J. Org. Chem. 1992, 57, 3706-3712

Photochemistry of 2,3-Di(1′-naphthyl)oxiranes. Spectral and Kinetic Behavior of Carbonyl Ylides in Condensed Media[1]

K. B. Clark,[*,†] K. Bhattacharyya,[‡] P. K. Das,[*,‡] J. C. Scaiano,[†] and A. P. Schaap[§]

Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, Canada K1A 0R6, Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, and Chemistry Department, Wayne State University, Detroit, Michigan 48202

Received October 25, 1991 (Revised Manuscript Received March 12, 1992)

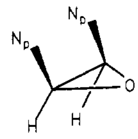
The photochemistry of *cis*- and *trans*-2,3-di(1′-naphthyl)oxiranes (*c*- and *t*-**1**) has been studied by nanosecond laser flash photolysis in fluid solution. Direct photolysis (λ_{exc} = 248, 266, 308 nm) produces carbonyl ylides which are characterized by broad, structureless absorption bands in the visible region (450–650 nm, $\lambda_{max} \sim 545$) and unusually short lifetimes (14–22 ns) in a variety of solvent systems. Triplet energy transfer to the oxiranes results in formation of naphthalene-like triplets (λ_{max} = 410–420 nm, $\tau_T < 80$ ns) which act as precursors to carbonyl ylides that exhibit spectra ($\lambda_{max} \sim$ 540–570) similar to those formed via direct excitation but are longer lived (τ = 40–70 ns). In contrast to triplet sensitization, there is no evidence of triplet oxiranes formed via direct excitation. Direct photolysis of the oxiranes appears to result in singlet-mediated photochemistry which initially gives rise to one-bond fragmentation yielding the ultra-short-lived ground-state ylides. Direct photolysis also leads to the formation of 1-naphthaldehyde and 1-naphthylcarbene via either two-bond fragmentation of the singlet excited oxirane or fragmentation of the ground-state carbonyl ylides. A portion of the fragmentation process appears to occur adiabatically as evidenced by the observation of triplet 1-naphthaldehyde in the transient absorption phenomena. In acetonitrile, the transient absorption spectra from direct laser photolysis (308 nm) reveal evidence for photoionization of the oxiranes giving radical cations ($\lambda_{max} \sim$ 620 nm).

Introduction

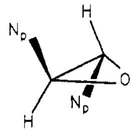
The photochemistry of three-membered heterocycles and their conversion to 1,3-dipoles via carbon–carbon bond fragmentation has intrigued photochemists for years. In addition to being the principal intermediates in 1,3-dipolar cycloadditions,[2] 1,3-dipoles, commonly referred to as ylides, are known to play important roles in a host of thermal and photoinduced processes such as isomerization and photooxygenation of three-membered heterocycles, thermochromism/photochromism, alkene ozonolysis, and photocyclization of aromatic enamines and their sulfur analogues.[3] In general, under ambient reaction conditions, 1,3-dipoles are elusive in nature taking on a transitory existence. Their involvement has been established by inference through chemical trapping, for instance, as cyclic adducts from reactions with dipolarophiles and as products from reaction with alcohols and HX-type reagents.

Classically, direct observations of transient ylides have been made spectroscopically by photogenerating them as stable species in low-temperature rigid matrices. In more recent years direct observation of ylides in condensed media at room temperature has been made possible by time-resolved laser flash photolysis.[3] The time-resolved technique is particularly suited for studies on the kinetic behavior of 1,3-dipolar intermediates which is essential for a detailed understanding into the mechanisms of the reactions in which they are implicated.

Recently, the electron-transfer photosensitization of *cis*- and *trans*-2,3-dinaphthyloxiranes in the presence of oxygen has been shown to result in photooxygenation of the oxiranes to stereochemically pure *cis*-ozonides.[4] Addition of singlet oxygen, O_2 ($^1\Delta_g$), to the resultant carbonyl ylides has been implicated in the mechanism of ozonide formation. The absorption–emission spectral properties of both *cis*- and *trans*-2,3-di(1′-naphthyl)oxirane (*c*- and *t*-**1**, respectively) and their corresponding photochemistry in 3-methylpentane glass at 77 K have been examined by Becker and co-workers.[5] They reported the formation of colored species with absorption in the 480–650 nm region ($\lambda_{max} \sim$ 570 and 575 nm for *c*- and *t*-**1**, respectively) and also formation of 1-naphthaldehyde and 1,2-di(naphthyl)ethylene. An earlier paper[6] has described the photochemical ring opening of 2,3-di(2′-naphthyl)oxiranes leading to transient carbonyl ylides. To evaluate the possibility for participation of 1,3-di(1′-naphthyl)carbonyl ylides in the ozonolysis of naphthyloxiranes we describe here their transient special properties from photolysis of *cis*- and *trans*-2,3-di(1′-naphthyl)oxiranes (*c*- and *t*-**1**) in fluid solutions.



c-**1**



t-**1**

N_p = 1-naphthyl

Experimental Section

General Considerations. Melting points were determined on a Kofler hot-stage microscope apparatus. The ^{1}H NMR spectra were recorded on a Varian Em-360 (60-MHz) spectrometer in deuteriochloroform and are reported in parts per million downfield of tetramethylsilane. Mass spectra were recorded on a Hewlett-Packard 5970A series GC–MS instrument. Ground-state absorption spectra were recorded in Cary 3 and 219 spectrophotometers. Steady-state emission spectra were recorded in EPA solution using Perkin-Elmer LS-5 and SLM spectrofluorimeters.

Materials. 2-Methyltetrahydrofuran (Aldrich) was distilled from lithium aluminum hydride before use. All other solvents (Aldrich, spectrophotometric grade, 99+% or Fisher Scientific, spectranalyzed) were used as received.

***cis*- and *trans*-2,3-Di(1′-naphthyl)oxiranes (*c*- and *t*-1).** The oxiranes *c*- and *t*-**1** were synthesized together according to the procedure of Mark.[7] 1-Naphthaldehyde (16.6 g, 0.106 mol)

[†] Steacie Institute for Molecular Sciences.

[‡] University of Notre Dame.

[§] Wayne State University.

(1) National Research Council of Canada, Publication No. 33287.

(2) Huisgen, R. *1,3-Dipolar Cycloaddition Chemistry*; Wiley: New York, 1984; Vol. 1.

(3) Das, P. K. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1987; Vol. 2, p 35.

(4) (a) Schaap, A. P.; Siddiqui, S.; Prasad, G.; Palomino, E.; Sandison, M. *Tetrahedron* **1985**, *41*, 2229. (b) Schaap, A. P.; Siddiqui, S., Prasad, G., Palimino, E., Sandison, M. *J. Am. Chem. Soc.* **1984**, *106*, 6087.

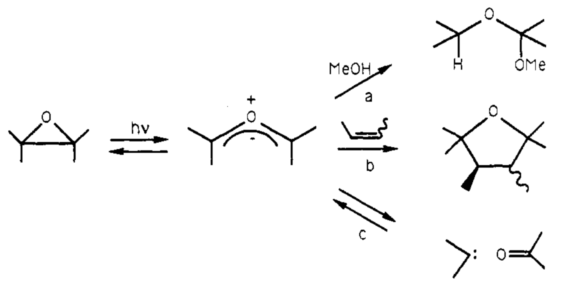
(5) Becker, R. S.; Bost, R. O.; Kolc, J.; Bertoniere, N. R.; Smith, R. L.; Griffin, G. W. *J. Am. Chem. Soc.* **1970**, *92*, 1302.

(6) Das, P. K.; Griffin, G. W. *J. Org. Chem.* **1984**, *49*, 3452.

(7) Mark, V. *Organic Synthesis*; J. Wiley and Sons: New York, 1963; Collect. Vol. V, p 358.

0022-3263/92/1957-3706$03.00/0 © 1992 American Chemical Society

Scheme I



was placed with 20 mL of benzene in a 100-mL three-necked, round-bottomed flask equipped with addition funnel, magnetic stirrer, and reflux condenser. To this solution was added dropwise HMPT (10 g, 0.061 mol) in 5 mL of dry ethyl ether. Care was taken to ensure that the temperature of the solution did not rise above 31 °C during the addition of HMPT. The reaction mixture was then heated to 50 °C for 0.5 h at which time the solvent was stripped on a rotary evaporator. The remaining oil was washed with water and then taken up in pentane. The pentane extract was then washed (2 × 100 mL) with water. The pentane was removed by rotary evaporation and the light yellow solid recrystallized from methanol yielding 8.4 g of a white solid of which the ^{1}H NMR spectrum revealed that both the cis and trans isomers were present in almost equal proportions (47:53 cis/trans). The isomers were separated by spinning TLC using a Chromatotron (Harrison Research Model 7924T) on a 2-mm-thick silica gel disk (0.75 g of material per separation). The mixture was eluted using 10% ether/hexane to give *trans*-2,3-di(1'-naphthyl)oxirane (*t*-1), mp = 142.5–143.5 °C (after recrystallization from cyclohexane and then 10% benzene in hexane) (lit.[8] mp = 140–141 °C) and *cis*-2,3-di(1'-naphthyl)oxirane (*c*-1), mp 170–171 °C (after recrystallization from cyclohexane and then 10% benzene in hexane) (lit.[8] mp = 168–169 °C). ^{1}H NMR assignments agree well with the literature.[4a,5,8]

***trans*-2,3-Di(1'-naphthyl)oxirane (*t*-1)**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.20–8.06 (m, 14 H), 4.40 (s, 2 H).

***cis*-2,3-Di(1'-naphthyl)oxirane (*c*-1)**: ^{1}H NMR (60 MHz, $CDCl_3$) δ 7.20–8.21 (m, 14 H), 4.99 (s, 2 H).

trans-2,3-Di(1'-naphthyl)oxirane was also prepared in a separate synthesis in order to further differentiate between the cis and trans isomers.[8a] Briefly, oxirane *t*-1 was prepared by treatment of *trans*-1,2-di(1'-naphthyl)ethene[9] with *m*-chloroperbenzoic acid in dichloromethane. After purification the resulting oxirane exhibited physical properties identical to that listed above for *t*-1.

Laser Flash Photolysis. The laser flash photolysis experiments carried out at the Radiation Laboratory employed three pulsed laser sources, namely, a Molectron UV-400 nitrogen laser (337.1 nm, 8 ns, 2–3 mJ/pulse), a Lambda-Physik EMG MSC100 excimer laser (248 or 308 nm, ca 20 ns, ≤100 mJ/pulse), and a Quanta-Ray DCR-1 Nd-YAG laser (266 nm, fourth harmonic, 6 ns, ≤20 mJ/pulse). In order to minimize multiphoton processes, the high-intensity laser pulses from the Nd-YAG and excimer systems were defocused and/or appropriately attenuated. Details of the kinetic spectrophotometer and data collection/processing system are given elsewhere.[10] Most of the experiments were carried out in cells of 2–3-mm path lengths using a front-face geometry with an angle of 20–30° between the directions of laser and monitoring beam incidence. For a few experiments, a right angle geometry and 1-cm × 1-cm cells were used minimizing contributions from spurious and/or genuine emissions. The solutions used for laser flash photolysis were deoxygenated by saturating with high-purity argon.

The laser flash photolysis experiments carried out at the National Research Council of Canada were performed using the pulses from a Molectron UV-24 Nitrogen laser (337.1 nm, ca. 8 ns, ≤15 mJ/pulse), a Lumonics TE-860-2 excimer laser with a Xe/HCl gas mixture (308 nm, 5-ns pulses, ≤20 mJ/pulse) or a Lumonics EX-510 excimer laser with XeCl gas mixture (308 nm, 8-ns pulses, ≤50 mJ/pulse), and a Lumonics HY750 Nd/YAG laser (fourth harmonic, 266 nm, 10-ns pulses, ≤45 mJ/pulse). Samples were contained in 7- × 7-mm^2 quartz cells for 266- and 308-nm excitation. In the case of 337.1-nm excitation, 3- × 7-mm^2 quartz cells were used. In most cases flow samples were used to prevent complicating emissions resulting from the buildup of fluorescent products. Solutions were generally deoxygenated by purging with nitrogen. Unless otherwise stated, all experiments were carried out between 292 and 295 K. Further details of the apparatus at the NRCC have been reported elsewhere.[11,12]

Results and Discussion

1. Steady-State Absorption and Emission. The similarity of the low-energy UV absorption bands of *c*- and *t*-1 (230–330 nm) in acetonitrile at 296 K to that of naphthalene suggest that these bands are essentially due to the isolated naphthalene moiety. Interestingly, under similar conditions of instrumental resolution, the UV–vis absorption spectrum of the cis isomer exhibited vibrational structure unlike that of the trans isomer, which was featureless. This fine structure in the UV absorption spectrum of *c*-1 indicates that the singlet state survives a number of vibrations and hence is longer lived than that of *t*-1.[13]

Both *c*- and *t*-1 fluoresce weakly in fluid solutions at room temperature. As in the absorption studies both isomers exhibit naphthalene-like fluorescence, with similar vibronic structure (0,0 bands at 327 nm (88 kcal/mol)) in acetonitrile.

2. Low-Temperature Photolysis. Ylide Absorption Spectra. Prolonged irradiation of *c*- and *t*-1 at 253 or 315 nm in EPA glasses at 77 K leads to a pink coloration of the media. The absorption spectra of the resultant product(s) responsible for the pink coloration show maxima at 560 and 570 nm for *c*- and *t*-1, respectively. On the basis of rate of coloration, *t*-1 appears more photolabile than *c*-1. The development of color occurs about 1 order of magnitude faster upon photolysis of *t*-1 than in the case of *c*-1. The photoinduced coloration disappears with gradual warming of the glass to room temperature. Similar observations have been reported by Becker et al.[5]

As shown by experiments with *t*-1, the pink coloration in the low-temperature glasses becomes bleached upon irradiation with visible light. These properties, as well as similarities with the absorption spectra of other carbonyl ylides derived from related aryl oxiranes,[2] lead us to a tentative assignment (vide infra) of the pink coloration to carbonyl ylides resulting from photochemical ring opening of *c*- and *t*-1.

3. Laser Flash Photolysis Studies. 3.1. Triplet Sensitization. Rate of Energy Transfer. Triplet sensitization studies were carried out in acetonitrile and benzene solutions using 337.1-nm excitation. A variety of aromatic ketones were used as sensitizers including acetophenone, butyrophenone, benzophenone, and 4,4'-di-

---

(8) (a) We noted that in a recent publication[8b] the assignments to *c*-1 and *t*-1 had apparently been reversed accidentally. (b) Zimmerman, H. E.; Caufield, C. E.; King, R. K. *J. Am. Chem. Soc.* **1985**, *107*, 7732.

(9) (a) *trans*-1,2-Di(1-naphthyl)ethene was prepared following a literature procedure from 1-naphthaldehyde and 1-naphthylmethyltriphenylphosphonium chloride.[9b–d] (d) Drefahl, G.; Lorenz, D.; Schnitt, G. *J. Prakt. Chem.* **1964**, *295*, 143. (c) Wong, J. P. K.; Fahmi, A. A.; Griffin, G. W.; Bhacca, N. S. *Tetrahedron* **1981**, *37*, 3345. (d) Tagaki, W.; Inoue, I.; Yano, Y.; Okonogi, T. *Tetrahedron Lett.* **1974**, 2587.

(10) (a) Das, P. K.; Encinas, M. V.; Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965 and references cited therein. (b) Chattopadhyay, S. K.; Das, P. K.; Hug, G. L. *Ibid.* **1982**, *104*, 4507 and references cited therein.

(11) (a) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747. (b) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(12) Kazanis, S.; Azarani, A.; Johnston, L. J. *J. Phys. Chem.* **1991**, *95*, 4430.

(13) Calvert, J. G.; Pitts, J. N. *Photochemistry*; J. Wiley and Sons: New York, 1966; p 583.

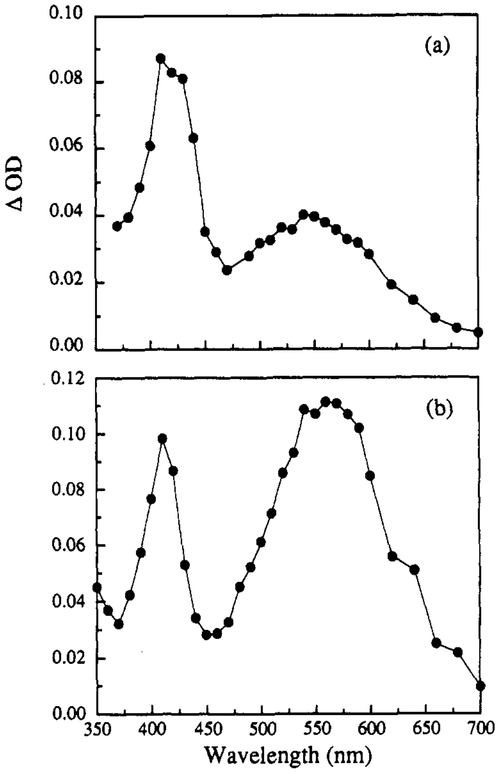


Figure 1. Transient absorption spectra of triplet excited oxirane and ground-state ylide recorded 50 and 20 ns after 337.1-nm excitation of a solution of 0.25 M butyrophenone and 0.005 M *cis*- (a) and 0.015 M *trans*-2,3-di(1′-naphthyl)oxirane (b), respectively, in benzene under nitrogen at 20 °C.

methoxybenzophenone. 4,4′-Dimethoxybenzophenone was particularly convenient as a sensitizer since the donor triplet could be conveniently monitored at a wavelength (ca. 700 nm) where complications due to contributions from product transient absorptions were negligible. This enabled measurement of quenching rate constants, k_q^T, for the triplet donor by *c*- and *t*-1. Linear plots were obtained

$$k_{obs} = k_0 + k_q^T[Ox] \qquad (1)$$

based on equation 1 where k_{obs} and k_0 are the pseudo-first-order rate constants for triplet decay in the presence and absence of oxirane (Ox), respectively. The slopes from k_{obs} vs [Ox] plots provided k_q^T's of 8.8 and 7.4 × 10^9 M^{-1} s^{-1} for *c*- and *t*-1, respectively, in benzene. Quenching of the other ketone triplets by the naphthyloxiranes is also expected to be diffusion-controlled.

Spectral and Kinetic Phenomena. Triplet sensitization of oxiranes *c*- and *t*-1 under conditions of nearly complete quenching of the triplet donors resulted in the formation of two short-lived transients with maxima at 410–420 and 540–570 nm as shown in Figure 1. The transients centered at 410–420 nm formed from the cis and trans isomers decayed with different rates. In acetonitrile at room temperature ([Ox] ≥ 25 mM) these signals decayed in 70 and 25 ns for *c*- and *t*-1, respectively. The transients centered in the 540–570-nm region have kinetic profiles comprising of clean first-order formation and decay (Figure 2b). The formation/decay profiles of these signals indicate that the transients centered at 410-420 nm are the precursors for the long-wavelength transients centered in the 540–570-nm region.

The short-wavelength transients (λ_{max} = 410–420 nm) are assignable as naphthalene-localized triplets of the naphthyloxiranes. This is based primarily on the similarity of the transient absorption spectra with that of triplet naphthalene and triplet 1-methylnaphthalene (λ_{max} = 420 nm). In addition, triplet excited 2,3-di(2′-naphthyl)oxiranes (the β-substituted derivatives) also absorb in this region (λ_{max} = 430 nm).[6] The transients absorbing at longer wavelengths (λ_{max} = 540–570 nm) are assigned as ground-state carbonyl ylides formed via ring opening of the triplet excited oxiranes (Scheme IIa). This assignment is based primarily on the spectral similarity to carbonyl ylides formed via photolysis of *cis*- and *trans*-2,3-di(2′-naphthyl)oxiranes (λ_{max} = 530 nm).[6]

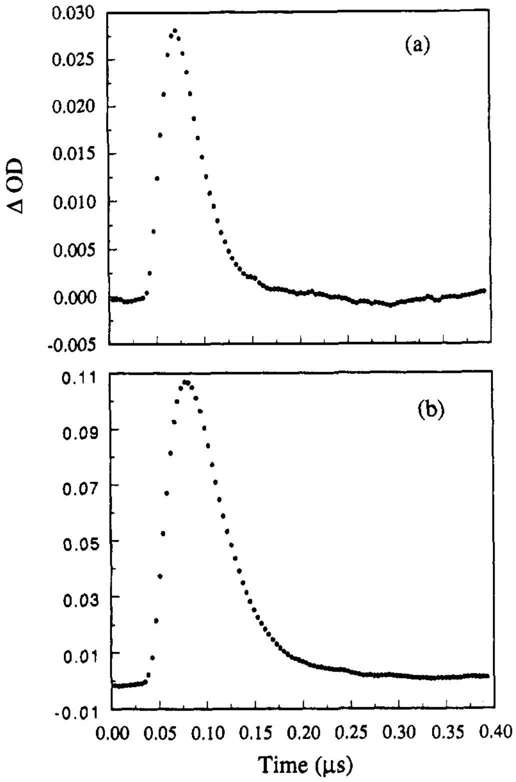
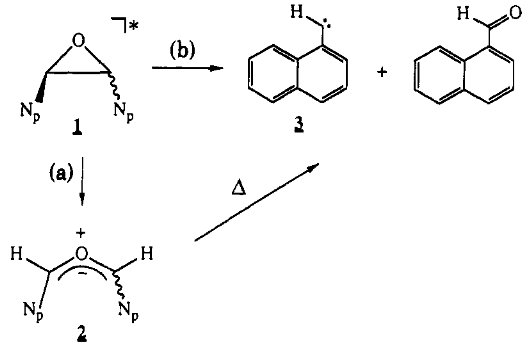


Figure 2. Decay of transient absorption at (a) 410 nm (triplet oxirane) and (b) 550 nm (ylide) observed upon 337.1-nm excitation (N_2 saturated, room temperature) of solutions of benzophenone in acetonitrile containing 0.015 M *trans*-2,3-di(1′-naphthyl)oxirane.

Scheme II



Additional evidence that the 410–420-nm signals are precursors to the 540–570-nm signals was provided by ferrocene quenching experiments. Addition of ferrocene to the solutions resulted in quenching of the 410–420-nm signals. In an experiment where *c*-1 acted as triplet quencher ([Ox] ≈ 25 mM) to benzophenone triplets in acetonitrile we monitored the 410–420-nm absorption at variable ferrocene concentrations (0–4 mM). The bimolecular rate constant for quenching of the 410-nm signal by ferrocene was observed to be 4.5 × 10^9 M^{-1} s^{-1}. The progressive increase in the rate of growth of the 540-nm signals with increasing ferrocene concentrations confirmed that these originated through the intermediacy of the ferrocene-quenchable, shorter wavelength species (λ_{max} = 410–420 nm). An alternative assignment in terms of ylide triplets (biradical in nature) is not tenable, since ring-opened triplets are not expected to react efficiently with ferrocene via an energy-transfer mechanism. We estimate from the ground-state absorptions of the ylides that their lowest excited singlet energies (E_S) are less than 45 kcal/mol. The corresponding triplet energies (E_T) should therefore be less than 30 kcal/mol (based on singlet–triplet energy separation expected for a π,π^* transition).[14] Ferrocene ($E_T \sim$ 38–41 kcal/mol)[15] would not be a favorable energy acceptor toward this type of triplet.

Attempts at quenching the long-wavelength transients (λ_{max} = 540–570 nm) with maleic anhydride (MA), a strong dipolarophile, were made in order to corroborate the assignment as ground-state carbonyl ylides. Unfortunately, given the ultrashort lifetimes of these transients (40 and 70 ns for ylides derived from *c*-1 and *t*-1, respectively) at room temperature it was difficult to detect any influence on their lifetime. However, in toluene at −40 °C where the ylide formed from *t*-1 lived ca. 400 ns, addition of small amounts of MA (maximum concentration 0.005 M) clearly lead to quenching of the transients. From a plot of k_{exptl} vs [MA] the rate constant was determined to be $(7.5 \pm 0.3) \times 10^8$ M^{-1} s^{-1} in toluene at 233 K.

It is interesting to note that the triplet arising from *c*-1 is longer lived than that of *t*-1 (τ_T = 70 and 25 ns, respectively, in acetonitrile). This suggests that ring opening is more favoured in the triplet of the trans isomer. Becker et al. also observed that in the low-temperature photolysis of these oxiranes (−196 °C in 3-methylpentane) the ylide derived from *t*-1 was formed faster than that derived from the cis isomer.[5] The triplet excitation delocalization between the two naphthyl substituents in *t*-1 incorporates a through-bond interaction involving the C–C σ bond and thus may facilitate the C–C bond cleavage.

No residual absorptions corresponding to longer-lived transients were observed after completion of the nanosecond decay of the transients absorbing at 410–420 and 540–570 nm produced under triplet sensitization.

Analysis of the photolysate after steady-state triplet sensitization (λ_{exc} = 350 nm) of the oxiranes in cyclohexane resulted in small amounts of 1-naphthaldehyde indicating that some carbonyl ylides undergo fragmentation instead of ring closure. Very little 1-(methylcyclohexyl)naphthalene, the carbene/solvent adduct, was observed under these conditions.

3.2 Direct Photolysis. Steady-state photolysis (λ_{exc} = 300 nm) of *c*- and *t*-1 in cyclohexane at room temperature results in a "clean" photolysate comprised of only two products, 1-naphthaldehyde and 1-(methylcyclohexyl)naphthalene. These products are derived from a photofragmentation reaction where 1-naphthaldehyde and 1-naphthylcarbene are the products.

3.2.1 Short Time Scales. Excitation of *c*- and *t*-1 (λ_{exc} = 248, 266, and 308 nm) in a variety of solvents (acetonitrile, benzene, cyclohexane, methylcyclohexane, and trifluoromethyltoluene) gave similar absorption spectra at nanosecond time scales. The spectra from both isomers are dominated by a rather broad but very strong absorption band (λ_{max} ca. 545) as shown in Figure 3. The transient, which is formed within the laser pulse duration, is very short lived (15–22 ns, solvent dependent) and decays with clean first-order kinetics (Figure 3, inset). Excitation of *t*-1 at 266 nm in methanol as well as 2-methyl-2-propanol also gave the short-lived transient (λ_{max} = 545 nm) with lifetimes of 29 and 33 ns, respectively. Similar experiments carried out for *c*- and *t*-1 in oxygen-saturated acetonitrile and cyclohexane showed that the presence of O_2 had no visible effect on either the yield or decay of the transient.

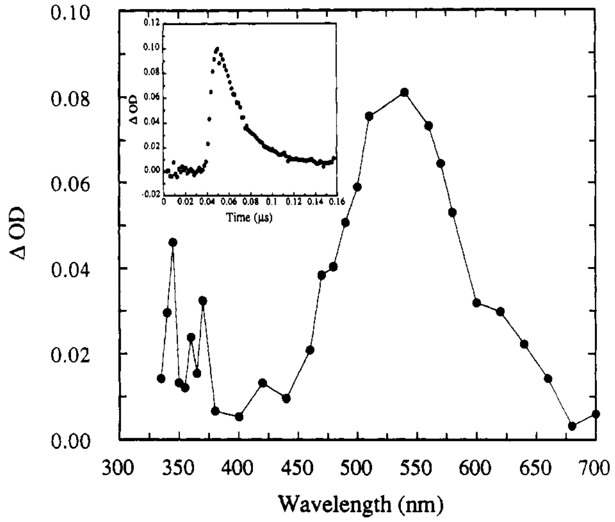


Figure 3. Transient absorption spectrum of ylide measured 10 ns after 308-nm excitation of *trans*-2,3-di(1′-naphthyl)oxirane (0.1 mM) in (trifluoromethyl)toluene under nitrogen at 18 °C. Inset: Decay of the transient absorption monitored at 540 nm after 308 nm excitation.

The spectral similarity of these transients with that of the photogenerated carbonyl ylides in low-temperature glasses (allowing for a redshift in the maxima in low-temperature glasses) leads us to assign these spectral bands as ground-state carbonyl ylides, **2**, products of the photochemical ring opening of oxiranes *c*- and *t*-1 (Scheme IIa). In terms of spectral location, the absorption bands observed in this study bear strong resemblance to the carbonyl ylides (λ_{max} = 530 nm) derived from photolysis of *cis*- and *trans*-2,3-di(2′-naphthyl)oxirane.[6]

The transients were quenched by maleic anhydride in toluene at −40 °C where the ylide formed from *t*-1 lived ca. 300 ns. The rate constant was determined to be $(6.0 \pm 1.1) \times 10^8$ M^{-1} s^{-1} which is somewhat slower than that determined for the triplet-sensitized process discussed earlier ($(7.5 \pm 0.3) \times 10^8$ M^{-1} s^{-1}).

3.2.2 Long Time Scales. Photolysis in Acetonitrile. Laser flash photolysis of *c*- and *t*-1 at 308 nm in acetonitrile resulted in transient absorption spectra exhibiting three major absorption bands with maxima at 385, 480, and 620 nm when monitoring at longer (μs) time scales (Figure 4). The 385 and 620 nm signals have complex decay kinetics on the microsecond time scale and are observed only in acetonitrile. The absorption spectrum (λ_{max} 385 nm) and the kinetic behavior of this transient are identical to that of nitrile ylide **4** which results due to reaction of 1-naphthylcarbene **3** and the solvent as shown in Scheme IIIa. The carbene is formed either via two-bond fragmentation of the oxirane or via decay of the carbonyl ylide (vide infra) as shown in Scheme II. Reaction of 1-naphthylcarbene with nitriles to form nitrile ylides is a known reaction.[16]

The species absorbing at ca. 620 nm in acetonitrile is tentatively assignable to oxirane radical cations derived from photoionization. This absorption band was not observed in any other solvent used in the study. These

---

[14] McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice-Hall: Englewood Cliffs, NJ, 1969.

[15] Herkstroeter, W. G. *J. Am. Chem. Soc.* **1975**, *97*, 4161.

[16] Barcus, R. L.; Hadel, L. M.; Johnston, L. J., Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928.

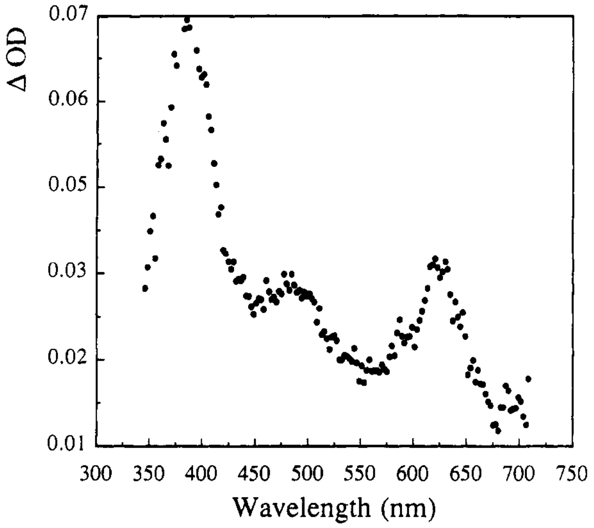
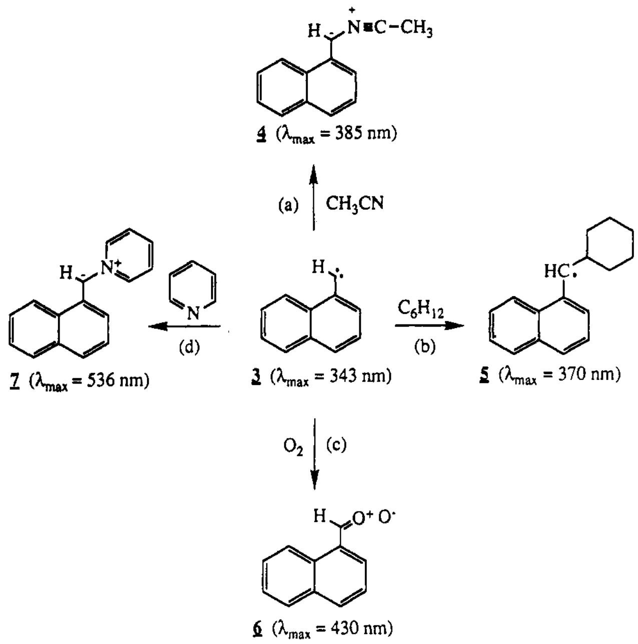


Figure 4. OMA transient absorption spectrum of nitrile ylide, triplet 1-naphthaldehyde, and radical-cation measured 0.5 μs (20-ns gate) after 308-nm excitation of *cis*-2,3-di(1′-naphthyl)oxirane (0.7 mM) in acetonitrile under nitrogen at 19 °C.

Scheme III



species have been generated by photoinduced electron transfer from the oxiranes to cyanoaromatic singlets and exhibit similar spectral and kinetic behaviour.[21] Photoconductivity experiments performed using 266-nm excitation of *t*-1 in acetonitrile (undistilled) resulted in weak conductance that decayed with first-order kinetics (8–9 μs, Figure 5c) lending support to the radical-cation assignment.

The transient with λ_{max} at 485 nm has a lifetime of 2 μs (Figure 5b). The lifetime of the transient was thoroughly quenched in oxygen-saturated solutions and also by 1,3-cyclohexadiene with a diffusion-controlled rate constant (k_q = 6.0 × 10^9 M^{-1} s^{-1}) suggesting that it is triplet in nature. It is easily identified as triplet 1-naphthaldehyde as shown by the similarity of the spectra, kinetics, and quenching properties of this species with those of independently generated triplet 1-naphthaldehyde under similar conditions. Similar results were obtained for 248- and 266-nm photolysis. 1-Naphthaldehyde is formed in the fragmentation reaction that also produces 1-naphthylcarbene. The observation of 1-naphthaldehyde triplet in the course of direct excitation of *c*- or *t*-1 suggests that an adiabatic fragmentation process occurs to a nonnegligible extent. On the basis of previous studies we expected 1-naphthaldehyde to be formed in the ground state along with the carbene via decay of the ground-state ylide. We were surprised to observe triplet 1-naphthaldehyde, and initially reasoned that it was the result of a biphotonic process involving excitation of 1-naphthaldehyde during the laser pulse duration. Laser intensity dependence studies indicate, however, that the yield of 1-naphthaldehyde triplet is monophotonic. Flow was used throughout the study precluding the accumulation of signals resulting from absorption by photoproducts. We tentatively conclude that at least some of the photofragmentation may be adiabatic in nature. We cannot eliminate the possibility that these signals result from 1-naphthaldehyde present as an impurity in the starting material although we find no evidence for its presence.

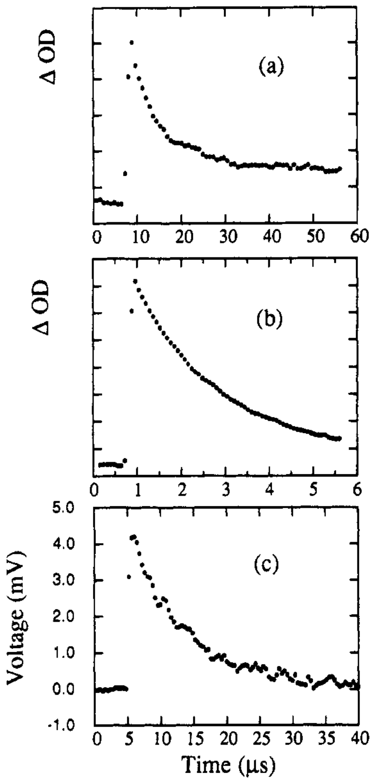


Figure 5. (a) and (b) Decay of the transient absorption at 370 nm (nitrile ylide) and 480 nm (triplet 1-naphthaldehyde) following 308-nm excitation of *trans*-2,3-di(1′-naphthyl)oxirane in nitrogen-saturated acetonitrile at 20 °C. (c) Kinetic trace for decay of conductance following 266-nm excitation of *t*-1 in oxygen-saturated acetonitrile at 20 °C tentatively assigned to the radical cation exhibiting absorbance with λ_{max} = 620 nm.

As discussed in Section 3.1, there is no evidence of 1-naphthaldehyde triplet in the sensitization experiments even though the aldehyde is present as a product in the photolysate. Photofragmentation to give excited 1-naphthaldehyde must occur directly via the oxiranes and not by decay of the corresponding ground-state ylides in the direct photolysis. The possibility that adiabatic photofragmentation could also occur from the first singlet excited state of the ylides (formed either in the laser pulse duration or by adiabatic ring opening of the oxiranes) does not seem energetically viable since we estimate the singlet excited-state energy, E_s, for these ylides to be ca. 45 kcal/mol.

From the laser flash photolysis studies, we estimate the fluorescence lifetimes of *c*- and *t*-1 to be <10–12 ns in

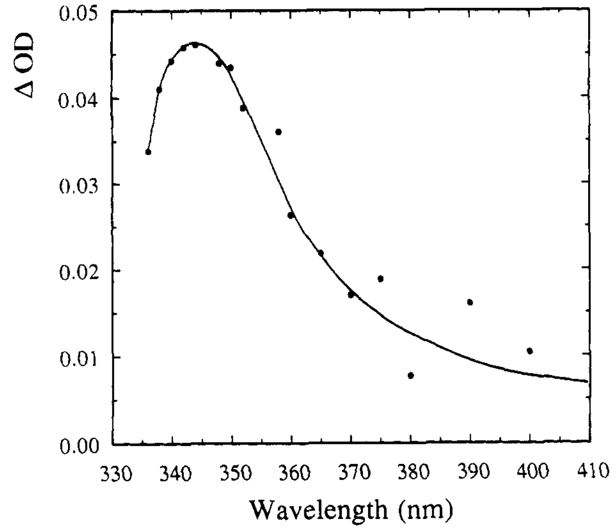


Figure 6. Transient absorption spectrum of 1-naphthylcarbene recorded 20 ns after 308-nm excitation of *trans*-2,3-di(1'-naphthyl)oxirane (0.1 mM) in N_2-saturated (trifluoromethyl)toluene at room temperature. The solid line is simply an "artist fit".

degassed acetonitrile at room temperature. No evidence can be found for short-lived signals centered in the 420-nm region that would indicate the participation of naphthalene-centered triplets in the direct photolyses of the oxiranes. It appears that direct excitation results in singlet excited-state-mediated photochemistry which leads to one- and two-bond fragmentation of the oxirane over intersystem crossing and luminescence. This contrasts the triplet-mediated photochemistry induced by energy transfer from triplet sensitizers where oxirane ring opening (1-bond cleavage) to give carbonyl ylides appears to be the primary photoprocess.

3.2.3 Reactions of 1-Naphthylcarbene. Direct observation of the carbene was made in trifluoromethyltoluene, a relatively unreactive solvent toward carbenes. Griffin and Horn have reported the maximum of 1-naphthylcarbene to be ca. 355 nm but suggested that the true maximum is blue-shifted since the diazomethane precursors that were used in that study underwent considerable ground-state depletion in this region.[17] We encountered difficulties with strong emissions in this region, but by employing 308-nm laser excitation a transient absorption spectrum was obtained from photolysis of *t*-1 at nanosecond timescales. Figure 3 reveals a sharp absorption (λ_{max} = 345 nm (5-ns resolution)) possibly due to 1-naphthylcarbene along with the very intense absorption at 540 nm belonging to the carbonyl ylide. A signal with maximum at 370 nm is also observed on this nanosecond time scale and may be due to 1-naphthylmethyl radical 5 (Scheme IIIb).[16,17] Strong emissions in the 300–430-nm region created distortions in the signals preventing reliable kinetic studies to be made on short time scales. An absorption spectrum of the same system was taken at the same time scale but with 2-nm resolution (Figure 6). This spectrum clearly reveals the carbene with λ_{max} = 343 nm. This is slightly redshifted from the value of 333 nm predicted for 1-naphthylcarbene (ground-state triplet) by Scaiano and co-workers.[16]

1-Naphthylcarbenes are also known to react rapidly with oxygen to give carbonyl oxides, 6 (Scheme IIIc).[18] Carbonyl oxide (λ_{max} = 430 nm) was readily detected upon photolysis of *c*- and *t*-1 in O_2-saturated isooctane or benzene (Figure 7). When pyridine was added to the same solutions, a strong, readily detectable absorption with λ_{max} at 536 nm was formed. The corresponding transient absorption spectrum is exhibited in Figure 8. The signal is long-lived with a lifetime of ca. 8 μs in the O_2-saturated benzene. We attribute the signal to a pyridine ylide, 7, formed by the reaction of 1-naphthylcarbene with pyridine (Scheme IIId). A number of pyridine ylides have been reported in the literature[19,20] including that for pyridine ylide 7 itself.[16]

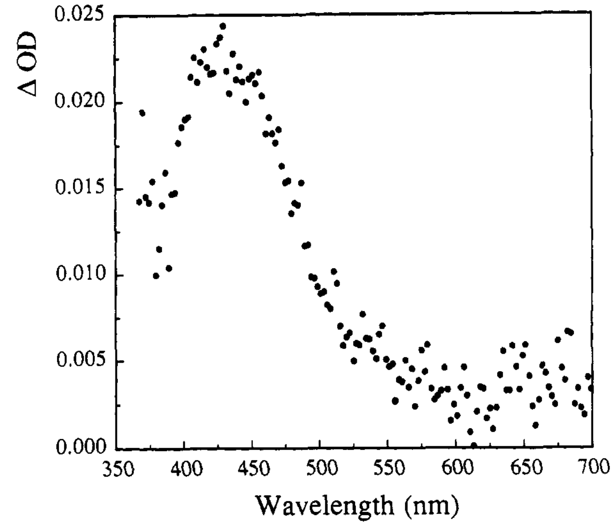


Figure 7. OMA transient absorption spectrum of carbonyl oxide measured 2.5 μs (20-ns gate) following 308-nm excitation of *trans*-2,3-di(1'-naphthyl)oxirane (0.1 mM) in O_2-saturated benzene at room temperature.

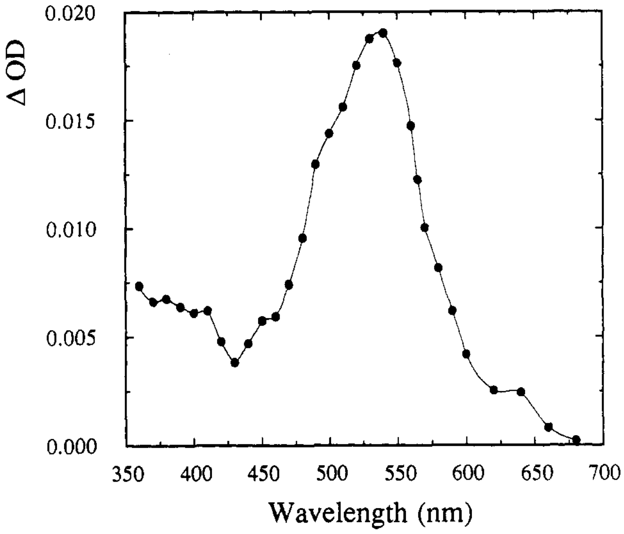


Figure 8. Transient absorption spectrum of pyridine ylide recorded 2.5 μs following 308-nm excitation of *trans*-2,3-di(1'-naphthyl)oxirane in N_2-saturated benzene containing 0.1 M pyridine at room temperature.

3.3 Temperature Dependence of Ylide Lifetimes. As revealed in the previous sections, the ylide spectra are very

---

[17] Griffin, G. W.; Horn, K. A. *J. Am. Chem. Soc.* **1987**, *109*, 4919.

[18] (a) Werstiuk, N. H.; Casal, H. L.; Scaiano, J. C. *Can. J. Chem.* **1984**, *62*, 2391. (b) Casal, H. L.; Tanner, M.; Werstiuk, N. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 4616.

[19] (a) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1990**, *112*, 3915. (b) Liu, M. T. H.; Bonneau, R. *J. Am. Chem. Soc.* **1989**, *111*, 6873. (c) Bonneau, R.; Liu, M. T. H. *J. Chem. Soc., Chem. Commun.* **1989**, 510. (d) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Doyle, M. P.; Liu, M. T. H. *Tetrahedron Lett.* **1989**, *30*, 1335. (e) Jackson, J. E.; Soundararajan, N.; Platz, M. S.; Liu, M. T. H. *J. Am. Chem. Soc.* **1988**, 110, 5595.

[20] Boate, D. R.; Johnston, L. J.; Kwong, P. C.; Lee-Ruff, E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 8858.

[21] Das, P. K. Unpublished results.

Table I. Eyring Parameters for the Decay of the Short-Lived Transients (λ_{max} ~ 530–550 nm) in 2-Methyltetrahydrofuran[a,b]

substrate	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
c-1	7.2 ± 0.3	0.7 ± 1.3
t-1	6.4 ± 0.5	−2.5 ± 2.1

[a] Excitation wavelength = 248 nm. [b] Temperature range (196–298 K).

similar, irrespective of the geometry (cis or trans) of the oxirane precursor or the mode (singlet or triplet) through which they are formed, although the kinetics of ylide decay differ. Inference as to the nature of the ylide geometries (i.e., exo,exo, endo,exo, or endo,endo) are therefore precluded. Kinetically and spectrally distinct carbonyl ylides in fluid solution have been identified in the case of *cis*- and *trans*-diphenyloxiranes.[22]

The ylide lifetimes increased dramatically (monitoring at 540 nm) in low-temperature fluid solution. For example, in 2-methyltetrahydrofuran the observed lifetimes are 1.24 and 1.07 μs for *c*- and *t*-1 at −44 and −49 °C, respectively (λ_{exc} = 248 nm). The activation parameters for the decay of the ylides obtained from their respective Eyring plots ($r > 0.99$) determined over the temperature range, T = 196–298 K (λ_{exc} = 248 nm) are exhibited in Table I. The slight difference in activation parameters may suggest that geometrically unique ylides are formed from the *cis*- and *trans*-oxirane isomers.

3.4 Implications to Electron-Transfer Photooxygenation. It has been shown that under electron-transfer photosensitization by cyanoaromatics in O_2 saturated acetonitrile the di(1′-naphthyl)oxiranes produce ozonides.[4a] The proposed mechanism for this reaction suggests the formation of an ylide and singlet oxygen, O_2 ($^1\Delta_g$), via back-electron transfer from superoxide anion to oxirane radical cation and subsequent interception of the ylide by O_2 ($^1\Delta_g$) to form ozonides stereospecifically. In view of the ultrashort lifetimes of these ylides in solution at room temperature, reaction with O_2 ($^1\Delta_g$) via diffusionally controlled encounters appears very unlikely. The only manner in which O_2 ($^1\Delta_g$) can effectively react with an ylide is while they exist as a geminal pair in the solvent cage. To establish experimentally the involvement of carbonyl ylides as distinct species in the photooxygenation of 2,3-dinaphthyloxiranes will be a challenge due to the difficulty of intercepting these unusually short-lived intermediates.

Summary

The results for the 2,3-di(1′-naphthyl)oxiranes (α-naphthalene derivative) differ dramatically from the photochemistry of 2,3-di(2′-naphthyl)oxiranes (β-naphthalene derivative) which give relatively long-lived (0.4–0.6 μs), triplet-derived carbonyl ylides.[6] Under conditions of triplet sensitization *cis*- and *trans*-2,3-di(1′-naphthyl)oxirane undergo ring opening via naphthalene-centered triplets to yield short-lived (40 and 70 ns in benzene, respectively) 1,3-di(1′-naphthyl)carbonyl ylides which appear to revert primarily back to starting oxirane.

In contrast, direct excitation of the oxiranes leads to no observable triplets. Singlet-mediated photochemistry may dominate for direct excitation which leads to one- and two-bond fragmentation of the oxiranes. One-bond cleavage results in ultra-short-lived ylides (14–22 ns) that exhibit slightly different spectral properties (blue-shifted) to those derived via triplet sensitization. 1-Naphthylcarbene and 1-naphthaldehyde are products presumably formed via fragmentation of the ground-state ylides. Some evidence exists for adiabatic contributions to the fragmentation reaction as evidenced by the observation of triplet 1-naphthaldehyde in the transient absorption phenomena. Formation of triplet 1-naphthaldehyde presumably results from adiabatic two-bond photofragmentation of singlet excited naphthyloxiranes, a reaction that would initially yield ground-state singlet 1-naphthylcarbene and singlet excited 1-naphthaldehyde. We are currently attempting to define the specific details of this process using picosecond spectroscopic techniques.

Acknowledgment. The work described herein was in part supported by the office of the Basic Energy Sciences, Department of Energy (U.S.). This is Document No. NDRL No. 3466 from the Notre Dame Radiation Laboratory. K.B.C. thanks the Natural Sciences and Engineering Research Council of Canada for a Visiting Scientist Fellowship. A.P.S. thanks the U.S. Army Office for financial support.

Registry No. *c*-1, 13528-49-9; *t*-1, 13528-48-8; **3**, 4399-95-5; **6**, 140663-21-4; **7**, 140663-22-5; HMPT, 680-31-9; 1-naphthaldehyde, 66-77-3.

---

[22] Kumar, C. V.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*, 5639.