Communications to the Editor

Time-Resolved Laser Flash Spectroscopic Study of Benzyl Radical Pairs in Micelle Cages

Nicholas J. Turro,* Ming-Fea Chow, Chao-Jen Chung,
Yoshifumi Tanimoto, and Gregory C. Weed

Chemistry Department, Columbia University
New York, New York 10027

Received September 22, 1980

Photolysis of benzyl ketones provides a convenient means of producing triplet, spin-correlated geminate radical pairs.[1] In nonviscous, homogeneous solution these radical pairs rapidly ($\lesssim 10^{-9}$ s) become random free radicals.[2] Spin correlation is destroyed when the radical fragments have separated sufficiently to allow exchange forces to become negligible relative to weak, random, magnetic forces experienced by the individual radical centers, i.e., the spin-correlated triplet radical pair develops singlet character. Micelles have been shown to provide a unique type of "solvent cage" for a radical pair.[3] The hydrophobic portion of the micelle provides a restricted volume of space of dimensions which allow the exchange interaction between the radical center to rapidly decrease to very small values, but at the same time the micelle preserves the compositional correlation of geminate radical pairs for relatively long periods of time ($\gtrsim 10^{-5}$ s).[5] We report here a time-resolved laser flash spectroscopic investigation of triplet benzyl radical pairs produced in micelles. A study of transient absorption of benzyl radicals as a function of (1) isotopic composition and structure of the parent ketone, (2) magnetic field, and (3) the presence or absence of an aqueous phase radical trap provides support for the occurrence of two types of geminate benzyl radical pairs: a fast decaying pair and a slow decaying pair.

The structures of the ketones[6] employed in this study are shown in Chart I. Typically, a given ketone in aqueous solutions of hexadecyltrimethylammonium chloride (HDTCl) was excited by a 15-ns pulse of 249-nm light produced by an excimer laser.[7] Under these conditions a transient, whose spectral characteristics (λ_{max} 320 nm) are in good agreement with those of benzyl radical in homogeneous solution, is produced.[8a] The decay of benzyl radical absorption in methanol and in isooctane cleanly follows second-order kinetics in the time range of 50–50 000 ns. Thus, as expected,[8b] the disappearance of benzyl radicals in homogeneous solution, in the time range of interest, occurs predominantly via combination of random free radicals. In the same time domain, the decay of benzyl radicals (monitored by absorbance or optical density, Figure 1) in micellar solution is complex, but can be analyzed in terms of a "fast" first-order decay (rate constant, k_f) and a "slow" first-order decay (rate constant, k_s), i.e., in terms of eq 1, where $I(t)$ is the measured optical density at time t, I_f

$$I(t) = I_f \exp(-k_f t) + I_s \exp(-k_s t) \tag{1}$$

and I_s are fitting parameters, and k_f and k_s are the rate constants for the fast and slow decays, respectively.

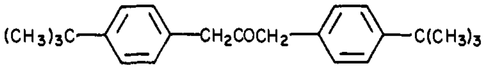
Chart I. Structures Employed in This Study

$C_6H_5CH_2COCH_2C_6H_5$

DBK

$C_6H_5{}^{13}CH_2CO{}^{13}CH_2C_6H_5$

DBK-*2,2′*-^{13}C



DtB-DBK

Table I. Rate Constants for Decay of Benzyl Radicals in Micellar Solution

	$k_f \times 10^6$, s^{-1} ^{b}		$k_s \times 10^6$, s^{-1} ^{c}	
ketone^a	0 G	400 G	0 G	400 G
DBK	2.5 ± 0.3	1.4 ± 0.1	0.021 ± 0.003	0.025 ± 0.003
DBK-*2,2′*-$^{13}C_2$	3.4 ± 0.3	2.3 ± 0.2	0.023 ± 0.001	0.026 ± 0.003

^{a} Ketone concentration: 4×10^{-4} M; HDTCl concentration: 0.05 M. Observation 320 nm. Samples N_2 purged. ^{b} First-order rate constant for fast decaying benzyl radicals. See text for discussion. Typical plot shown in Figure 1. ^{c} First-order rate constant for "slow" decaying benzyl radicals. See text for discussion.

Figure 2 summarizes a working mechanism for the interpretation of the data in Table I. From data in the literature,[9] the time scale for decarbonylation of $C_6H_5CH_2CO$ radicals is of the order of 10^{-8} s. Therefore, we expect decarbonylation to be nearly complete at the initial time periods investigated (~50 ns), and, as a result, the first significant transient species detected in our measurements are expected to be spin-correlated triplet benzyl radical pairs. Since the *total* benzyl radical concentration is being monitored in our experiments, the decay of benzyl radical absorption may be due to paths a, b, or c (it is assumed that formation of a singlet radical pair in a micelle is rate determining for a combination event). In the time region analyzed (~50–50 000 ns), a path involving radical escape followed by micelle reentry may be ruled out as a significant contributor for combination of benzyl radicals based on the following arguments: (1) The decay by such a path would follow second-order kinetics, whereas the observed fast and slow decays are both first order. (2) Although benzyl radicals escaping from micelles[10,11] have been found to be efficiently scavenged by aqueous Cu(II), the fast and slow decays are identical in the absence of Cu(II) or in the presence of 4×10^{-3} M Cu(II). (3) The fast and slow decays of 4-*tert*-butylbenzyl radicals are comparable to those for benzyl radicals. (4) The time scale for the slow process is of the order (~10^{-4} s) expected for electronic spin relaxation of benzyl radicals.[12]

An applied magnetic field and ^{13}C substitution cause a striking variation in the magnitude of k_f but influence k_s to a much less significant degree (Table I). The effects are consistent with the working mechanism of Figure 2. Thus, for DBK the decrease (2.5×10^6–1.4×10^6 s^{-1}) in k_f upon going from 0 to 400 G (Figure 1 and Table I) is consistent with a decrease in the rate of ISC of triplet correlated pairs because of the Zeeman splitting[13a] of

---

[1] (a) Engel, P. S. *J. Am. Chem. Soc.* **1970**, *92*, 6074. (b) Robbins, W. K.; Eastman, R. H. *Ibid.* **1970**, *92*, 6076.

[2] Frank, J.; Rabinowitch, E. *Trans. Faraday Soc.* **1934**, *30*, 120. Rabinowitch, E.; Wood, W. *Ibid.* **1936**, *32*, 1381. Noyes, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2042; **1956**, *78*, 5486.

[3] Turro, N. J.; Cherry, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 7431.

[4] Fendler, J. H.; Fendler, E. J. "Catalysis in Micellar and Macromolecular Systems"; Academic Press: New York, 1975.

[5] For example, the exit rate of toluene from HDTCl micelles can be estimated to be ~5×10^5 s^{-1} from literature data: Almgren, M.; Grieser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279.

[6] The synthesis of DBK-*2,2′*-$^{13}C_2$ described in a full paper: Turro, N. J.; Chow, M. F.; Kraeutler, B. *J. Am. Chem. Soc.*, in press.

[7] For a description of the experimental setup, see: Turro, N. J.; Aikawa, M.; Butcher, J. A. *J. Quantum Electronics* **1980**, *QE-16*, 1218.

[8] (a) McAskill, N. A.; Sangster, D. F. *Aust. J. Chem.* **1977**, *30*, 2107 and references therein. (b) Lehni, M.; Schuh, H.; Fischer, H. *Int. J. Chem. Kinet.* **1979**, *11*, 705.

[9] Brunton, G.; McBay, H. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1977**, *99*, 4447. Robbins, W. K., Eastman, R. H. *Ibid.* **1970**, *92*, 6077. Perkins, M. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* **1974**, 297.

[10] Turro, N. J.; Kraeutler, B.; Anderson, D. R. *J. Am. Chem. Soc.* **1971**, *101* 7435.

[11] Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Weed, G.; Kraeutler, B. *J. Am. Chem. Soc.* **1980**, *102*, 4843.

[12] Walling, C.; Lepley, A. R. *J. Am. Chem. Soc.* **1972**, *94*, 2007.

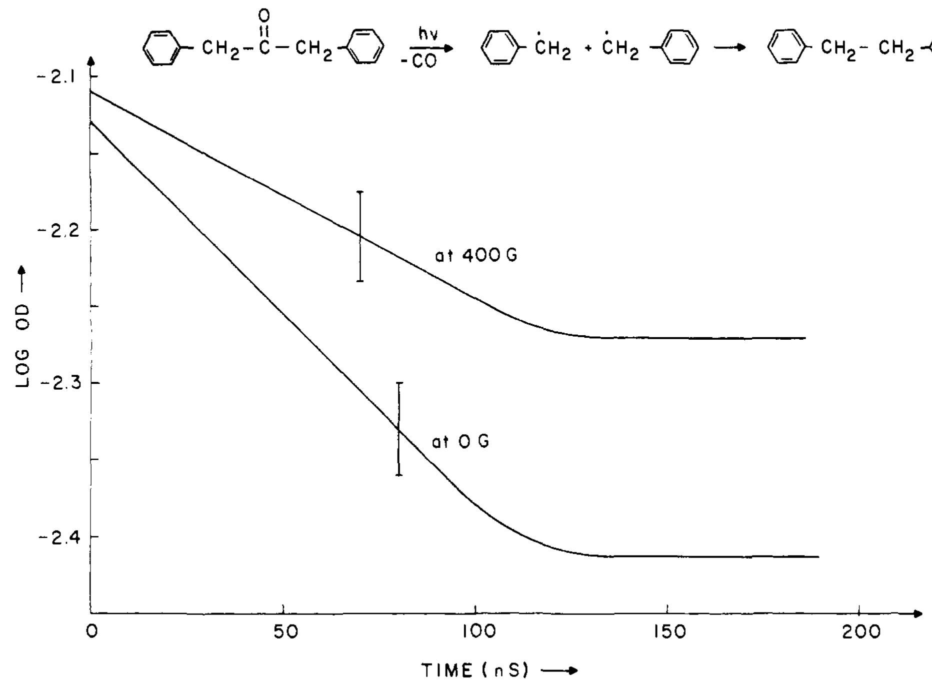


Figure 1. Decay of benzyl radical absorption in the "short time" domain (~50–200 ns) in the earth's magnetic field (~0 G) and a magnetic field of 400 G.

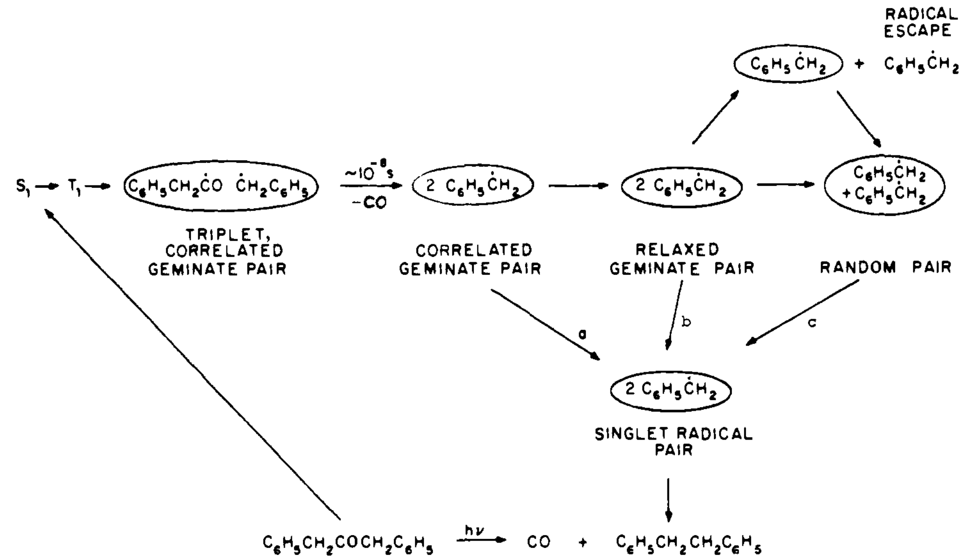


Figure 2. Schematic representation of the mechanism proposed for interpretation of the results of Figure 1 and Table I. Light absorption to form S_1 and molecular ISC to form a triplet is followed by α cleavage to form a triplet correlated geminate pair. It is postulated that decarbonylation occurs with preservation of spin correlation and formation of a geminate benzyl radical pair. This pair undergoes ISC by two pathways corresponding to the different decays of Figure 1: (a) a faster hyperfine induced ISC to produce a singlet radical pair and (b) a slower spin–lattice relaxation which also produces singlet radical pairs. Since combination of the singlet radical pairs is expected to be very fast in the time domain of interest, the ISC processes are rate limiting. Other pathways for recombination, such as escape followed by reentry (overall path c), correspond to a much longer time scale than that monitored in this report.

the T_+ and T_- levels; the increase (2.5×10^6–3.4×10^6 s^{-1}) in k_f upon going from dibenzyl ketone (DBK) to DBK-$2,2'$-$^{13}C_2$ is consistent with an increase in the rate of ISC because of the magnetic isotope effect[13b] of ^{13}C. At 0 G the measurable fraction of fast decaying pairs in the time domain <200 ns is 47 ± 7% (10 independent experiments), whereas at 400 G, the fraction of fast decaying pairs in the time domain <200 ns decreases to 31 ± 2% (6 independent experiments). The faster rate of ISC of $C_6H_5{}^{13}CH_2\cdot$ radical pairs is also consistent with the observation[11] that the cage effect for DBK-$2,2'$-$^{13}C_2$ is substantially higher than that for DBK. The lack of a substantial magnetic isotope effect or magnetic field effect on the rate constant k_s (Table I) is consistent with the assignment of the slow decay to the recombination of geminate benzyl radical pairs which have undergone spin relaxation by a random spin–lattice mechanism.

Addition of Cu(II) to samples does not measurably alter the decay of either the fast or the slow component. This result and the observation that laser excitation of 4,4′-di-*tert*-butyldibenzyl ketone produces a fast and slow decay that are quite comparable ($k_f \simeq 2.6 \times 10^6$, $k_s \simeq 0.023 \times 10^6$ s^{-1}) to those found for DBK,

---

(13) (a) At 0 G, hyperfine coupling induces intersystem crossing (ISC) between all three (degenerate) sublevels (T_+, T_-, and T_0) of the triplet radical pair and the singlet state of the radical pair. An external field whose strength is greater than the hyperfine coupling will only leave the degeneracy of T_0 and S and inhibit ISC. As a result, the decay of spin correlated benzyl radical pairs (which is rate limited by ISC) will decrease. For a discussion of the effect of Zeeman splitting on ISC of radical pairs, see: Closs, G. *Proc. Int. Cong. Pure Appl. Chem.* **1971**, *23* (4), 19. Lawler, R. G. *Prog. Nucl. Magn. Reson. Spectrosc.* **1973**, *9*, 147. (b) Buchachenko, A. L. *Russ. Chem. Rev.* **1976**, *45*, 375.

provide substantial evidence that neither the slow nor fast decay involves benzyl radicals that escape from HDTCl micelles.[14]

Only recently have time-resolved magnetic field effects on the dynamics of radical pairs been measured.[15-18] Our results confirm many of the conclusions concerning the behavior of radical pairs in micelles that were proposed on the basis of steady state measurements.[19] It is noteworthy that the time scales for geminate reactions of radical pairs in micelles are now confirmed, by direct spectroscopic measurement, to be several orders of magnitude greater than the time scale for analogous processes in homogeneous solution.

In summary, the laser flash excitation of DBK in HDTCl solution produces geminate triplet radical pairs in micelle aggregates. These geminate pairs decay by two major pathways in the time domain 50–50 000 ns: ISC of spin-correlated triplet radical pairs followed by combination of singlet radical pairs to form diphenylethane (k_f) and recombination of relaxed geminate radical pairs to form diphenylethane (k_s). The rate of spin correlated ISC is substantially decreased by application of a magnetic field of 400 G and is substantially increased by ^{13}C in the CH$_2$ groups of the benzyl radicals. The relaxed geminate radical pairs are not sensitive to either magnetic effect. The escape of benzyl radicals from micelles occurs on a longer time scale than that explored in this investigation.

Acknowledgment. We thank the Air Force Office of Scientific Research and the National Science Foundation for their generous support of this research. We also thank Drs. H. Hayashi and S. Nagakura for informing us of their results on the photolysis of DBK in anionic sodium dodecyl sulfate micelles. Dr. Gary Lehr is thanked for his important comments relevant to the interpretation of the data.

---

[14] This conclusion follows from the observation that 4-*tert*-butylbenzyl radical pairs undergo nearly 100% geminate micellar cage recombination.

[15] Werner, H. J.; Staerk, H.; Weller, A. *J. Chem. Phys.* **1978**, *68*, 2419. Schulten, K.; Staerk, H.; Weller, A.; Werner, H.-J.; Nickel, B. *Z. Phys. Chem.* **1976**, *NF101*, 441.

[16] Michel-Beyerle, M. E.; Krieger, H. W.; Haberkorn, R.; Seidlitz, H. *Chem. Phys.* **1979**, *42*, 441.

[17] Sakaguchi, Y.; Nagakura, S.; Hayashi, H. *Chem. Phys. Lett.* **1980** *72*, 420.

[18] Closs, G.; Miller, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 1639.

[19] Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369.

Polymerization of Acetylenes, 1,3-Dienes, and Allyl Halides on Active Uranium Powder

T. C. Wen, C. C. Chang, and Y. D. Chuang

Institute of Nuclear Energy Research
Hsinchu, Taiwan, Republic of China

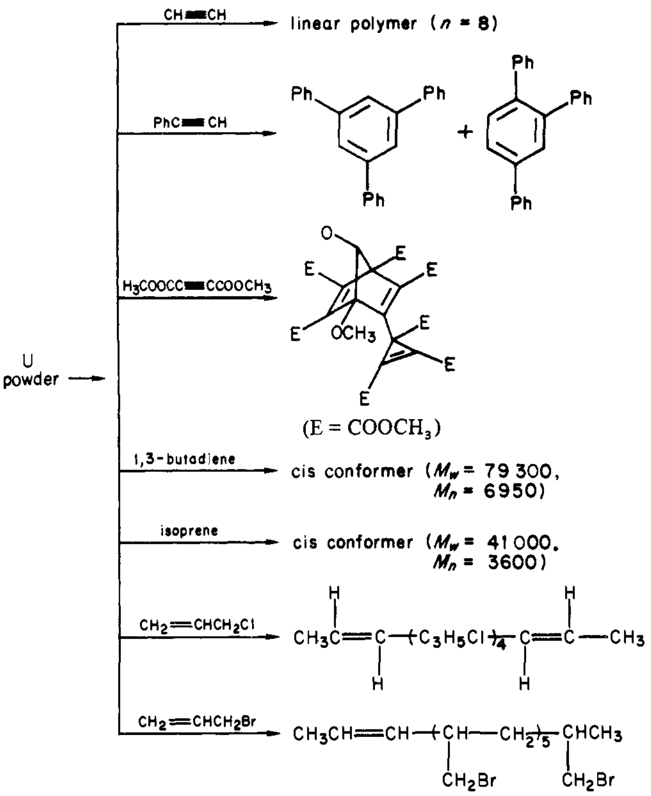
J. P. Chiu and C. T. Chang*

Department of Chemistry, National Tsing Hua University
Hsinchu, Taiwan, Republic of China

Received November 10, 1980

During the past decade there has been a considerable upsurge of research activity in the chemistry of metal vapors, aiming mainly at the facile syntheses of organometallic complexes and the initiation of a variety of chemical reactions by active metal atoms or cluster.[1] A hitherto unnoticed but related technique of producing large quantities of active uranium metal powders by means of electrolytic amalgamation has recently been shown to provide a simple and energy-saving route to organouranium compounds and other related materials.[2] The higher activity of this uranium powder in comparison with that from other methods is demonstrated by its very high reactivity in the synthesis of uranocene.[3] Other pronounced features of this metal powder have been further revealed in its reactions with various substrates, giving rise to various kinds of hydrocarbons, oligomers, and polymers. The metal powder was repeatedly used for five times, and its catalytic activity remained virtually unchanged.

Scheme I



In this communication we describe the reactions of the uranium powder with acetylenes, 1,3-dienes, and allyl halides at room temperature, which outlines unexpected results as shown in Scheme I. This work demonstrates the first example of an f-block element induced polymerization.

All operations were carried out in an N$_2$-flushed glove bag or an evacuated system. The starting material, uranium amalgam, was prepared as previously described.[4] The uranium amalgam was washed with dilute HCl, water, and acetone and finally placed in an apparatus designed for the decomposition and removal of mercury at 150 °C and 10^{-4} torr. Liquid organic substrates were then introduced onto the thereby obtained black, fresh uranium powder, whereas the gaseous substrates were cocondensed with benzene on the powder. The reactions of 10 g of uranium powder with dimethyl acetylenedicarboxylate (4 mL), phenyl acetylene (5 mL), and acetylene (4 mmol) gave different kinds of polymers. Kauer et al.[5] and Lacount et al.[6] heated dialkyl ethers of acetylenedicarboxylic acid at 85 °C for 10 days and at 120 °C for several hrs, respectively, to obtain the tetramer tetramethyl 4-methoxy-5-[1,2,3-tris(methoxycarbonyl)-2-cyclopentenyl]-1-oxabicyclo[2.2.1]hepta-2,5-diene-1,2,3,6-tetracarboxylate, whereas in the presence of our uranium catalyst the reaction proceeds at room temperature to give 70% yield in only 2 h. The reaction mixture was filtered, and unreacted substrate was pumped out.

---

[1] (a) P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972); (b) K. J. Klabunde, *Acc. Chem. Res.*, **8**, 393 (1975); (c) K. J. Klabunde, and T. O. Murdock, *J. Org. Chem.*, **44**, 3901 (1979).

[2] C. C. Chang, N. K. Sung-Yu, C. S. Hseu, and C. T. Chang, *Inorg. Chem.*, **18**, 855 (1979); L. C. Wang, H. C. Lee, T. S. Lee, W. C. Lai, and C. T. Chang, *J. Inorg. Nucl. Chem.*, **40**, 507 (1978).

[3] R. D. Rieke and Lee D. Rhyne, *J. Org. Chem.*, **44**, 3445 (1979); D. F. Stark and A. Streitweiser, *J. Am. Chem. Soc.*, **95**, 342 (1973).

[4] L. C. Wang, H. H. Hung, H. C. Lee, and C. T. Chang, *J. Chem. Soc., Chem. Commun.*, 124 (1975).

[5] J. C. Kauer and H. E. Simmons, *J. Org. Chem.*, *33*, 2721 (1968).

[6] E. Legoff and R. B. Lacount, *Tetrahedron Lett.*, **24**, 2333 (1967).

0002-7863/81/1503-4576$01.25/0