by using the Cary 14 spectrophotometer. For fluorescence quantum efficiency measurements, the concentrations of naphthalene, as a standard, and of all sulfones were adjusted so that the absorptions of the systems were practically the same at λ_{ex} 310 nm. The measured fluorescence intensities (I_f) at the wavelength corresponding to the maximum of fluorescence were used to calculate the quantum efficiencies (I_f) relative to sulfone **9**. Small variations, in the absorbances values (A) at λ 310 nm were included in the calculation. The quantum yields (Table V) were then calculated according to the following expression:[27]

$$\frac{\Phi_f}{\Phi_f'} = \frac{I_f(1 - 10^{-A'})}{I_f'(1 - 10^{-A})}$$

Fluorescence Decay Time (τ_s). The fluorescence decay times were calculated from the Stern–Volmer relationship for oxygen quenching of the fluorescence emission in cyclohexane[17] according to the following expression:

$$L_0/L = 1 + \tau_s k_q[Q']$$

where L and L_0 are the fluorescence intensities with and without air, τ_s is the mean decay time of the deaerated solution, k_q is the quenching rate constant for oxygen, and [Q′] is the concentration of dissolved oxygen. The value of $k_q[Q']$ was taken as $6 \times 10^7\ s^{-1}$.[17] The fluorescence intensity measurements were first obtained with samples deaerated with argon and then repeated after saturation with air, to give the L_0 and L values. The results, together with k_f values calculated from the expression $k_f = \phi_f\tau_s^{-1}$, are presented in Table V.

Fluorescence of the Sulfones 8, 13, and 14. The spectra were obtained in EPA (ether:isopentane:ethanol = 5:5:2). The emission maxima were observed at 317 nm for **8** (λ_{ex} 254 nm), 348 for **13** (λ_{ex} 310 nm), and 343 nm for **14** (λ_{ex} 310 nm).

Fluorescence of the Sulfones 7, 9, and 10. The spectra were obtained in cyclohexane at excitation wavelength of 310 nm (Table V).

(27) Calvert, J. G.; Pitts, J. N., Jr. "Photochemistry"; Wiley: New York, 1966; p 800.

Phosphorescence of the Sulfones 7, 9, and 10. The phosphorescence spectra were observed in chloroform glass at 77 °C. The emission maxima were found at 468 (onset 405) nm for **7** (broad), 480 nm for **9**, and 475 nm for **10**. (Table VI).

Phosphorescence of the Sulfones 8, 13, and 14. The phosphorescence spectra were observed in EPA glass at 77 K. The emission maxima were found at 410, 433, and 460 nm for **8** (λ_{ex} 254 nm), 495, 530, 570, and 620 nm for **13** (λ_{ex} 310 nm), and 484, 518, 557, and 602 nm for **14** (λ_{ex} 310 nm) (Table VI).

F. CIDNP Investigations. All CIDNP measurements were performed on a Bruker WP 80-MHz FT NMR spectrometer with a ^1H probe modified for irradiation of the sample through a lens–fiber optic light pipe arrangement (see Figure 3).

The unfiltered light of a Varian 300 W EIMAC VIX 300 UV Xe–Hg lamp irradiated the sample. The spectra were obtained from Fourier transformations of 5–10 free induction decays recorded at ca. 20°–60° flip angles and 2-s pulse delay.

Approximately 10 mg of the sample to be analyzed was dissolved in 0.5 mL of a deuterated solvent, usually C_6D_6 and placed in either a Pyrex or a quartz NMR tube. Certain additives were used to elucidate the nature of the photochemical mechanism. Tri-*n*-butyltin hydride and bromotrichloromethane were added as radical scavengers. Benzophenone (E_T = 68.6 kcal/mol),[16] acetophenone (E_T = 73.7 kcal/mol),[16] and xanthone (E_T = 74.0 kcal/mol)[16] were added as triplet sensitizers. The results are listed in Table VII and in Figures 1 and 2.

Acknowledgment. The support for this work was provided by the National Institutes of Health (GM 16611) and the University of Kansas General Research Fund. Support for the purchases of the Bruker WP80 FTNMR with the photo-CIDNP probe and the PE 555 UV-vis spectrometers (CHE 77-07826 and 78-03307) is gratefully acknowledged. The assistance of Prof. G. W. Everett in the CIDNP experiments is especially appreciated. B.M. thanks the International Research and Exchange Program for partial support.

Mechanistic Studies of the Photodecomposition of Arylmethyl Sulfones in Homogeneous and Micellar Solutions

Ian R. Gould,[†] Chen-ho Tung,[†] Nicholas J. Turro,*[†] Richard S. Givens,[‡] and Bogdan Matuszewski[‡]

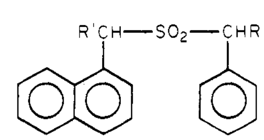
Contribution from the Department of Chemistry, Columbia University, New York, New York 10027, and the Department of Chemistry, University of Kansas, Lawrence, Kansas 66044. *Received June 30, 1983*

Abstract: The mechanism of photodecomposition of aryl sulfones has been investigated by using both steady-state and time-resolved techniques. Direct evidence for radical and triplet-state intermediates is provided. A correlation is found between the dynamics of reaction of the intermediate triplet states with the stabilities of the intermediate radicals.

The photoactivity of aryl sulfones was first reported by Cava et al.[1] who found that upon irradiation these compounds efficiently lose molecular sulfur dioxide and yield products typical of radical coupling reactions. The quantum yields for reaction of a series of aryl sulfones have been determined under both direct photolysis and triplet-sensitized reaction conditions.[2] It was found that both the singlet and triplet states of these compounds are photoreactive and that the relative amount of reaction from each state was structure dependent. For example, the photocleavage of dibenzyl sulfone (DBS) **1a** was found to occur both from singlet and triplet states. For the naphthyl benzyl sulfone **2a** reaction was found

p-RPhCH$_2$SO$_2$CHR′Ph

1a, R = R′ = H
1b, R = CH_3; R′ = H
1c, R = H; R′ = CH_3



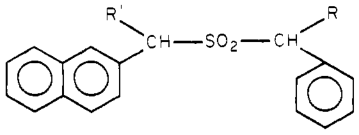
2a, R = R′ = H
2b, R = CH_3; R′ = H
2c, R = H; R′ = CH_3

to occur mainly from the triplet state; however, for the β-naphthyl sulfone **3a** the singlet state was determined to be the more pho-

[†]Columbia University.
[‡]University of Kansas.

(1) Cava, M. P.; Schlessinger, R. H.; VanMeter, J. P. *J. Am. Chem. Soc.* **1964**, *86*, 3173.

0002-7863/84/1506-1789$01.50/0



3a, R = R' = H
3b, R = CH_3; R' = H
3c, R = H; R' = CH_3

tolabile. Subsequent work with stereochemically defined **1c**, **2b,c**, and **3b,c** showed that equilibration of the chiral carbon's stereochemistry occurred faster than radical coupling to form the hydrocarbon product. Additionally, racemization of the sulfone was more efficient for the cases of methyl substitution on the naphthyl side (**2c** and **3c**) and occurred only in the singlet manifold.[2d] Furthermore, when irradiation was performed in deuterated or hydroxylic solvents, no deuterium was found to be incorporated in the recovered sulfone nor was there any evidence for ether or alcohol products. These results were taken as evidence that the primary reaction step involves reversible cleavage to form radical intermediates which further decompose with loss of SO_2 to yield the coupling products.[2]

The chemistry of benzylic radical pairs in micellar media and in the presence of external magnetic fields can potentially provide information concerning the multiplicity of radical pair reactions.[3-5] Accordingly, we have investigated the photochemistry of aryl sulfones as possible radical pair precursors. In particular, we have examined the effects of micellization, triplet sensitization, and magnetic fields on the photoproducts from these compounds. In addition, we have used the powerful technique of pulsed-laser photolysis to determine directly the nature and reaction dynamics of the transient intermediates in these reactions. The results of these experiments provide direct evidence as to the nature of the intermediates and to the multiplicity and dynamics of the intermediate excited states.

Experimental Section

Sulfones **1**–**3** were prepared according to a procedure described previously.[2d] Spectrograde solvents were used in all cases. Steady-state irradiations were performed in argon- or nitrogen-purged solutions at 254 nm for sulfone **1** and >300 nm for **2** and **3**. Irradiations using acetophenone and acetone as triplet sensitizers were performed by using a high intensity monochromator (15-nm band pass) at 350 nm and 313 nm, respectively. Experiments in the presence of an external magnetic field were performed with the aid of a 3000-G permanent magnet. Analysis of products was by GLC. The determination of the percentage of cage reaction for radicals A and B which yield the normal coupling products AA, AB, and BB is given in eq 1.[5]

$$\% \text{ cage} = \frac{AB - AA - BB}{AA + AB + BB} \qquad (1)$$

Pulsed laser experiments were performed by using a Lambda Physik Excimer Laser (248 nm, 308 nm, and 351 nm, pulse width ≤ 20 ns) and a standard transient absorption system as previously described.[6]

Results

Steady-State Experiments. Irradiation of sulfone **1b** in acetonitrile results in a 100% yield of diphenylethane, *p*-tolylphenylethane, and di-*p*-tolylethane. Analysis of these products according to eq 1 reveals that negligible cage reaction occurs in this case (Table I). A similar result is observed for acetone-sensitized decomposition of this sulfone. Irradiation of **1b** in sodium dodecyl sulfate (SDS) micelles[3,7] results in a change in the distribution of diphenylethane products (100% yield). The extent of cage reaction for this system is determined to be 82%. Application of a 3000-G external magnetic field results in a decrease in the cage value to 40% for the micellar system. Identical values for cage reaction (82%, earth's field; 40%, 3000 G) are determined for this reaction sensitized by acetone in SDS micelles (Table I).

Table I. Effect of Micellization and External Magnetic Field on the Cage Effects for Reaction of Sulfones and Dibenzyl Ketone[a]

	acetonitrile		SDS, 5×10^{-2} M	
compd	direct	sensitized	direct,[b] %	sensitized, %
1b[c]	6%	4%	82 (40)	81 (40)
2a[d]			82 (45)	82 (45)
2b[d]	24%	19%	82 (45)	82 (32)
3a[d]			100 (100)	90 (60)
DBK[e]	0%	0%	35 (20)	

[a] All numbers are accurate to ±8%. [b] Numbers in parentheses represent cage values determined in the presence of a 3000-G external magnetic field. [c] Acetone used as triplet sensitizer. [d] Acetophenone used as triplet sensitizer. [e] See ref 15.

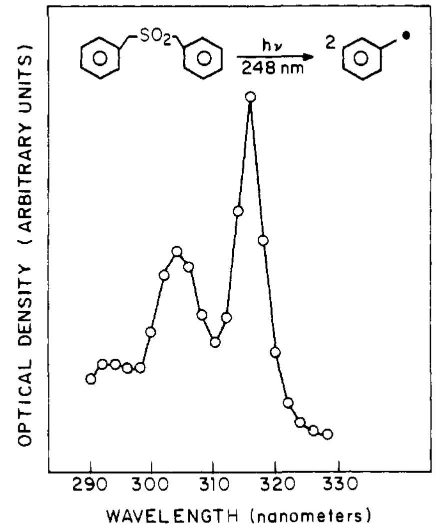


Figure 1. Transient absorption spectrum of benzyl radicals formed upon photolysis of DBS (**1a**) in acetonitrile 0.5 μs after laser pulse.

Similar behavior is observed for photodecomposition of sulfones **2a** and **2b** in homogeneous and micellar solution (Table I). For the naphthyl sulfones acetophenone was used as the triplet sensitizer. For sulfone **2b** a small (24%) but significant cage effect is observed in homogeneous solution. A dramatic change in the steady-state behavior is observed for sulfone **3a**. In this case direct photolysis leads to 100% cage in SDS micelles in the presence or absence of an external magnetic field. However, a cage reaction of 90% is found when a triplet sensitizer is used. Additionally, the cage value drops to 60% for the sensitized reaction in a field of 3000 G.

Time-Resolved Experiments. Pulsed-laser photolysis of sulfone **1a** in acetonitrile by using 248-nm excitation light gives rise to strong transient absorption signals which are assigned to benzyl radicals by comparison with absorptions formed upon photolysis of dibenzyl ketone (DBK) (Figure 1).[8] As with benzyl radicals from DBK, the absorption signals decay via second-order processes in the microsecond timescale in well-degassed solutions. However, unlike DBK no grow-in of radical absorption is observed in the nanosecond timescale. At sufficiently low laser power, photolysis of DBK results in a "two-step" production of benzyl radicals. A fast formation of absorption is observed "in the pulse" due to the primary cleavage step followed by a slower grow-in of absorption due to loss of carbon monoxide by the primary product phenacyl radical.[9] No corresponding growth could be detected for DBS

(2) (a) Givens, R. S. *Org. Photochem.* **1981**, *5*, 227. (b) Givens, R. S.; Matuszewski, B. *Tetrahedron Lett.* **1978**, 861. (c) Givens, R. S.; Olsen, R. J.; Wylie, P. L. *J. Org. Chem.* **1979**, *44*, 1608. (d) Givens, R. S.; Hrinczenko; B.; Liu, J. H.-S.; Matuszewski, B.; Tholen-Collison, J. *J. Am. Chem. Soc.*, preceding paper in this issue.
(3) Turro, N. J.; Kraeutler, B. *Acc. Chem. Res.* **1980**, *13*, 369.
(4) Turro, N. J. *Proc. Natl. Acad. Sci.* **1983**, *80*, 609.
(5) Turro, N. J. *Pure Appl. Chem.* **1981**, *53*, 259.
(6) Turro, N. J.; Aikawa, M.; Butcher, J. A., Jr. *J. Quant. Electronics* **1980**, *QE-16*, 1218.
(7) Turro, N. J.; Gratzel, M.; Braun, A. M. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 675.
(8) McAskill, N. A.; Sangster, D. F. *Aust. J. Chem.* **1977**, *30*, 2107.

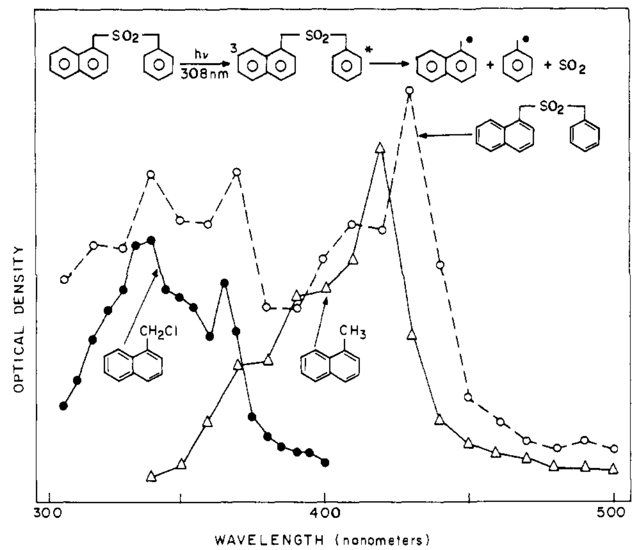


Figure 2. Transient absorption spectra observed upon laser photolysis of sulfone **2a**, (chloro-α-methyl)naphthalene, and α-methylnaphthalene in acetonitrile solution.

even at temperatures as low as −90 °C. Thus, we conclude that loss of SO_2 from the primary radical product occurs at a rate of at least 10^8 s^{-1} at room temperature. It is conceivable that the rate of loss of SO_2 from the intermediate sulfonyl radical is very slow relative to the time scale of our analysis of the absorption decay, so that a build-up of absorption due to loss of SO_2 would not be observed.[10] This possibility was considered unlikely because the quantum yield[2b] of diphenylethane for photolysis of DBS is ca. 0.60 (i.e., loss of SO_2 from the radical intermediate is efficient) implying a rapid rate of loss of SO_2, which has been confirmed by recent ESR measurements.[10b] Laser photolysis of sulfones **1b** and **1c** gives rise to clean absorptions due to benzyl, *p*-tolyl, and *sec*-phenethyl radicals, respectively.[11a] In no cases were significant absorptions observed in the region of 340 nm, and therefore, we exclude the possibility of participation of benzyl cation or anion[11b] in these reactions under these conditions.

Laser photolysis of sulfones **2** and **3** results in transient absorption spectra that are significantly different from those characteristic of sulfones **1**. A typical example is shown for sulfone **2a** in Figure 2. The spectrum may be separated into two components: the absorptions at wavelengths less than 380 nm (λ_{max} 340 nm) are assignable to naphthyl radicals, since laser photolysis of α-(chloromethyl)naphthalene gives rise to identical transient absorptions in the region[11a] (Figure 2). The absorptions in the visible region (λ_{max} 420 nm) are almost identical with those due to α-methylnaphthalene triplet[12] (Figure 2). Thus, we assign the 420-nm absorptions for the naphthyl sulfones to the lowest triplet states of these compounds. Analysis of the transient spectra for **2a** as a function of time reveals that the 420-nm absorption is progressively replaced by that at 340 nm. Furthermore, it is clear that the time-resolved decay of the 420-nm band occurs concomitantly with a growth in absorption of the 340-nm band (Figure 3). Thus, we can say that the triplet state of this sulfone cleaves to yield radical products. In this case absorptions due to the benzyl radical are small with respect to those of the naphthyl radical. Radical absorptions are easily observed for the α-naphthyl sulfones **2**; however, the β-substituted sulfones **3** give rise to smaller absorption signals in the UV region. Indeed, for sulfone **3a** no grow-in of transient absorption can be observed when monitoring at 340 nm. The differing reactivities of the sulfones **2** and **3** can be characterized by comparison of the lifetimes of the triplet states of these compounds monitored at 420 nm (Table II). Also summarized in Table II are the results of a study of the temperature dependence of the triplet decay parameters. Significant temperature dependence for triplet decay was observed for sulfones

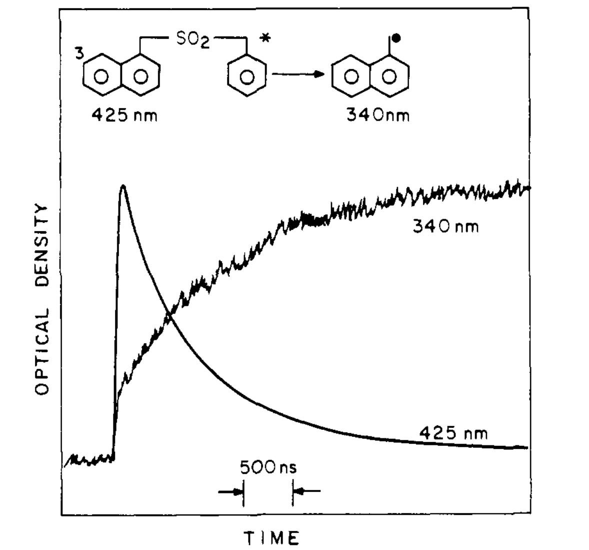


Figure 3. Oscillogram showing decay of sulfone **2a** triplet state observed at 420 nm, and concomitent growth of naphthyl radical absorption observed at 340 nm.

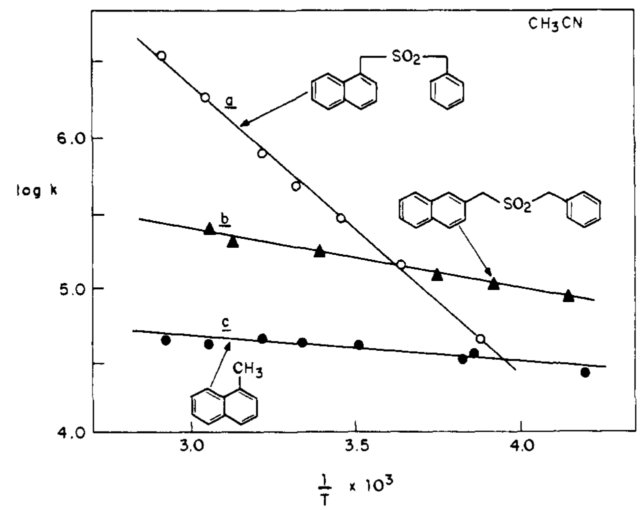


Figure 4. Arrhenius plots showing temperature dependence of log k_r for sulfone **2a**, log k_{obsd} for sulfone **3a**, and log k_{obsd} for α-methylnaphthalene in acetonitrile solvent.

Table II. Kinetic Data for Triplet State Reactivity for Naphthyl Sulfones in Acetonitrile

sulfone	k_{obsd}[a]	E_a, kcal/mol	log A, s^{-1}	$k_{20°}$ calcd, s^{-1} [d]
2a[b]	4.7×10^5	9.0 ± .2	12.2 ± .3	3.1×10^5
2b[b]	6.5×10^5	9.1 ± 1.0	12.7 ± .8	8.3×10^5
2c[b]	2.0×10^6	8.2 ± .5	12.3 ± .4	1.5×10^6
3a[c]	1.7×10^5	1.9 ± .3	6.6 ± .3	
3b[c]	3.7×10^5	0.5 ± 0.9	5.9 ± 1.7	
3c[b]	6.8×10^4	11.1 ± 1.5	12.7 ± 1.7	2.7×10^4
α-methyl-naphthalene[c]	4.1×10^4	0.8 ± .5	5.2 ± .5	

[a] Observed rate constant for triplet decay at 243 K (k_{obsd}). [b] Activation parameters determined for k_r (eq 2 in text). [c] Activation parameters determined for k_{obsd}. [d] Calculated rate constant from Arrhenius parameters.

(9) (a) Turro, N. J.; Gould, I. R.; Baretz, B. H. *J. Phys. Chem.* **1983**, *87*, 531. (b) Lunazzi, L.; Ingold, K.; Scaiano, J. C. *Ibid.* **1983**, *87*, 529.

(10) (a) The authors would like to thank a referee for suggesting this possibility. (b) After submission of this manuscript, the authors learned of a study by Prof. K. U. Ingold which demonstrated that the rate of loss of SO_2 from the benzyl sulfonyl radical was $>2 \times 10^6$ s^{-1}. We thank Dr. Ingold for providing a preprint of this work.

(11) (a) Porter, G.; Strachan, E. *Trans, Faraday Soc.* **1958**, *54*, 1595. (b) Dorfman, L. M.; Sujdak, R. J.; Bockrath, B. *Acc. Chem. Res.* **1976**, *9*, 352.

(12) Labhart, H.; Heinzemann, W. "Organic Molecular Photophysics"; Birks, J. B., Ed.; Wiley: New York, 1973; Vol. 1 p 297.

Table III. Yield Data for Formation of Naphthyl Sulfone Triplets in Acetonitrile at Room Temperature

sulfone	ϕ_{REL}[a]	ϕ_{REL}^{ISC}[b]	ϕ_{ISC}[c]
2a	0.75	0.90	0.72
2b	0.58	0.74	0.59
2c	0.42	0.71	0.57
3a	1.9	0.83	0.66
3b	2.1	0.91	0.73
3c	1.8	0.78	0.62

[a] Yield of triplet absorption relative to naphthalene. [b] Intersystem crossing yield relative to naphthalene. [c] Intersystem crossing yields calculated assuming ϕ_{ISC} for naphthalene is 0.8 in polar solvents (vide supra, ref 14).

2 and **3c**. It is assumed that the rate constant (k_{obsd}) for triplet decay is given by eq 2a, in which k_r represents the rate constant

$$k_{obsd} = k_r + k_d \quad (2a)$$

$$k_r = k_{obsd} - k_{obsd}(N) \quad (2b)$$

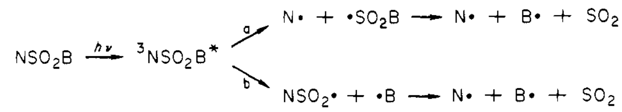
for the cleavage reaction, and k_d the sum of the other processes leading to triplet decay (intersystem crossing, impurity quenching, etc.). If we assume that the temperature dependence of k_d is given by that of the triplet decay of α-methylnaphthalene [k_{obsd}(N)], then subtraction of k_{obsd}(N) from k_{obsd} yields the temperature dependence of k_r. Since the decay rates of sulfones **3a** and **3b** show little variation with temperature, k_{obsd} only is analyzed for these compounds. Plots of k_r vs $1/T$ are linear (Figure 4) and yield the parameters summarized in Table II.

Direct observation of the triplet states of the naphthyl sulfones allows a determination of the absolute yields of these states from their corresponding singlet states. Pulsed-laser photolysis at 351 nm of solutions of benzophenone (10^{-2} M) in the presence of sulfone or naphthalene (10^{-2} M) results in excitation of the benzophenone exclusively, and subsequent transfer of 99% of the benzophenone triplet energy to the corresponding quencher. Since the intersystem efficiency for benzophenone is unity, absorptions due to quencher triplet must come from energy transfer from the benzophenone. Thus, observation of the maximum optical densities of the sulfone triplet states allows determination of their extinction coefficients relative to that of naphthalene. It is found that the extinction coefficients of the α-naphthyl sulfones (at 420 nm) are within experimental error equal to that of naphthalene, whereas those of the β-naphthyl sulfones are larger by a factor of 2.3.[13] Pulsed-laser photolysis of acetonitrile solutions of naphthalene and sulfones **2** and **3** of identical optical density at the excitation wavelength (OD = 0.4 at 308 nm) allows determination of the yields of each triplet state relative to naphthalene, since the extinction coefficients are known. Hence, intersystem crossing yields for each sulfone can be determined relative to naphthalene (Table III).[14]

Discussion

The laser photolysis experiments provide direct evidence that the photodecomposition reactions proceed via radical intermediates for each of the sulfones studied.[2a] In previous studies, we have used the reactions of triplet radical pairs as probes for micellar and magnetic field effects.[3,7] For example, the cage effect for the triplet benzyl radical pair produced from photolysis of DBK in homogeneous solution is found to be indistinguishable from zero.[15] However, in SDS micelles a cage value of 35% is observed.[15] Furthermore, it is found that in the presence of an external magnetic field of 3000 G, the cage effect falls to 20%.[15] In the present work we reverse the experiment and use the micelle and magnetic field effects to probe the reactivity of the radical pair. The observation of essentially zero cage reaction in homogeneous solution for sulfones **1b** and **2a** is entirely consistent with the assignment of triplet-state reactivity for these radical pair reactions.[16] Analogous to DBK we may also assign triplet-state reactivity to radical pairs from these precursors from the results of micelle and magnetic field effect experiments. Although a certain amount of singlet energy transfer may occur with the sensitizers used in the present study, that identical cage values are obtained for the sensitized reactions further supports the previous conclusions that the major decomposition pathways involve the triplet state. On the other hand, the results obtained with **3a** reveal that micellization or application of an external magnetic field have no effect on the cage reaction in this case. This behavior is entirely consistent with mostly singlet-state reactivity for this sulfone as previously suggested.[2]

Scheme I. Two Possible Cleavage Routes for Naphthyl Sulfones[a]



[a] Naphthyl and benzyl moieties are represented by N and B, respectively.

The cage reaction for the benzyl radical pair formed from DBS is significantly greater than that from DBK. This difference could reveal the presence of a certain amount of singlet state reactivity for this sulfone.[2] An alternative explanation arises from examination of eq 3. The main difference in the reaction dynamics

$$\text{Ar-X-Ar}' \xrightarrow{h\nu} \text{Ar-X}\cdot + \text{Ar}'\cdot \xrightarrow{k_{-x}} \text{Ar}\cdot + \text{Ar}'\cdot + \text{X} \quad (3)$$

of DBS compared to DBK lies in the rate of loss of the species X in eq 3. For DBK photolysis, loss of CO from the intermediate phenacetyl radical has been determined to be 6×10^6 s^{-1},[9] whereas the corresponding reaction in the DBS system proceeds at a much faster rate ($>10^8$ s^{-1}). The rate constants for exit of benzylic radicals from SDS micelles is estimated to be in the order of 10^6 s^{-1}.[18] Since loss of X from the primary radical pair derived from DBS will be faster than the corresponding process for DBK, then the secondary benzyl:benzyl radical pair from DBS will be formed closer together than that from DBK. Hence, intramicellar cage reactions will occur to a greater extent for DBS-derived radicals before exit of either radical into the water phase.

The main difference between the time-resolved observations for the benzyl and naphthyl sulfones is that in the latter case the triplet states are directly observed. Laser photolysis of the benzyl sulfones results in radical production "in the pulse" which indicates that the triplet states of these compounds are very short lived. For the naphthyl sulfones, the lowest triplet states are longer lived. This is undoubtedly due to the fact that the naphthyl sulfones have lower triplet energies than the benzyl analogues. The triplet energies of the benzyl sulfones have been determined by phosphorescence measurements to be ca. 70 kcal/mol, whereas those of sulfones **2** and **3** are typical of naphthyl compounds—ca. 60 kcal/mol.[2d]

Cleavage of the naphthyl sulfones can occur via either routes a or b as shown in Scheme I. It would be expected that path a would be favored, since this reaction originates from the lowest energy chromophoric component in the sulfone. Furthermore, this pathway would yield the more stable primary radical products.[19] Examination of the activation parameters summarized

(13) This curious behavior is not observed for comparison of α- and β-methylnaphthalene (vide supra, ref 12).

(14) Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

(15) (a) Turro, N. J.; Weed, G C. *J. Am. Chem. Soc.* **1983**, *105*, 1861. (b) Weed, G. C. Ph.D. Dissertation, Columbia University, 1981.

(16) Small or zero cage effects for singlet radical pairs are normally only observed for radical pairs which have unusually small rate constants for recombination (e.g., vide infra, ref 17).

(17) Koenig, T.; Fischer, H. "Free Radicals"; vol. 1, Kochi, J. K., Ed.; Wiley: New York, 1973; p 157.

(18) (a) Turro, N. J., Chow, M.-F.; Chung, C. J.; Tanimoto, Y.; Weed, G. C. *J. Am. Chem. Soc.* **1981**, *103*, 4574. (b) Almgren, M.; Grieser, F.; Thomas, J. K. *Ibid.* **1979**, *101*, 279. (c) Turro, N. J.; Zimmt, M. B.; Gould, I. R. *Ibid.* **1983**, *105*, 6347.

(19) For example, the difference in C–H bond dissociation energies to yield benzyl and α-methylnaphthyl radicals is approximately 3 kcal/mol (vide infra, ref 20).

in Table II reveals that this is the case. The rates of triplet cleavage appear to correlate well with the stabilities of the product naphthyl radicals. For example, methyl substitution in the position α to the naphthalene in sulfone **2** (**2c**) causes a decrease in activation energy for cleavage, whereas substituion on the benzene side (**2b**) has no effect on the cleavage activation parameters.[21] Similarly, for the β-substituted sulfones, methyl substitution on the benzene side has no effect, whereas substitution on the naphthyl side allows observation of an increased temperature dependence for triplet decay. These observations imply that the transition states for the cleavage reactions are product like. This, in turn, allows an explanation for the reluctance of the β-substituted sulfone triplet states to undergo reaction. Assuming that the A factor for cleavage of sulfone **3a** is the same as that of **2a**, then an increase in activation energy of 2 kcal/mol will decrease the reaction rate by two orders of magnitude. At room temperature under these conditions, the lifetime of the sulfone triplet state will be dominated by the processes which contribute to k_d in eq 2.

The preexponential factors for triplet decay of the β-sulfones and α-methylnaphthalene are typical of those expected if intersystem crossing, or bimolecular quenching reactions are the dominant modes of triplet decay.[22] The A factors for k_r for the α-naphthyl sulfones are typical of those observed for unimolecular cleavage reactions in which the number of degrees of freedom in the transition state are somewhat restricted.[24] For example, they are similar to those observed in isooctane solution for unimolecular loss of CO from phenacetyl radicals.[9]

Knowledge of the intersystem crossing yields for the naphthyl sulfones allows estimation of the extent of singlet-state reactivity. Examination of the data in Table III shows that the sulfone intersystem crossing yields are all less than that of naphthalene (assumed to be 0.8).[14] It is evident that the extent of singlet-state reactivity is not significantly different for the α- or β-substituted sulfones. Indeed, no clear trends in the intersystem crossing yields can be observed. These observations are consistent with the conclusion that the lack of triplet-state reactivity is the origin of the small quantum yields for cleavage of the β-substituted sulfones.

Conclusion

The use of micellar and magnetic field effects has provided information concerning the mechanisms of SO_2 photoextrusion for a variety of aromatic sulfones. Time-resolved optical-absorption experiments provide direct evidence as to the nature of reaction-state multiplicity, the nature of the cleavage step, and the identity of the transient intermediates in these reactions. A correlation is found between the dynamics of the cleavage steps and the energies of the triplet states and stabilities of the intermediate radicals.

Acknowledgment. The authors at Columbia thank the National Science Foundation and the Air Force Office of Scientific Research for their generous support of this research. The authors at Kansas thank the National Institutes of Health (GM 16611) for financial support. Bogdan Matuszewski acknowledge a leave of absence from A Mickiewicz University, Poznań, Poland.

Registry No. 1b, 88430-87-9; **2a**, 67168-90-5; **2b**, 88430-88-0; **2c**, 88430-89-1; **3a**, 67168-91-6; **3b**, 88430-90-4; **3c**, 88430-91-5; DBK, 102-04-5; SDS, 151-21-3; acetone, 67-64-1; acetophenone, 98-86-2; 1-(chloromethyl)naphthalene, 86-52-2; 1-methylnaphthalene, 90-12-0.

(20) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(21) The *sec*-phenethyl radical is ca. 2 kcal/mol more stable than the benzyl radical on the basis of hydrocarbon bond-dissociation energies (vide supra, ref 20).

(22) The observed activation parameters for triplet decay are consistent with those previously observed for naphthalene (vide infra, ref 23). The observation of significant temperature dependence for triplet decay in homogeneous solution is usually attributed to impurity quenching (ref 23). In the present case the rate-determining step for the decay of the nonreacting triplets under the present experimental conditions is probably quenching by residual oxygen or other impurities.

(23) Tsai, S. C.; Robinson, G. W. *J. Chem. Phys.* **1968**, *49*, 3184.

(24) Benson, S. W. "Foundations of Chemical Kinetics"; McGraw-Hill: New York, 1965.

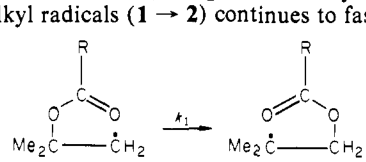
Mechanism of Rearrangement of β-(Acyloxy)alkyl Radicals[1]

L. R. C. Barclay,[2] J. Lusztyk,[3] and K. U. Ingold*[3a]

Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, K1A 0R6 Canada, and the Department of Chemistry, Mount Allison University, Sackville, New Brunswick, E0A 3C0 Canada. *Received July 14, 1983. Revised Manuscript Received November 23, 1983*

Abstract: Rate constants for the free radical rearrangement, $CF_3C(O)OCMe_2\dot{C}H_2$ (**1d**) $\rightarrow$ $CF_3C(O)OCH_2\dot{C}Me_2$ (**2d**), have been measured in $CF_2ClCFCl_2$ by kinetic EPR spectroscopy. This reaction is very significantly faster ($k_1^{75\,°C} = 7.0 \times 10^4$ s^{-1}) than the related rearrangement, $CH_3C(O)OCMe_2\dot{C}H_2$ (**1a**) $\rightarrow$ $CH_3C(O)OCH_2\dot{C}Me_2$ (**2a**) ($k_1^{75\,°C} = 4.5 \times 10^2$ s^{-1}), in hydrocarbon solvents. The potential cyclic intermediate radical, 2-(trifluoromethyl)-4,4-dimethyl-1,3-dioxolan-2-yl (**3d**), does not undergo ring opening to **2d**, at temperatures where the **1d** $\rightarrow$ **2d** rearangement is very fast. It is concluded that **3d** is not an intermediate in the trifluoroacetoxyl migration. It is also concluded on the basis of the k_1 values for **1a** and **1d** that these rearrangements involve a charge-separated transition state. The **1a** $\rightarrow$ **2a** rearrangement is very much faster in water ($k_1^{75\,°C} = 2.1 \times 10^4$ s^{-1}) than in hydrocarbon solvents, which provides additional support for a charge-separated transition state.

The mechanism of the 1,2 migration of acyloxy groups in β-(acyloxy)alkyl radicals (**1** $\rightarrow$ **2**) continues to fascinate chemists.[4-12] We[10] have recently confirmed Beckwith's suggestion[7,8] that at least some **1** $\rightarrow$ **2** rearrangements do not proceed via an



1 2

a, R = CH_3; b, R = C_6H_5; c R = c-C_3H_5; d, R = CF_3

(1) Issued as N.R.C.C. No. 23063.

(2) Mount Allison.

(3) (a) N.R.C.C. (b) Research Associate 1982–1984.

(4) Beckwith, A. L. J.; Ingold, K. U. In "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. I, Essay 4, pp 161–310.

(5) Surzur, J.-M.; Teissier, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1967**, *264*, 1981–1984; *Bull. Soc. Chim. Fr.* **1970**, 3060–3070.