molecule for probing the reorganization and stereoselective contributions to the electron-transfer process. The results of synthetic and electron-transfer experiments involving this ion will be presented in a subsequent publication.

Acknowledgment. We are thankful to J. Springborg and B. Søndergaard for providing some of the resolved cyclohexanediamine ligand and to the ANU Microanalytical Service. M.G.M. is grateful to the Australian National University for a Postgraduate Research Award.

Registry No. (*R*,*R*)-chxn, 20439-47-8; (*S*,*S*)-chxn, 21436-03-3; (−)-(*R*,*R*)-chxn·2HCl, 35018-63-4; (+)-(*S*,*S*)-chxn·2HCl, 35018-62-3; {(−)-chxn·H$_2$}{(+)-tartrate}, 39961-95-0; {(+)chxn·H$_2$}{hydrogen (+)-tartrate}$_2$, 39961-96-1; Δ-*lel*$_3$-[Co(chxn)$_3$]Cl$_3$, 37381-44-5; Δ-*lel*$_3$-[Co(chxn)$_3$](CF$_3$SO$_3$)$_3$, 92097-48-8; Λ-*ob*$_3$-[Co(chxn)$_3$]Cl$_3$, 31537-08-3; Λ-*ob*$_3$-[Co(chxn)$_3$](CF$_3$SO$_3$)$_3$, 92216-20-1; Λ-*lel*$_3$-[Co(chxn)$_3$]Cl$_3$, 59617-81-7; Λ-*lel*$_3$-[Co(diNOchar)]Cl$_3$, 92097-45-5; Λ-*lel*$_3$-[Co(diNOchar)]Cl$_2$·ClO$_4$, 92216-17-6; Δ-*lel*$_3$-[Co(diNOchar)]Cl$_3$, 92216-18-7; Δ-*lel*$_3$-[Co(diNOchar)](CF$_3$SO$_3$)$_3$, 92281-95-3; Δ-*lel*$_3$-[Co(NOsemichar)]Cl$_3$, 92125-50-3; Δ-*lel*$_3$-[Co(NOsemichar)](CF$_3$SO$_3$)$_3$, 92216-87-0; Δ-*lel*$_3$-[Co(diNOchar)](ClO$_4$)$_2$, 92097-47-7; Λ-*lel*$_3$-[Co(diAMchar·H$_2$)]Cl$_5$, 92125-51-4; Λ-*lel*$_3$-[Co(diAMchar·H$_2$)](CF$_3$SO$_3$)$_5$, 92216-90-5; Δ-*lel*$_3$-[Co(diAMchar)]Cl$_2$, 92216-91-6; Δ-*lel*$_3$-[Co(diAMchar)](CF$_3$SO$_3$)$_2$, 92218-46-7; Λ-*lel*$_3$-[Co(diAMchar·H$_2$)]$^{5+}$, 92281-99-7; Δ-*lel*$_3$-[Co(diAMchar)]$^{2+}$, 92125-53-6; Δ-*lel*$_3$-[Co(diAMchar·H$_2$)]Cl$_5$, 92216-85-8; Δ-*lel*$_3$-[Co(diAMchar)]ZnCl$_4$, 92125-54-7; [Co(AMNOchar·H)]Cl$_4$, 92125-52-5; (*R*,*R*)$_3$-diNOchar, 92097-44-4; (*S*,*S*)$_3$-diNOchar, 92216-15-4; Li$_2$ZnCl$_4$, 61420-95-9; HCHO, 50-00-0; NO$_2$CH$_3$, 75-52-5.

---

(32) Geue, R. J.; McCarthy, M. G.; Sargeson, A. M. unpublished data.

Communications to the Editor

Magnetic Effects on Chemical Reactions in the Absence of Magnets. Effects of Surfactant Vesicle Entrapped Magnetite Particles on Benzophenone Photochemistry

Pascal Herve, Faruk Nome,[1] and Janos H. Fendler*

Department of Chemistry
and Institute of Colloid and Surface Science
Clarkson University, Potsdam, New York 13676

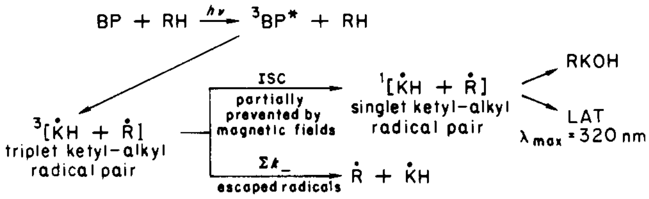
Received September 10, 1984

The paper reports the first observation of a substantial magnetic effect in the absence of an applied magnetic field: the dramatic alteration of benzophenone photochemistry by surfactant vesicle incorporated colloidal magnetite.

The influence of externally applied magnetic field on chemical reactions involving radical pairs is well documented.[2-6] A case in point is the photoreduction of benzophenone, BP, to an alcohol, RKOH (main product), and to light-absorbing coupling (minor) products, LAT.[7-10] Product formation has been rationalized in terms of the decay of photolytically generated benzophenone triplets, $^{3}\mathrm{BP}^{*}$, in the presence of a hydrogen donor, RH, to a triplet ketyl radical pair, $^{3}[\dot{\mathrm{K}}\mathrm{H} + \dot{\mathrm{R}}]$. The triplet ketyl radical pair undergoes, in turns, intersystem crossing to a singlet radical pair, $^{1}[\dot{\mathrm{K}}\mathrm{H} + \dot{\mathrm{R}}]$, governed by ISC, competetively with the escape of radicals from their cages (governed by Σk_-). The observed decrease of LAT on photolyzing BP in the presence of an externally applied magnetic field substantiated the mechanism shown in Scheme I.[7] Incorporation of BP in aqueous micelles increased the amount of LAT formed on photolysis and amplified the magnetic effects.[7,8]

Dioctadecyldimethylammonium chloride (DODAC) surfactant vesicles[11] were utilized in the present work as media for benzophenone photoreactions.[12] Repetitive bursts (2 Hz) of 266 nm, ca. 1 mJ, laser pulses mediated the benzophenone photoreduction.[13] The progress of the reaction was monitored by a Hewlett-Packard 8450 A Diode Array Spectrophotometer. The amount of LAT formed in DODAC vesicles, just like in aqueous micelles,[7] is appreciably greater than that in a pure solvent (Figure 1). The increase in LAT yields is probably due to the solubilization of the ketyl radicals with the hydroxyl groups hydrogen bonded to water in the head-group region of DODAC vesicles. There they are likely to be arranged with their phenyl rings oriented toward the bilayers where the counterradicals are located, which then facilate the formaton of para-coupled products.[9] Incorporation of colloidal magnetite (Fe$_3$O$_4$) particles[14] dramatically decreased the LAT yields (Figure 1) by increasing the fraction of those escaped to those undergone intersystem crossing (Scheme I).

Scheme I



Effects of DODAC vesicle incorporated magnetite particles have been substantiated by laser flash photolysis.[16] Benzophenone

---

(1) Permanent address: Departamento de Quimica, Universidade Federalde Santa Catarina, 88.000-Florianopolis, S.C., Brazil.

(2) Buchachenko, A. L. *Russ. Chem. Rev. (Engl. Transl.)* **1976**, *45*, 761–792.

(3) Haberkorn, R. *Chem. Phys.* **1977**, *19*, 165–179. Haberkorn, R. *Chem. Phys.* **1977**, *24*, 111–117. Haberkorn, R. *Chem. Phys.* **1977**, *26*, 35–46.

(4) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369–377.

(5) Steiner, U. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 228–233.

(6) Turro, N. J. *Proc. Natl. Acad. Sci. U.S.A.* **1983**, *80*, 609–621.

(7) (a) Scaiano, J. C.; Abuin, E. B. *Chem. Phys. Lett.* **1981**, *81*, 209–213. (b) Scaiano, J. C.; Abuin, E. B.; Stewart, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673–5679. (c) Scaiano, J. C.; Lougnot, D. J. *J. Phys. Chem.* **1984**, *88*, 3379–3382.

(8) Sakaguchi, Y.; Hayashi, H.; Nagakura, J. *J. Phys. Chem.* **1982**, *86*, 3177–3184.

(9) Scaiano, J. C.; Selwyn, J. C. *Photochem. Photobiol.* **1981**, *34*, 29–32.

(10) Scaiano, J. C. *J. Photochem.* **1973**, *2*, 81–118.

(11) Fendler, J. H. *Acc. Chem. Res.* **1980**, *13*, 7–13.

(12) Stock solutions, 3.6 × 10^{-3} M (stoichiometric surfactant concentration), of DODAC vesicles were prepared by the ultrasonic dispersal of 53.7 mg of DODAC in 25 ml of distilled water at 70 °C for 15 min by the microtip of the Branson sonicator set at 70 W. Stock solutions were diluted tenfold by water for all photochemical experiments. Hydrodynamic diameters of the 3.6 × 10^{-4} M DODAC vesicles were determined to be 1100 ± 100 Å by dynamic light scattering. Recrystallized benzophenone was introduced by injection in MeOH to give a final concentration of 8.0 × 10^{-5} M.

(13) Reed, W.; Guterman, L.; Tundo, P.; Fendler, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 1897–1907.

(14) Magnetite (Fe$_3$O$_4$) particles were prepared by adding 30% ammonium hydroxide to equal volumes of 0.9 M FeCl$_3$·6H$_2$O and 0.6 M FeCl$_2$·4H$_2$O.[15] Settling of the magnetic particles was facilitated by placing the solution in a beaker on a magnet. The precipitate was washed 6 times with 3% NH$_4$OH and stabilized by the addition of 10^{-3} M lauric acid. Cosonication of appropriate ratios of DODAC and lauric acid stabilized magnetites resulted in magnetic particle containing surfactant vesicles. Sizes of magnetite carrying DODAC vesicles were determined to be 1400 ± 100 Å. Vesicle incorporated magnetite particles remained stable at least a month. Saturation magnetization of 1.2 × 10^{-3} M Fe$_3$O$_4$ in 2 × 10^{-3} M DODAC vesicles was determined to be 0.25 G by means of a vibrationg magnetometer. Concentrations of Fe$_3$O$_4$ were determined by atomic absorption using a Perkin-Elmer Model 5000 spectrometer by dissolving Fe$_3$O$_4$ containing vesicles in concentrated HCl.

(15) Khalafalla, S. E.; Reimers, G. W. *IEEE Trans. Magn.* **1980**, *MAG-16*, 178–183.

0002-7863/84/1506-8291$01.50/0

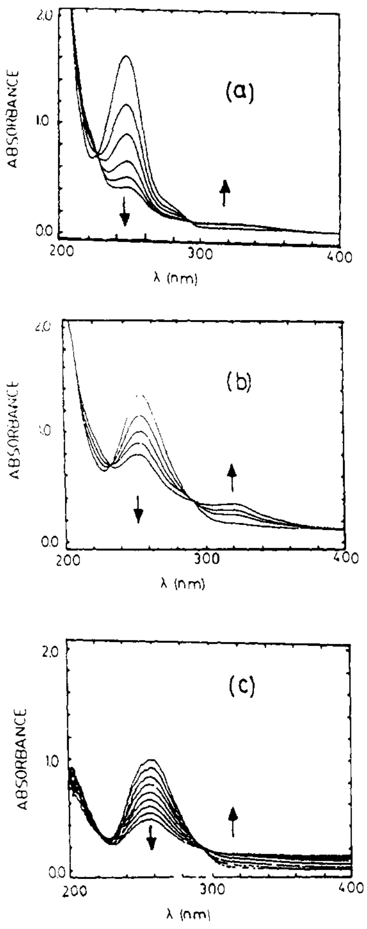


Figure 1. Absorption spectra of 8 × 10^{-5} benzophenone in cyclohexane (a), in 2 × 10^{-3} M DODAC vesicles (b), and in 2 × 10^{-4} M DODAC vesicles incorporating 1.24 × 10^{-4} M Fe_3O_4 (c). The arrows indicate the directions of spectral change as functions of increasing amounts of absorbed 266-nm laser energies.

triplets, $^3BP^*$, and the subsequently formed ketyl radicals both absorb at 545 nm. Addition of 10^{-3} M 1,4-cyclohexadiene (RH in Scheme I) efficiently quenched $^3BP^*$, which resulted in the clear separation of two consecutive decays: a fast one, due to the decay of $^3BP^*$ and intersystem crossing, and a slower one, due to $\dot{K}H$ (Figure 2). The ratio of absorbance obtained by extrapolating the longer lived component to zero time, A_e, to the absorbance observed immediately after the laser flash, A_0[7a,b] is a measure of the importance of the escape process:

$$\frac{A_e}{A_0} = \frac{\Sigma k_-}{\Sigma k_- + k_{ISC}} \tag{1}$$

As seen in the insert of Figure 2, introducing increasing amounts of magnetite per DODAC vesicle resulted in increased amounts of escaped KH. The effect obtained with 0.6 molar ratio of Fe_3O_4/DODAC (87.6 ± 3%) corresponds, within the limits of experimental error, to the maximum effect attainable.[17] The magnitude of the magnetic effects in the absence of magnets is the same as that found by applying an external field of approximately 2000 G.[7] In fact, an increase of exit from 55% to 84% was observed in dodecyltrimethylammonium chloride when a 2000-G magnetic field was applied.[7]

The determined binding contant, $K = 2 \times 10^4$ M^{-1}, indicated the complete incorporation of benzophenone into the magnetite carrying DODAC vesicles. Magnetic effects reported here originate, therefore, in the localization of benzophenone within the influence of single-domain magnetic particles confined in the matrices of surfactant vesicles. Single-domain magnetic particles have effectively split the triplet sublevels of the radical pair localized in close proximity and slowed down its intersystem crossing from the T_+ and T_- sublevels.[2-6] This, in turn, enhanced the efficiency of radical escape which has manifested in decreased LAT production (Scheme I). Thus, the observed effect of the photochemistry of benzophenone is a direct result of the magnetic moment in the vicinity of the magnetic particles. We are not unaware of the significance of finding magnetic effects in the absence of magnets and are currently exploring the potential applications of this phenomenon.

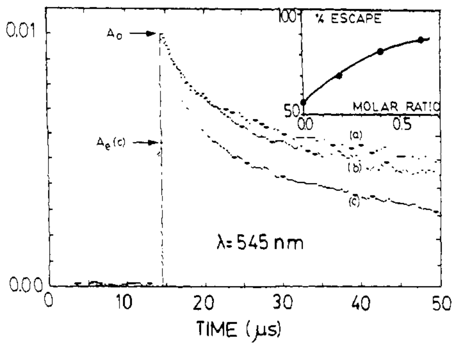


Figure 2. Laser flash photolysis of 8 × 10^{-5} M benzophenone in DODAC vesicles containing 0 (a), 0.205 (b), and 0.620 (c) molar ratios of Fe_2O_4. Excitation by 266-nm 8-ns pulses, observation at 545 nm. A_e and A_0 values indicated in the figure were obtained by computer extrapolations. Insert: Plots of percent of the escaped radicals as functions of the molar ratio Fe_3O_4 to DODAC (according to eq 1).

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged. Faruk Nome thanks CNPq Brazil for a fellowship. Pascal Herve thanks the French Government for a partial Paul Valery fellowhsip.

---

[16] Using the fourth harmonic of a Quanta-Ray DCR-1A Nd:YAG laser as the excitation source.[13]

[17] 85 = 55 + $^2/_3$ (100 − 55).[7]

Concerning the Lifetime of the Second Excited Singlet State of Adamantanethione

K. J. Falk, A. R. Knight, A. Maciejewski,[1] and R. P. Steer*

Department of Chemistry, University of Saskatchewan
Saskatoon, Saskatchewan, Canada S7N 0W0

Received September 24, 1984

Thiones are prominent among the growing group of organic molecules known to react chemically and/or fluoresce from excited singlet states higher than S_1.[2,3] Of the various aromatic, aralkyl, and alicyclic thiones which are members of this group, only two, thiobenzophenone and adamantanethione, have been the subject of extensive investigations of their S_2 photochemistry.

Excitation in the first strong absorption band of adamantanethione (**1**) near 250 nm populates the second excited singlet state, of $^1(\pi,\pi^*)$ character.[4] The end products of illuminating **1** at 254 nm in cyclohexane solution arise from the net insertion of the thione into C–H bonds of the solvent and from dimerization. There is good evidence that a free radical mechanism is operative.[5,6] Kinetic arguments, based on concentration quenching and quenching by 1,1′-azoisobutane, have been used to determine that the reactive precursor to both insertion and dimerization products has a lifetime of ca. 250 ps.[5-7] It has always been assumed in the aforementioned work that the reactive precursor is the second

---

[1] On leave from A. Mickiewicz University, Poznan, Poland.

[2] Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farneth, W. *Chem. Rev.* **1978**, *78*, 125–145.

[3] de Mayo, P. *Acc. Chem. Res.* **1976**, *9*, 52–59.

[4] Lawrence, A. H.; Liao, C. C.; de Mayo, P.; Ramamurthy, V. *J. Am. Chem. Soc.* **1976**, *98*, 3572–3579.

[5] Law, K. Y.; de Mayo, P.; Wong, S. K. *J. Am. Chem. Soc.* **1977**, *99*, 5813–5815.

[6] Law, K. Y.; de Mayo, P. *J. Am. Chem. Soc.* **1979**, *101*, 3251–3260.

[7] An earlier estimate[4] of ca. 130 ps was revised.