Supplementary Material Available: Spectroscopic and analytical data for compounds **5** and **8–18** and experimental procedures for the preparation of compounds **8** and **16** (10 pages). Ordering information is given on any current masthead page.

---

(24) For such substitutions of chiral allylic acetals[24a,b] and carbamates,[24c] see: (a) Fujiwara, J.; Fukutani, Y.; Hasegawa, M.; Maruoka, K.; Yamamoto, H. J. Am. Chem. Soc. 1984, 106, 5004. (b) Alexakis, A.; Mangeney, P.; Ghribi, A.; Marek, I.; Sedrani, R.; Guir, C.; Normant, J. Pure Appl. Chem. 1988, 60, 1. (c) Denmark, S. E.; Marble, L. K. J. Org. Chem. 1990, 55, 1984.

Example of Diffusion-Limited Behavior in the Reaction of a Geminate Radical Pair in Micelles[1]

C. Bohne,[2] M. S. Alnajjar,[3] D. Griller,*,[2] and J. C. Scaiano*,[2]

Division of Chemistry
National Research Council of Canada
Ottawa, Canada K1A 0R6
Pacific Northwest Labs
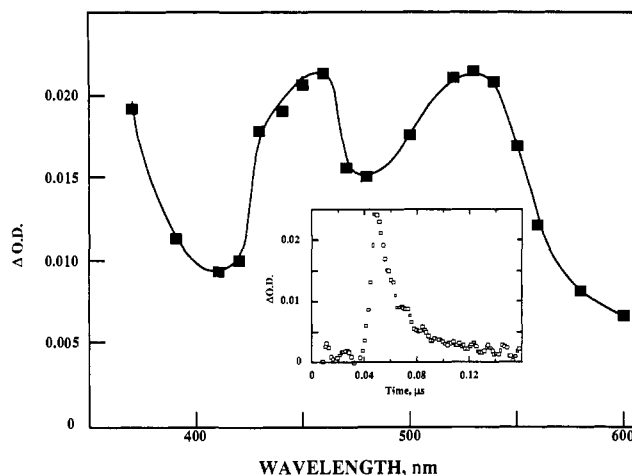*P.O. Box 999, Richland, Washington 99352*

Received August 23, 1990
Revised Manuscript Received December 14, 1990

Triplet-derived, carbon-centered radical pairs in micelles undergo geminate processes in a few hundred nanoseconds.[4–8] In this time, the two radicals in a given micelle undergo several encounters. However, for reaction to take place between them, the radical pair must first cross from the triplet to the singlet state. That crossing can be slowed down further by applying a magnetic field that induces Zeeman splitting of the triplet sublevels. Earlier work has indicated that hyperfine couplings play an important role in controlling the decay of these radical pairs.[9]

The rate constant, k_{reacn}, for radical-pair reaction within a micelle is determined by diffusional processes and spin interactions. It can be expressed in terms of the rate constant for radical–radical encounters, k_e, and the probability, f, that a given encounter will have singlet character, eq 1.[10]

$$k_{reacn} = k_e f \qquad (1)$$

For a triplet-derived radical pair, the maximum value of f will be 0.25 if the radicals can separate over large distances so that the electron-exchange interaction, J, vanishes. However, this situation does not often arise in micelles where separation is limited

(1) Issued as NRCC-32322.
(2) NRCC.
(3) Pacific Northwest Labs. This work was partially supported by the Office of Basic Energy Sciences of the U.S. Department of Energy under Contract DE-AC06-76RLO-1830.
(4) Scaiano, J. C.; Abuin, E. B.; Stewart, L. C. J. Am. Chem. Soc. 1982, 104, 5673.
(5) Gould, I. R.; Zimmt, M. B.; Turro, N. J.; Baretz, B. H.; Lehr, G. F. J. Am. Chem. Soc. 1985, 107, 4607.
(6) Closs, G. L.; Forbes, M. D. E.; Norris, J. R., Jr. J. Phys. Chem. 1987, 91, 3592.
(7) Levin, P. P.; Kuz'min, V. A. Izv. Akad. Nauk SSSR, Ser. Khim. 1988, 298.
(8) Turro, N. J.; Zimmt, M. B.; Gould, I. R. J. Phys. Chem. 1988, 92, 433.
(9) This has been the subject of a recent comprehensive review: Steiner, U. E.; Ulrich, T. Chem. Rev. 1989, 89, 51.
(10) Evans, C. H.; Scaiano, J. C. J. Am. Chem. Soc. 1990, 112, 2694.

Figure 1. Transient absorption spectra following excitation of benzophenone (3 mM) in SDS micelles (0.2 M) in the presence of thiophenol (29 mM) ca. 6 ns after the laser pulse. The insert shows a decay trace recorded at 540 nm.

by the phase boundary. Here, f will roughly depend upon J^{-1} and hence on r, the average separation between the radicals.[11] By contrast, k_e is proportional to r^{-n} ($2 \leq n \leq 3$). The intramicellar encounter time $(1/k_e)$ can be expected to be of a magnitude comparable to those observed for excimer formation and energy transfer in related (but larger) micelles; these values are in the 50–100-ns range.[12,13]

It has long been known that magnetic resonance properties such as differences in g values and/or hyperfine interactions control spin-state relaxation. To date, most of the experiments have focused upon the role of hyperfine interactions. We reasoned that in order to identify a system with very fast spin relaxation we should investigate radicals with broad or undetectable EPR lines. In this work, we have deliberately introduced a radical with a very anisotropic g tensor as partner in a triplet radical pair and show that this property can induce rapid loss of triplet character.

The system investigated involved the reaction of benzophenone triplet with thiophenol, reaction 2. Laser flash photolysis (337 or 308 nm) was used to monitor the triplet at 600 nm to avoid interference from $Ph_2C^\bullet OH$ (λ_{max} 540 nm) or $PhS^\bullet$ (λ_{max} 450 nm).[14] In benzene, $k_2 = (2.6 \pm 0.4) \times 10^8$ M^{-1} s^{-1}, as determined from the effect of thiophenol on the rate of benzophenone triplet decay.

$$^3Ph_2CO^* + PhSH \rightarrow Ph_2C^\bullet OH + PhS^\bullet \qquad (2)$$
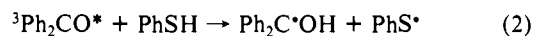
When benzophenone (0.003 M) was photolyzed in sodium dodecyl sulfate (SDS; 0.2 M) micelles, the ketone triplet decayed predominantly by hydrogen abstraction from the surfactant ($\tau \sim 300$ ns).[4] However, addition of thiophenol shortened the triplet lifetime (reaction 2) monitored at 600 nm, and at thiol concentrations ≥ 0.03 M (which leads to occupancies >7), it was below our detection limit (<5 ns). At this point, abstraction from the surfactant can be neglected. The transient spectrum corresponds to the thiyl (450 nm)[15] and ketyl (540 nm) radicals (Figure 1). The lifetimes for both transients were ca. 20 ns (see insert in Figure 1) and independent of further addition of thiol. There was no residual absorption following the decay, indicating that radical escape from the micelle was negligible and that decay took place

(11) Wertz, J. E.; Bolton, J. R. Electron Spin Resonance. Elementary Theory and Practical Applications; McGraw-Hill: Toronto, 1972. The relationship between J and r depends upon orbital overlap and falls off rapidly at larger interradical distances: Tse, J. C., unpublished results.
(12) Infelta, P. P.; Grätzel, M. J. Chem. Phys. 1979, 70, 179.
(13) Rothenberger, G.; Infelta, P. P.; Grätzel, M. J. Phys. Chem. 1979, 83, 1871.
(14) Details of our laser photolysis system have been reported elsewhere: Scaiano, J. C. J. Am. Chem. Soc. 1980, 102, 7747. Scaiano, J. C.; Tanner, M.; Weir, D. J. Am. Chem. Soc. 1985, 107, 4396.
(15) Ito, O.; Matsuda, M. J. Am. Chem. Soc. 1979, 101, 5732.

by intramicellar radical–radical reaction. Application of an external field ($\leq$3.2 kG) had no effect on the experiment. The size of SDS micelles can be increased with the addition of NaCl.[16–18] The ketyl lifetime increases to 40 and 70 ns with the addition of 0.4 and 0.6 M NaCl, respectively.

Hyperfine interactions, which are common in other systems, cannot account for the rapid relaxation observed in these experiments, since larger interactions in other systems have not caused similar effects.[4,9] Moreover, $Ph_2C^\bullet OH$ has been used in numerous experiments where triplet character has been preserved for hundreds of nanoseconds[4,19] so that the properties of its g tensor cannot account for the relaxation. We interpret our results in terms of rapid relaxation related to the g tensor for $PhS^\bullet$.

Relaxation that comes from g-tensor anisotropy is magnetic field dependent but at the fluxes used in these experiments cannot contribute to rapid relaxation.[20] However, both transverse (T_1) and longitudinal (T_2) relaxation times associated with *spin rotational relaxation* are significant. They are defined in eq 3, where τ_0 is the rotational relaxation time and δ_g represents the shift of g-tensor components from the free-electron value,[20] e.g., $\delta g_x = g_x - 2.002\,319$.

$$T_1^{-1} = T_2^{-1} = \frac{(\delta g_x{}^2 + \delta g_y{}^2 + \delta g_z{}^2)}{9\tau_0} \tag{3}$$

The principal values of the g tensor for $PhS^\bullet$ are 2.003, 2.003, and 2.017.[21] While those for $Ph_2C^\bullet OH$ are not known, we have used representative values for the structurally related radical $(CH_3)C^\bullet(OH)CO_2{}^-$, viz., 2.0037, 2.0036, and 2.0031, respectively.[21] These values lead to g(isotropic) = 2.003 47, which is close to the value of 2.0030 observed for $Ph_2C^\bullet OH$ in fluid solution.[21]

Values of τ_0 depend upon solvent viscosity and radical size and are therefore difficult to define in micelles where viscosities are inhomogeneous and poorly defined. However, $T_1 + T_2$, for $PhS^\bullet$, must be less than the radical-pair lifetime ($\sim$20 ns). Substitution into eq 3 gives $\tau_0 = 2 \times 10^{-13}$ s, which is in accord with values of 10^{-12} to 10^{-13} s observed for small organic molecules in hydrocarbon solvents.[22] Values of τ_0 in this range lead to T_1-($Ph_2C^\bullet OH$) in the neighborhood of 1 μs which are consistent with the fact that this radical does not itself induce rapid relaxation in numerous experiments described in the literature.[9] Thus, spin rotational relaxation induced by $PhS^\bullet$ accounts for rapid relaxation observed in this work.

Our results by themselves cannot rule out spin–orbit coupling (SOC) as the mechanism for rapid relaxation; however, our preference for an interpretation based on the g tensor should be examined in the context of other studies involving oxygen,[19,23] germanium-centered[24], and benzenesulfonyl[24] radicals. In the last two cases modest magnetic field effects and micellar escape were observed in SDS micelles.[24] This argues against atomic mass as a key parameter.

An implication of this result is that the lower limit for the rate constant, k_c, for encounters between radicals in SDS micelles must be $\sim$5 × 10^7 s^{-1}, i.e., the reciprocal of the experimental lifetime of the radical pairs. Thus, in radical pairs where spin rotational relaxation is not rapid and radical-pair lifetimes are ca. 1 μs, the value of f must be $\leq$10^{-2}; see eq 1.

The dominant effect found in this study is related to the shift of the components of the g tensor from the free-spin value. Thus organic radicals, in which one of the principle values in the g tensor is ca. 2.02, will be capable of reducing triplet-pair lifetimes in micelles to the nanosecond time domain. Radicals such as peroxyl and perthiyl fall into this category.[21]

The present results indicate that organic radicals in which a component of the g tensor differed by unity from the free-spin value would actually be capable of inducing relaxation within the 50-ps lifetime that characterizes a geminate radical pair in the solvent cage. Transient radicals in this category would have broad EPR lines that would be essentially undetectable in homogeneous solution. Examples are alkoxyl and alkanethiyl radicals which, in non-hydrogen-bonding solvents, have extremely anisotropic g tensors due to electron exchange between the degenerate p orbitals.[25] For such "EPR invisible" radicals, all encounters should lead to reaction and f (eq 1) will approach unity.

(25) Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1618.

Photoelectron Spectrum of Cyclopropenylidene and Weak Bonds in Cyclopropenyl Radical

Horst Clauberg and Peter Chen*,1

Mallinckrodt Chemical Laboratories
Harvard University, Cambridge, Massachusetts 02138

We report the direct determination of the heat of formation for cyclopropenylidene (c-C_3H_2) by photoelectron spectroscopy. An adiabatic ionization potential of 9.15 ± 0.03 eV is measured for the carbene produced in a molecular beam by supersonic jet flash pyrolysis of 3-chlorocyclopropene. Insertion of this ionization potential into a thermochemical cycle yields $\Delta H_f(C_3H_2) = 114 \pm 4$ kcal/mol. In addition, the homolytic C–H bond dissociation energy for cyclopropenyl radical is determined to be 61 ± 6 kcal/mol. *The reduced bond strength in C_3H_3 radical is found to be in quantitative agreement with a proposed general relationship of radical bond strengths to carbene singlet–triplet splittings.*

Time-of-flight (TOF) mass and photoelectron spectrometers and the flash pyrolytic nozzle source are described elsewhere.[2] Laser light at 118.2 nm (10.49 eV) for photoionization was generated by frequency-tripling the Nd^{3+}:YAG third harmonic in a xenon cell.[2] 3-Chlorocyclopropene was synthesized and purified according to the procedure by Breslow.[3] Flash pyrolysis of 3-chlorocyclopropene (1500 °C, 10–50 μs contact time) resulted in clean loss of HCl, as shown in Figure 1. Comparison of the TOF mass spectra with heat off and heat on shows that conversion to C_3H_2 is clean and complete. We find no detectable secondary reactions of the carbene. Similar pyrolyses[4] of chloroform and α-deuterated vinyl chlorides indicate that α-elimination of HCl (DCl) is facilitated only for a singlet ground state carbene like cyclopropenylidene. Isomeric C_3H_2 species, propadienylidene and

(16) Turro, N. J.; Zimmt, M. B.; Lei, X. G.; Gould, I. R.; Nitsche, K. S.; Cha, Y. *J. Phys. Chem.* **1987**, *91*, 4544.

(17) Kalyanasundaram, K. *Photochemistry in Microheterogeneous Systems*; Academic Press: New York, 1987.

(18) Boens, N.; Luo, H.; Van der Auweraer, M.; Reekmans, S.; De Schryver, F. C.; Malliaris, A. *Chem. Phys. Lett.* **1988**, *146*, 337.

(19) Evans, C.; Ingold, K. U.; Scaiano, J. C. *J. Phys. Chem.* **1988**, *92*, 1257.

(20) Lüders, K.; Salikhov, K. M. *Chem. Phys.* **1987**, *117*, 113.

(21) Fischer, H.; Paul. H. Organic C-Centered Radicals. In *Landolt-Börnstein: Magnetic Properties of Free Radicals*; Fischer, H., Hellgewe, K. H.d, Eds.; Springer-Verlag: Berlin, 1977; New Series, Vol. 9, Parts B and C.

(22) Assink, R. A.; Jonas, J. *J. Chem. Phys.* **1972**, *57*, 3329.

(23) Levin, P. P.; Kuz'min, V. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1987**, 1003.

(24) Hayashi, H.; Sakaguchi, Y.; Mochida, K. *Chem. Lett.* **1984**, 79. Hayashi, H.; Sakaguchi, Y.; Tsunooka, M.; Yanagi, H.; Tanaka, M. *Chem. Phys. Lett.* **1987**, *136*. 436.

(1) David and Lucile Packard Fellow, NSF Presidential Young Investigator.

(2) (a) Minsek, D. W.; Chen, P. *J. Phys. Chem.* **1990**, *94*, 8399. (b) Blush, J. A.; Park, J.; Chen, P. *J. Am. Chem. Soc.* **1989**, *111*, 8951.

(3) Breslow, R.; Ryan, G.; Grover, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 988.

(4) Chen, P., unpublished data.