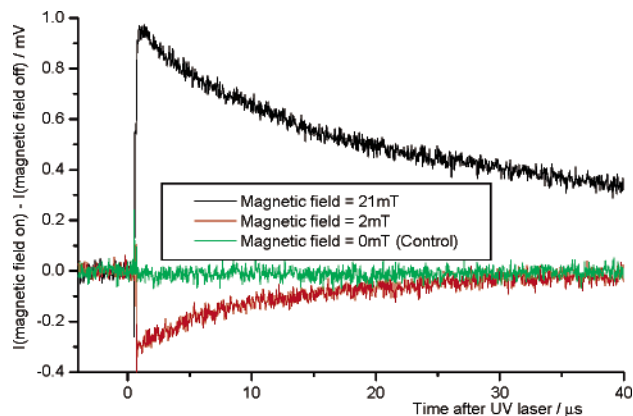
Figure 2. Subtracted decay curves (magnetic field on−magnetic field off) for radical A in cyclohexanol at three different field values. The number of free radicals is increased at 21 mT and reduced at 2 mT relative to zero magnetic field.
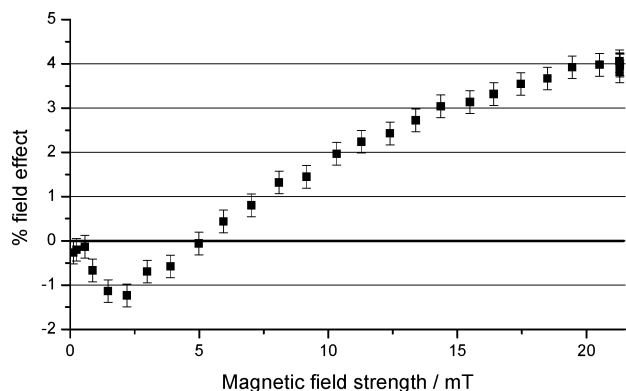

Figure 3. Magnetic field effect (calculated using I(field on) − I(field off)/I(field off) for integrated intensities 1−2 μs after laser irradiation) versus magnetic field for 266 nm irradiation of α-HP in cyclohexanol.

number of averages. Subtracting the field-off curve from the field on one reveals any effect of the magnetic field. As a control experiment, the same process can be performed without connecting the pulsing unit to the coils. This confirms the reproducibility of the experiment in that the curves obtained in such an experiment truly subtract to zero. Figure 2 shows the subtraction obtained for magnetic fields of 21 and 2 mT along with the control experiment. In the absence of a current pulse to the Helmholtz coils, the magnetic field measured at the sample, using a Hall Effect probe, was zero, indicating no residual field in the coils. All of the experiments were performed in the presence of Earth's magnetic field.

The predicted effect of the field, based on the RPM, is to increase the number of free radicals surviving at high (21 mT) field since those $T_{\pm 1}$ born radical pairs are energetically incapable of interconverting to a singlet configuration and recombining. The predicted effect of a much weaker field is a reduction in the number of free radicals surviving as the effect of the field is to slightly increase the rate of singlet−triplet-state mixing in the RP. Clearly both predictions are borne out in practice. The complete magnetic field dependence over the range of magnetic fields available is shown in Figure 3.

The radical decay curves exhibit complex kinetics due to both geminate pair (pseudo-first-order) and freely diffusing pair (f-pair, second-order) recombination. In fact, on the observed timescales, the decay is dominated by the slower f-pair recombination. The initial magnitudes of the decay curves differ in the presence and absence of a magnetic field due to the effect on the rapid geminate

recombination. It is thus likely that the observed magnetic field effects arise from both geminate and freely diffusing RPs.

The field effect appears not to be completely saturated at 21 mT, which given the calculated $B_{1/2}$ value[7] of the RP of 3.27 mT (using literature hyperfine couplings[8]), implies that incoherent spin relaxation is occurring on a timescale comparable to the RP lifetime. This implies a relatively long RP lifetime, which seems reasonable given that a weak field is also capable of influencing singlet−triplet state mixing in the RP. When acetonitrile is employed as a solvent, the lifetime of the RP is reduced substantially due to the large reduction in viscosity. In this case, the RP does not live long enough for a magnetic field to influence singlet−triplet spin-state mixing, and so no magnetic field effects are observed at all at any available field value. The results are particularly significant in that they indicate that without any special modification of solvent environment, a very weak magnetic field can influence free radical yields. There are clear implications for the investigation of MFEs in biological systems. The instrumentational significance of these results is that the use of time-resolved infrared allows the study of RP systems inaccessible to UV−vis absorption and fluorescence measurements. Moreover, the technique yields sufficient sensitivity to measure field effects of 1% or even less. This corresponds to an absolute change in infrared intensity at the detector of 0.001%.

In conclusion, the radical recombination reaction of radicals generated from the photolysis of α-HP was studied on a microsecond time scale using time-resolved mid-infrared spectroscopy. The reaction was found to exhibit opposite magnetic field dependencies at 2 and 21 mT, the effect at low-field being the first such observation for neutral free radicals in isotropic solution. These results are clearly the starting point for a thorough investigation into the effects of geminate and freely diffusing pairs, RP structure, solvent viscosity, relaxation, and so forth, along with full kinetic analyses. Such an investigation is currently being undertaken.

References

(1) For review articles, see: (a) Woodward, J. R. *Prog. React. Kinet.* **2002**, *27* (3), 165. (b) McLauchlan, K. A.; Steiner, U. *Mol. Phys.* **1991**, *73* (2), 241.

(2) There is a fairly large collection of literature. For examples, see: (a) Sheppard, A. R.; Kaune, T. W.; Poole, C.; Kelsh, M. A. *Epidemiology* **2000**, *11*, 624. (b) Lacy-Hulbert, A.; Metcalfe, J. C.; Hesketh, R. *FASEB J.* **1998**, *12*, 395.

(3) See the following and references therein: (a) Ritz, T.; Thalau, P.; Phillips, J. B.; Wiltschko, R.; Wiltschko, W. *Nature* **2004**, *429*, 177. (b) Ritz, T.; Adem, S.; Schulten, K. *Biophys. J.* **2000**, *76*, 707.

(4) Many examples can be found: (a) *Dynamic Spin Chemistry*; Nagakura, S., Hayashi, H., Azumi, T., Eds.; Kodansha/Wiley: Tokyo/New York, 1998. (b) Steiner, U. E.; Ulrich, T. *Chem. Rev.* **1989**, *89*, 51.

(5) Anisimov, O. A.; Grigoryantz, V. M.; Kiyanov, S. V.; Salikhov, K. M.; Molin, Yu. N. *Teoret. Eksper. Khim.* **1982**, *18*, 292. (b) Fischer, H. *Chem. Phys. Lett.* **1983**, *100*, 255. (c) Hamilton, C. A.; Hewitt, J. P.; McLauchlan, K. A.; Steiner, U. E. *Mol. Phys.* **1988**, *65*, 423. (d) Shkrob, I. A.; Tarasov, V. F.; Buchachenko, A. L. *Chem. Phys.* **1991**, *153*, 443. (e) Batchelor, S. N.; Kay, C. W. M.; McLauchlan, K. A.; Shkrob, I. A. *J. Phys. Chem.* **1993**, *97*, 13250. (f) Stass, D. V.; Lukzen, N. N.; Tadjikov, B. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1995**, *233*, 444. (g) Stass, D. V.; Tadjikov, B. M.; Molin, Yu. N. *Chem. Phys. Lett.* **1995**, *235*, 511. (h) Saik, V. O.; Ostafin, A. E.; Lipsky, S. *J. Chem. Phys.* **1995**, *103*, 7347. (i) Saik, V. O.; Lipsky, S. *Chem. Phys. Lett.* **1997**, *264*, 649. (j) Sacher, M.; Grampp, G. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 971. (k) Eveson, R. W.; Timmel, C. R.; Brocklehurst, B.; Hore, P. J.; McLauchlan, K. A. *Int. J. Radiat. Biol.* **2000**, *76*, 1509.

(6) For discussion and references, see: Woodward, J. R. *Prog. React. Kinet.* **2002**, *27* (3), 165.

(7) Werner, H.-J.; Staerk, H.; Weller, A. *J. Chem. Phys.* **1978**, *68*, 2419.

(8) Wu, C.-H.; Jenks, W. S.; Koptyug, I. V.; Ghatlia, N. D.; Lipson, M.; Tarasov, V. F.; Turro, N. J. *J. Am. Chem. Soc.* **1993**, *115*, 9583.

JA043945F