Spectroscopy and Kinetics of Triplet 4-Methylbenzenesulfonylnitrene

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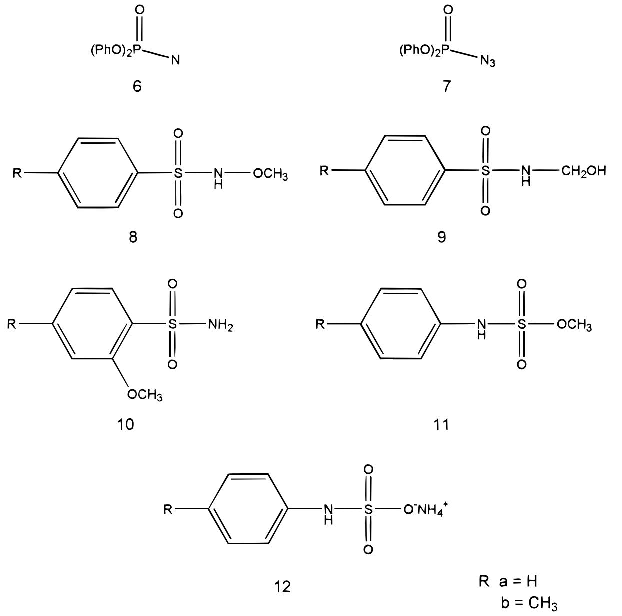
Triplet 4-methylbenzenesulfonylnitrene **3** was studied by solution phase laser flash photolysis, low-temperature absorption spectroscopy, and low-temperature EPR spectroscopy. Upon laser flash photolysis of 4-methylbenzenesulfonyl azide **1** in ethanol, absorption maxima were observed at 325 and 460 nm while in cyclohexane, a single maximum was observed at 310 nm. The short-wavelength absorptions were assigned to the triplet nitrene. There was no evidence that hydroxylic solvents catalyzed intersystem crossing from the singlet to the triplet state of **3**. After irradiation of **1** in an EPA glass at 77 K, a band at 313 nm was observed. The zero-field splitting parameters from the EPR spectrum of the nitrene in an EPA glass at 77 K were $|D/hc| = 1.471\ \mathrm{cm}^{-1}$ and $|E/hc| = 0\ \mathrm{cm}^{-1}$. Remarkably, **3** was not stable at 77 K in EPA. Irradiation of **1** also produced a second nitrene species, possibly (4-methylphenyl)nitrene, with $|D/hc| = 0.9840\ \mathrm{cm}^{-1}$ and $|E/hc| = 0\ \mathrm{cm}^{-1}$. The decay of the 325 nm transient was first order in ethanol ($\tau = 8.96 \pm 0.48\ \mu$s), methanol ($\tau = 8.18 \pm 0.08\ \mu$s), and methanol-$d_4$ ($\tau = 8.02 \pm 1.76\ \mu$s).

Introduction

Unlike the case with carbenes, attempts to observe triplet nitrenes through laser flash photolytic techniques have been hindered by two severe problems, inefficient intersystem crossing to the triplet and sluggish triplet reactivity.[1−5] Most singlet nitrenes react more rapidly than they undergo intersystem crossing to the triplet nitrene. Formation of the triplet is a minor pathway. In such cases, the triplet concentration is below detection limits. Often singlet nitrenes undergo rearrangements, particularly in nonnucleophilic solvents.[6,7] In solvents with sufficient nucleophilicity, the singlet nitrenes are trapped, and ylides are formed. These products of intra- and intermolecular reactions can be observed spectroscopically. Laser flash photolytic techniques have been applied almost exclusively to arylnitrenes.[1−3] The tendency of singlet arylnitrenes, particularly phenylnitrene, to rearrange to ketenimines led to confusion over the assignment of transients observed upon flash photolytic decomposition of aryl azides. Only in the last decade has a coherent scheme been developed for phenylnitrene reactivity on the basis of product studies, ambient temperature laser flash photolysis (LFP), and low-temperature EPR, IR, absorbance, and luminescence spectra.[1] It is possible by carefully choosing conditions to detect and assign observed transients to triplet nitrenes, ketenimines, or ylides. The detection of triplet arylnitrenes illustrated the second impediment usually encountered. Although the products of intermolecular triplet nitrene reactions such as hydrogen abstraction have been observed in product studies,[6,7] their reactivity has been too sluggish to obtain absolute rate constants through LFP. These apparent hydrogen abstraction products may have been formed by photoreduction of the azide precursor also. Transient lifetimes were dominated by triplet nitrene dimerization or dependent on precursor concentration.[1,8,9]

CHART 1



It would be desirable to find nitrenes whose singlet states are resistant to rearrangement and whose triplet states are sufficiently reactive for the acquisition of absolute rate constants. Then, substituent effects on the absolute rate constants of triplet nitrenes could be investigated. Recently, we have reported that triplet (diphenoxyphosphoryl)nitrene **6** (Chart 1) fulfills these criteria.[10] Previous product studies had shown that the reactions of (diethoxy)- and (diphenoxyphosphoryl)nitrenes were straightforward.[11,12] No products attributable to singlet rearrangement were found. Singlet phosphorylnitrenes react with hydrocarbons at diffusion control[12] and exhibit the lowest selectivity observed for any nitrene.[11b,13] Upon LFP of diphenyl phosphorazidate **7** in ethanol, a transient with an absorption maximum at 340 nm was observed.[10] Although its lifetime was unaffected by the presence of oxygen, triethylsilane, isoprene, or 1,4-cyclohexadiene, the transient decay was first order in ethanol, ethanol-d_6, methanol, and methanol-d_4. 4-Methylbenzenesulfonylnitrene is another possible candidate for study through laser flash photolytic techniques.[14] Relative to other classes of nitrenes, the singlet states of sulfonylnitrenes are resistant to rearrangement.[13] The selectivity of methanesulfonylnitrene is only slightly greater than that of phosphorylnitrenes,[13,15] indicating that singlet sulfonylnitrenes are highly reactive. As with phosphorylnitrenes, those structural features that enhance the reactiv-

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ity of the singlet may also increase the triplet nitrene reactivity sufficiently for the acquisition of absolute rate constants.

Although potentially useful, sulfonylnitrenes are not ideal candidates for study. Unlike phosphorylnitrenes whose reactions are relatively simple, both sulfonylnitrenes and sulfonyl azides exhibit a rich chemistry.[13,16] It is often unclear whether the products of thermolytic or photolytic decomposition of sulfonyl azides arise from a sulfonylnitrene or the azide itself. EPR spectroscopy provides strong evidence that sulfonylnitrenes are generated from the photolysis of sulfonyl azides at low temperatures.[17] At ambient temperatures in solution, the situation is more complex. Lwowski classified photolysis of azides as an occasionally useful method of generating sulfonylnitrenes.[18] There are three possible sources of complications; alternate mechanistic pathways may yield apparent nitrene products, rearrangement of singlet sulfonylnitrene, and elimination of SO_2 from either the azide precursor or the nitrene itself. Both ground state and excited state azides may react to yield the same products as nitrenes. Sulfonyl azides may undergo a 1,3-dipole addition with some olefins at ambient temperature followed by elimination of nitrogen to give aziridines.[13,16] Addition of a sulfonylnitrene to a double bond would also produce an aziridine. Normally, elevated temperatures are required for the 1,3-dipole addition. Often the photolysis of sulfonyl azides with olefins results in tar formation and polymerization.[13] Triplet nitrenes produce the corresponding amines and amides through consecutive hydrogen abstractions. It has long been known that reduction of excited state azides gives the same products.[13] Radicals react with azides in the presence of suitable hydrogen donors such as 2-propanol to yield the apparent products of triplet nitrenes.[19] Maslak demonstrated that the phosphoramidate observed upon sensitized photolysis of diethyl phosphorazidate was solely attributable to the triplet nitrene.[12b] Unfortunately, such evidence is unavailable for sulfonyl azides. Although sulfonylnitrenes are resistant to rearrangement relative to other nitrenes, evidence for a photo-Curtius rearrangement has been found. Gas phase pyrolysis of benzenesulfonyl azide produced azobenzene.[20] Lwowski et al. found products that were consistent with phenyl migration to nitrogen upon irradiation of benzenesulfonyl azide in methanol.[21] Benzenesulfonamide, a potential triplet nitrene product, and *N*-methoxybenzenesulfonamide attributed to singlet nitrene insertion into the methanol O−H bond were also observed. Alternative mechanisms precluding benzenesulfonylnitrene as an intermediate were also proposed to explain the isolated compounds. As an added complication, each product was shown to be photolabile. The photolysis of 4−methylbenzenesulfonyl azide in methanol gave unexpected products.[22] A third characteristic of sulfonyl azides not encountered with phosphoryl azides was their tendency to eliminate SO_2 through radical chain processes.[23,24] Radical initiators were found to catalyze the decomposition of some sulfonyl azides. However, 4−methylbenzenesulfonyl azide was shown to generate little SO_2 upon thermolysis. In aprotic solvents, C−H insertion products have been considered to arise from a nitrene intermediate.[21a,23b]

Given the complexity of sulfonyl azide and sulfonylnitrene chemistry, one may question their suitability for LFP. The example of the carbene fluorenylidene may be useful.[2,25,26] The reactions of the triplet state carbene are readily observable with LFP. Yet, product studies show that with hydrocarbons, the reaction of the singlet state predominates. Triplet state reactions constitute minor pathways. This illustrates that LFP can be applied effectively to species even when they represent a minor side reaction. If several criteria are met, LFP may be applied to triplet 4-methylbenzenesulfonylnitrene with success. Upon formation of the singlet nitrene from the precursor azide, intersystem crossing to the triplet must be efficient enough to generate spectroscopically detectable concentrations. Thermolysis of 4-methylbenzenesulfonyl azide in cyclohexane produces 4−methylbenzenesulfonamide in 5% yield.[23b] It is uncertain whether the appearance of this product is due to the triplet nitrene. However, if the sulfonamide does arise from a triplet nitrene intermediate, a 5% yield could indicate that sufficient concentrations of the triplet nitrene will be present for observation by LFP. Also, it must be possible to distinguish the sulfonylnitrene from other possible species that may appear in a transient spectrum. Photolysis of **1** may be expected to proceed along the pathways outlined in Scheme 1. This representation has been simplified for clarity and does not include potential decomposition with loss of SO_2 by either the azide or nitrene or the potential rearrangement of the singlet nitrene. For **1**, at ambient temperatures, these appear to be minor pathways. To apply LFP, intermediates from these pathways must be undetectable, not interfere with triplet nitrene absorption, or be readily distinguishable from the triplet.

Experimental Section

4-Methylbenzenesulfonyl azide **1** was prepared according to the method described by Leffler and Tsuno.[24b] 4-Methylbenzenesulfonamide **5** (Aldrich) was recrystallized from ethanol. Ethanol (MCB Reagent) was distilled from Mg under nitrogen. Cyclohexane (Aldrich spectrophotometric grade) was distilled from Na under nitrogen. 2-Methyltetrahydrofuran (2-MTHF) and 1,4-cyclohexadiene (Aldrich) were distilled from LAH under nitrogen. Isoprene (Aldrich) was dried over LAH and distilled under nitrogen. Distilled water was passed through a Barnstead NANOpure II filter. All other materials were used without further purification.

IR were obtained with a Perkin Elmer 683 infrared spectrophotometer. ^{1}H NMR were recorded on a Hitachi Perkin Elmer R-24B spectrometer (60 MHz). Absorption spectra were obtained on a Cary 1 spectrophotometer. Melting points were recorded on a Thomas Hoover melting point apparatus.

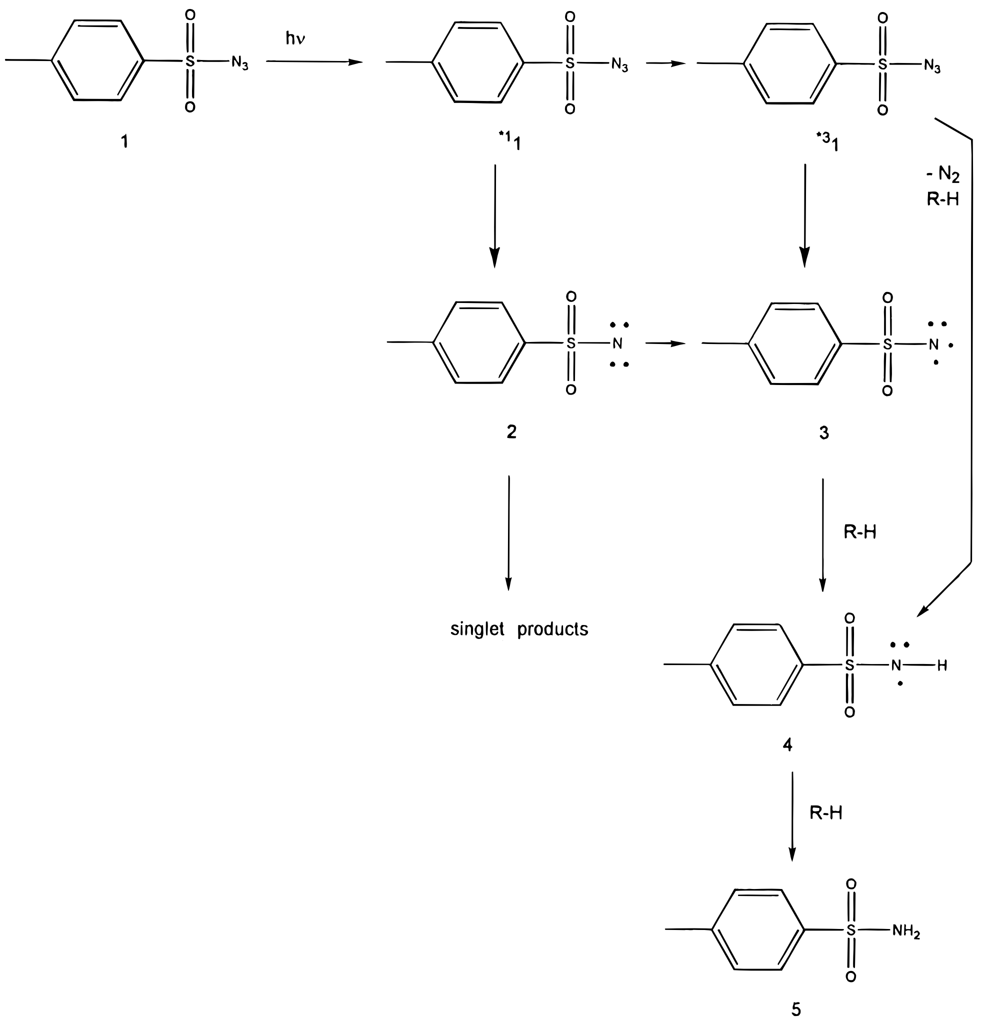
Laser Flash Photolysis. The laser flash photolysis apparatus used to acquire transient absorption spectra and lifetimes has been described previously.[10] Samples were irradiated with pulses from a frequency-quadrupled Nd-YAG laser (266 nm, <35 mJ, 5 ns) in either suprasil quartz 1 cm path length static cells or flow cells. Solutions were deaerated with a stream of deoxygenated nitrogen passing through the static cells or flow cell reservoir. Solution concentrations were adjusted so that the absorbance was 0.5−1.0 at 266 nm.

Low-Temperature Absorption Spectra. Solutions were deaerated by four freeze/pump/thaw cycles in a suprasil quartz 0.3 cm path length cell. Absorption spectra at 77 K were obtained by placing the cell in a quartz Dewar fitted with optical windows filled with liquid nitrogen. Spectra of the sample before and after irradiation (254 nm) in the Dewar were then acquired using the Cary 1 spectrophotometer.

Low-Temperature EPR Spectra. Solutions of **1** (0.1 M) were deaerated by bubbling nitrogen through them in 4 mm o.d. suprasil quartz tubes. Samples were placed in a quartz optical Dewar filled with liquid nitrogen and irradiated in a mini-Rayonet photochemical reactor (Southern New England Ultraviolet Co.) (254 nm). EPR spectra were obtained using either a Varian E-112 X-band spectrophotometer or a Bruker ESP 300 X-band spectrophotometer.

Irradiation of 4-Methylbenzenesulfonyl Azide in Methanol. Aliquots (1 mL) of a 2.0×10^{-2} M solution of **1** in

SCHEME 1



methanol were deaerated by four freeze/pump/thaw cycles in a 15 mm i.d. suprasil quartz tube. Samples were irradiated for 10 min in the aforementioned mini-Rayonet photochemical reactor. Photosylates were analyzed by GC or GC−MS. Gas chromatographic analyses were carried out on a FID-equipped Shimadzu GC-14A gas chromatograph using a 15 m × 0.53 mm i.d. Rtx-5 capillary column (Restek) in isothermal mode at 110 °C. GC−MS analyses were carried out on a TCD-equipped HP-5890 Series II gas chromatograph in tandem with a HP-5971A mass selective detector (Tri-State University). A 30 m × 0.25 mm i.d. DB-5 capillary column (J & W Scientific) was used with a temperature program from 150 to 200 °C with a 20 °C/min ramp. He was used as the carrier gas for both instruments.

Results and Discussion

Laser flash photolysis (266 nm) of 4-methylbenzenesulfonyl azide **1** in ethanol produced a transient spectrum with a strong absorption at 325 nm and a substantially weaker band at 460 nm (see Figure 1). Two species were present: one exhibited a first-order decay ($\tau_{325\ \mathrm{nm}} = 8.96 \pm 0.48\ \mu$s), while the other did not decay within 70 μs. Both species appeared within the laser pulse. The 460 nm absorption was too weak to obtain reliable kinetic data, but its lifetime was comparable to the 325 nm band. LFP of **1** in cyclohexane produced a transient spectrum with a maximum at 310 nm (see Figure 2). Although the transient absorption extended beyond 450 nm, a distinct band could not be discerned in this region.

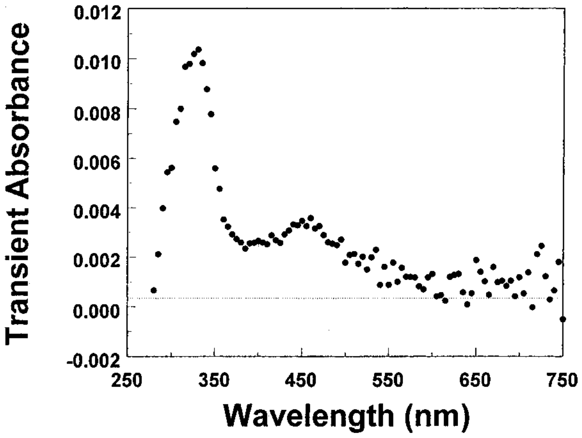


Figure 1. Transient absorption spectrum observed 500−540 ns after 266 nm laser flash photolysis of 6.54 × 10^{-4} M 4-methylbenzenesulfonyl azide **1** in ethanol (deoxygenated) at ambient temperature.

Transient absorption signal intensities were consistently weaker in hydroxylic solvents relative to those in cyclohexane. Enhanced triplet yields were observed in alcohols for (diphenoxyphosphoryl)nitrene,[10,11b] pentafluorophenylnitrene,[27] and 2,6-difluorophenylnitrene.[28] Platz has suggested that hydroxylic solvents catalyze intersystem crossing from the singlet to triplet state.[1] If the transients observed in ethanol and cyclohexane can be assigned to **3**, then the catalytic effect is negligible for this nitrene. A linear relationship between transient signal intensity at 310 nm and laser energy/pulse over

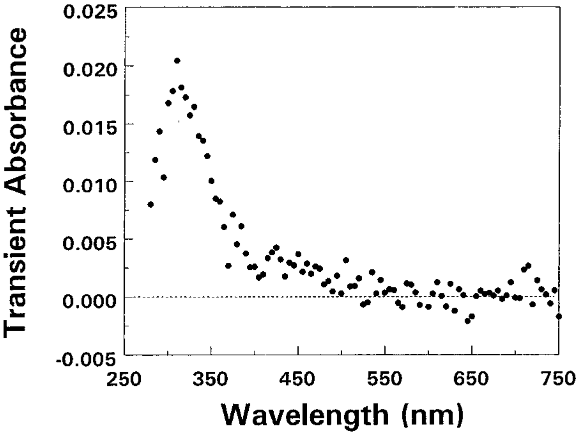


Figure 2. Transient absorption spectrum observed 200−1200 ns after 266 nm laser flash photolysis of 6.8×10^{-4} M 4-methylbenzenesulfonyl azide **1** in cyclohexane (deoxygenated) at ambient temperature.

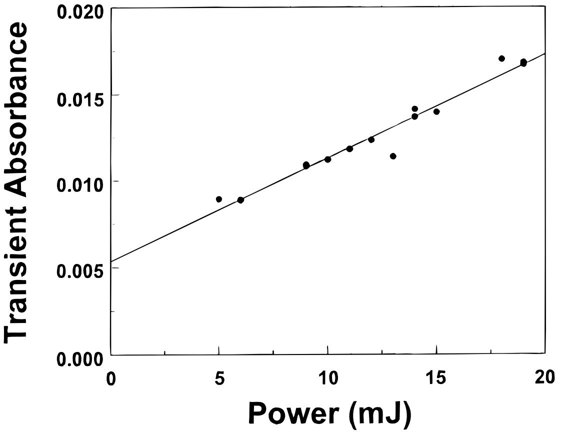


Figure 3. Plot of transient absorption at 310 nm vs laser power (mJ) upon flash photolysis of 6.33×10^{-4} M 4-methylbenzenesulfonyl azide **1** in cyclohexane (deoxygenated) at ambient temperature.

a 14 mJ range was observed (see Figure 3), indicating that the transient arises from a monophotonic process. The nonzero intercept is surprising. The transient absorbance at zero power roughly corresponds to that of the unidentified long-lived species and suggests that it is not a photoproduct.

The presence of oxygen or acid had no observable effect on the peak positions or their relative signal intensities in the spectrum in Figure 1. Transient spectra from LFP have been recently reported for arylnitrenium ions in acidic media.[29] No new transients were observed, and no enhancement of the 460 nm absorption was detected upon LFP of **1** in 70% ethanol/30% water using a 1:1 acetate buffer (2.0 mM). Similarly, there was no observable difference in the transient spectrum in a solution of **1** in 70% ethanol/30% water adjusted to a pH of approximately 2.6 with H_2SO_4. Failure to observe a nitrenium ion from a highly electron deficient nitrene is not surprising.

Irradiation (10 min, 254 nm) of **1** in an EPA glass (2:5:5 ethanol, 2-methylbutane, diethyl ether) at 77 K produced the spectrum in Figure 4 with an absorption maximum at 313 nm. This band overlapped with a tailing absorption whose maxima were obscured by the precursor. The species responsible for the 313 nm transient was not stable in EPA at 77 K. Also, it disappeared rapidly when the glass was annealed. Upon irradiation, the glass turned red. After warming to ambient temperature, the solution was yellow.

Irradiation (75 s, 254 nm) of **1** in an EPA glass at 77 K produced a spectrum consistent with 4-methylbenzenesulfonylnitrene. The zero-field splitting parameters (ZFSs) ($|D/hc| = 1.471$ cm^{-1}, $|E/hc| = 0$ cm^{-1}) were in reasonable agreement with those obtained by Smolinsky et al.[17a] in fluorolube ($|D/hc| = 1.442$ cm^{-1}, $|E/hc| = 0$ cm^{-1}). Both in EPA and in fluorolube, the peak corresponding to the overlap of the X_2 and Y_2 transitions was broad (300−350 G). In fluorolube, the nitrene was reported to be stable for 18 h, while in EPA it slowly decayed as had been noted in the matrix absorption spectra. Due to the higher concentrations of azide necessary for the EPR experiment, the red color of the matrix was more pronounced after irradiation. The color faded to orange over a time period that corresponded with the disappearance of the EPR signal. A second nitrene species was observed with **3** upon irradiation of the glass. Its ZFSs were $|D/hc| = 0.9840$ cm^{-1} and $|E/hc| = 0$ cm^{-1}. After prolonged irradiation (5 min) of **1**, the ratio of peak areas of the second nitrene species to **3** increased. These ZFSs approximate those found for (4-methylphenyl)nitrene ($|D/hc| = 0.9761$ cm^{-1}).[17c] Prolonged irradiation of **1** (up to 45 min) in the optical Dewar employed for matrix absorption spectroscopy did not result in the appearance of any new bands. Considering that the 313 nm band was weak and that irradiation into the absorption Dewar was inefficient relative to the EPR Dewar, it possible that a secondary photoproduct may not be observable in the matrix absorption spectra. Triplet phenylnitrene was shown to be light sensitive and photorearranged readily.[1] It would be tempting to assign the second species to (4−methylphenyl)nitrene arising from a photochemical reaction of **3**. The much longer lifetime of the nitrene at 77 K would allow for multiphotonic processes. As previously described, the arylnitrene product, azobenzene, was isolated in the pyrolysis of benzenesulfonyl azide.[20] Elimination of SO_2 was observed in the thermolysis of various alkyl- and arylsulfonyl azides.[23,24] No alkyl- or arylnitrene products were isolated, however, and radicals were believed to catalyze decomposition of the azide. Further EPR and products studies are being conducted to identify the second species and determine whether it is a photoproduct of **3** or formed concomitantly with it. Nonetheless, the EPR signal attributable to **3** and the 313 nm band in the matrix absorption spectrum are formed under similar conditions, and both are unstable in EPA at 77 K.

Abstraction of hydrogen by **3** from the solvent will produce the amidyl radical **4**. Conceivably, it could be the species responsible for the transient spectra in ethanol and cyclohexane. The most convenient method for generating such radicals is to irradiate the corresponding amine or amide in di-*tert*-butyl peroxide. The *tert*-butoxy radicals initially formed can abstract hydrogen from the nitrogen to give the radical which can detected through LFP.[30] Strong absorption by the peroxide

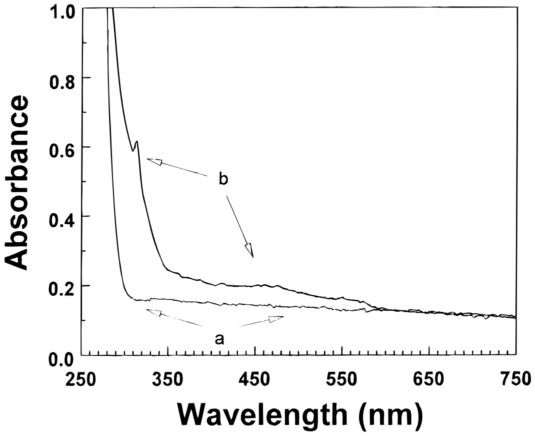


Figure 4. 2.73×10^{-3} M 4-methylbenzenesulfonyl azide **1** in EPA at 77 K: (a) before irradiation and (b) after irradiation for 10 min at 254 nm.

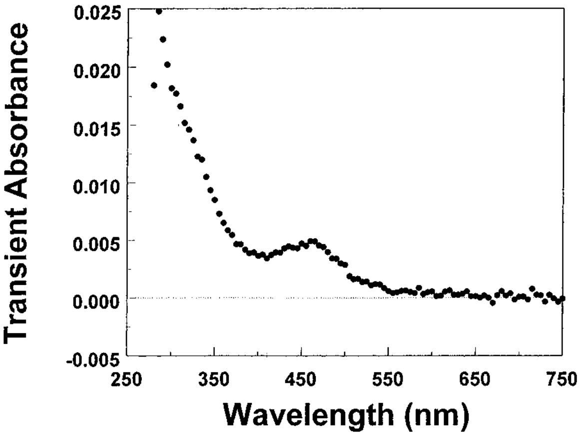


Figure 5. Transient absorption spectrum observed 400−1400 ns after 266 nm laser flash photolysis of 1.9×10^{-3} M 4-methylbenzenesulfonamide **5** in ethanol (deoxygenated) at ambient temperature.

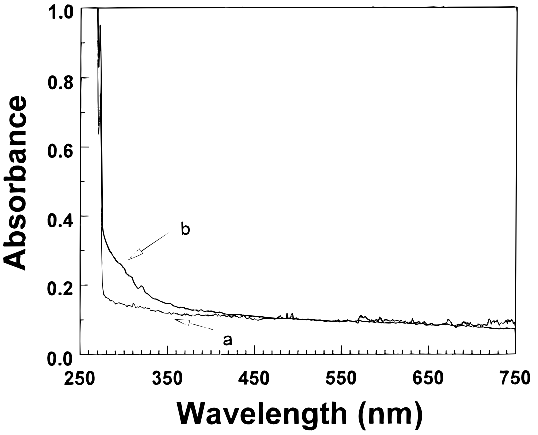


Figure 6. 1.17×10^{-2} M 4-methylbenzenesulfonamide **5** in EPA at 77 K: (a) before irradiation and (b) after irradiation for 15 min at 254 nm.

TABLE 1: Lifetimes of the Transients Assigned to 3 and 6 in Various Solvents

solvent	τ (μs)[a] of **3**	τ (μs) of **6**[b]
ethanol	8.96 ± 0.48	3.8 ± 0.6
ethanol-d_6		4.1 ± 0.8
methanol	8.18 ± 0.08	3.6 ± 0.4
methanol-d_4	8.02 ± 1.76	4.0 ± 1.0

[a] Errors are 2σ. [b] Reference 10.

below 320 nm limits the use of this method. A less satisfactory way to generate the amidyl radical would be to directly photolyze the sulfonamide. Upon LFP of **5** in ethanol, the transient spectrum consisted of a species with a strong tailing absorption with a maximum below 280 nm and a second weak maximum at 460 nm (see Figure 5). At 290 nm, the transient had a second-order decay ($2/k\epsilon = (2.02 \pm 0.79) \times 10^7$ cm s^{-1}) in ethanol. A similar spectrum was obtained in EPA at 77 K (see Figure 6), but the 460 nm peak was either not present or too weak to be observed. If this species is the amidyl radical **4**, then the transients produced upon LFP of **1** may be assignable to the triplet nitrene.

The decay of the 325 nm transient produced from the nitrene was first order in hydroxylic solvents (See Table 1). If this transient can be assigned to triplet 4−methylbenzenesulfonylnitrene, then the lifetimes demonstrate that it is less reactive than triplet (diphenoxyphosphoryl)nitrene **6**. The $|D/hc|$ value of **3** is smaller than that of triplet **6** ($|D/hc| = 1.5408$ cm^{-1}),[10] indicating greater spin delocalization in the former. Thus **3** would be expected to be more stable and less reactive than **6** despite the greater electron-withdrawing ability of the sulfonyl substituent relative to the phosphoryl substituent.[31] Due to the low number of runs, the lifetime in methanol-d_4 is less reliable than in methanol. The difference between lifetimes is probably negligible and shows that 4-methylbenzenesulfonylnitrene does not exhibit a significant kinetic isotope effect (KIE). Liang and Schuster reported that the reaction of triplet (4-nitrophenyl)nitrene with *N*,*N*-dimethyl-*tert*-butylamine had a surprisingly low KIE.[8] It was postulated that a rate-limiting electron transfer from the amine to the highly electron deficient nitrene to produce a radical ion intermediate had occurred. Small or negligible isotope effects would be expected for such a mechanism. No KIE was observed for the lifetimes of triplet **6** with alcohols.[10] This mechanism is currently under investigation for **3** and **6**. The 310 nm transient decay in cyclohexane was too long-lived to acquire kinetic data on our apparatus. The presence of 1,4-cyclohexadiene (0.106 M) in cyclohexane had no observable effect on the lifetime of the transient.

The presence of oxygen caused an anomalous decrease in the lifetime of **3** and its signal intensity in ethanol and cyclohexane. In air-saturated ethanol and cyclohexane, the transient signals were weaker. The transient decay was first order ($\tau = 328 \pm 44$ ns in cyclohexane and $\tau = 297 \pm 38$ ns in ethanol). Given that the concentration of oxygen in air-saturated cyclohexane is 2.3 mM,[32] the bimolecular rate constant for oxygen with **3** would be 1.4×10^9 M^{-1} s^{-1}. In air-saturated ethanol, the oxygen concentration is 2.07 mM,[32] which corresponds to $k_{\text{oxygen}} = 1.6 \times 10^9$ M^{-1} s^{-1}. Rate constants of this magnitude between oxygen and a nitrene are unexpected. Although it is known that nitrenes react with O_2,[33] the reactions are slow.[8] Liang and Schuster reported that the reaction of (4−nitrophenyl)nitrene with O_2 had a bimolecular rate constant less than 2×10^5 M^{-1} s^{-1}. Oxygen was found to have no effect on the lifetime of triplet (diphenoxyphosphoryl)nitrene.[10] The diffusion control rates at which **3** appears to react with O_2 are perplexing. We can only suggest that sulfonylnitrenes react with oxygen in a manner unlike other nitrenes. Breslow et al. found that cleavage of the S−N bond occurred in the thermolysis of **1** in the presence of *tert*-butyl hydroperoxide to produce the corresponding sulfinic acid.[23a] Perhaps, oxygen can react similarly.

Although it is possible to assign the reactive species responsible for the transient absorption spectra and the matrix absorption and EPR spectra to **3**, the anomalous rate of reaction with oxygen and the second species observed in the EPR indicate that care must be taken when making simplistic comparisons with triplet (diphenoxyphosphoryl)nitrene. With the latter, the chemistry is relatively straightforward. To understand why the sulfonylnitrene appears to be so reactive with O_2 and its instability in EPA at 77 K will require further product studies.

Preliminary results have been obtained for the photolysis of **1** in methanol which are germane to the assignment of the spectra to **3**. Previous product studies involving the photolysis of arylsulfonyl azides are contradictory. Horner and Christmann reported that irradiation of **1** in methanol produced **8b**, **10b**, **12b**, and an unidentified product.[22] **8b** is the expected product of singlet nitrene insertion into the O−H bond. No product of nitrene insertion into the C−H bond **9b** or triplet nitrene product **5** was reported. Minor product **10b** was the result of migration of the methoxy group in **8b**. Photolysis of benzenesulfonyl azide in methanol proceeded somewhat differently.[21] The product of singlet nitrene O−H insertion, **8a**, was isolated along with **11a** and **12a**. No C−H nitrene insertion product was observed, but the potential triplet product benzenesulfonamide was isolated in low yield. No **10a** due to rearrangement of **8a** was obtained. Instead, a product consistent with singlet nitrene rearrangement, **11a**, was isolated in this case. In our hands, irradiation of **1** in methanol for 15 min produced only two products on the basis of GC and GC−MS analysis. From its mass spectrum and comparison to an authentic sample, **5** was one of the photoproducts. Since 4-methylbenzenesulfonamide can arise from alternative pathways that do not involve the triplet nitrene as an intermediate, its presence is not confirmation of the assignment of the transient species to **3**. However, its complete absence would have been strong evidence against such an assignment. The second product had a molecular ion peak with $m/z = 201$. This is consistent with structures **8**−**11b**. The mass spectrum has a strong molecular ion which precludes **9b**. Assignment of the second product between the three remaining possibilities cannot be made with complete confidence on the basis of the mass spectrum alone until comparison with authentic samples are made. However, the simple O−H insertion product is the most reasonable candidate. Further investigations are underway. The significance of these preliminary results is that the potential triplet product is present.

Conclusions

The transient absorption produced upon LFP of **1** and the species observed in the matrix absorption and EPR spectra are tentatively assigned to the triplet nitrene **3**. It is comparable in nature to the triplet state of **6** whose character was shown to be intermediate between alkyl- and arylnitrenes. The ZFSs and lower reactivity indicate that electron delocalization is greater in **3**, although this is not reflected in the absorption spectra where the nitrene's strongest band in ethanol (325 nm) is blue shifted relative to that of **6** (345 nm). Several other features distinguish **3** from the phosphorylnitrene. It is unstable in an EPA matrix at 77 K and exhibits unique reactivity with oxygen. The detection of a second nitrene species suggests that **3** is photolabile or that there is an alternate photochemical reaction for the precursor azide. With the observation of **3** and **6**, there is now the opportunity to compare the effect of structure on the reactivity of nitrenes through LFP if sufficiently reactive substrates can be found. Recently, acyl azides have been employed in polymer surface modification.[34] The relatively simple chemistry of phosphoryl azides suggest that they may be potentially useful for such applications. The more complex behavior of sulfonyl azides illustrated here and in the cited papers make them less attractive candidates for polymer surface modification.

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