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Laser Flash Photolysis of Diphenylsulfonyldiazomethane: Detection of the Sulfene and a Sulfene–Pyridine Ylide

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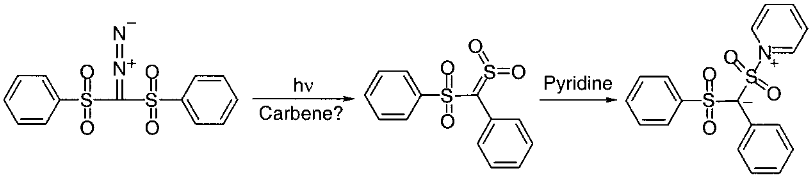
ABSTRACT



DSD Sulfene Sulfene-Pyridine Ylide

The photochemistry of diphenylsulfonyldiazomethane (DSD) was studied by means of nanosecond laser flash photolysis. The photochemical behavior of this molecule upon UV irradiation is characterized by sulfene formation, presumed to arise via Wolff rearrangement of a carbene. We were able to detect the sulfene and the sulfene ylide formed upon sulfene trapping by pyridine. Sulfene quenching by nucleophiles was also examined.

The photochemistry of compounds containing a diazo moiety invariably involves elimination of molecular nitrogen and typically yields the corresponding carbenes.[1−4] The behavior of carbenes derived from α-diazocarbonyls is dominated by facile Wolff rearrangement to form ketenes.[5−10] The hydrolysis of ketenes to carboxylic acids has made diazocarbonyls useful photoacid generators for the microlithographic industry.[11,12]

Deep-UV lithography requires the formulation of new photoresists with increased sensitivity. This higher sensitivity is achieved by generating a strong acid and employing it as a catalyst. The carboxylic acids produced by α-diazocarbonyl compounds are not satisfactory for this purpose, and stronger acids, e.g., sulfonic acids, are frequently the preferred photogenerated acids.[12] α-Diazosulfones are interesting because they are potential precursors of sulfonic acids. For these compounds, the initial formation of the carbene is followed by a sulfo-Wolff rearrangement to give the sulfene[13] which is hydrolyzed in water to yield the sulfonic acid.[14−16] While the reactions of α-ketocarbenes to yield ketenes have

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been the subject of intensive studies (vide infra), the corresponding reactions of α-sulfonylcarbenes and sulfenes have received less attention.[17] These studies have relied predominantly on the analysis of products from solvolysis of reaction intermediates. To the best of our knowledge, no time-resolved studies on the reactions of α-sulfonylcarbenes have been performed.

The utility of laser flash photolysis (LFP) with UV/vis detection in the study of α-diazocarbonyl compounds has been aided greatly by the use of various amines as "probe" molecules. These probes, typically pyridine, react with both carbenes and ketenes to form ylides with absorption in the optical region of interest, thereby allowing more complete kinetic analysis.[18−25]

In this work we report a LFP study of diphenylsulfonyldiazomethane (DSD), in which, for the first time, a sulfene was detected under reactive conditions[26] and a sulfene−pyridine ylide was detected by LFP. This allowed the behavior of the sulfene to be investigated via competition experiments.

DSD was prepared via the diazo transfer route commonly employed for α-diazoketones, starting from diphenylsulfonylmethane and *p*-toluenesulfonyl azide[27] (yield: 80%). The absorption spectrum of DSD in acetonitrile exhibits a main peak at 231 nm (log $\epsilon = 4.2$) and a weaker band at 376 nm (log $\epsilon = 2.0$).

The transient absorption spectra[28] obtained upon LFP (usually at 308 nm) of DSD in N_2-saturated acetonitrile at different delays after the laser pulse are shown in Figure 1. They show a UV maximum at 290 nm and a weaker band extending up to 370 nm. From the kinetic analysis, two transients can be observed and fitted to a biexponential decay. The shorter lifetime is 50 μs (monitored at 290 nm, see Figure 1) and the longer one 11 ms. Oxygen does not affect the lifetime of either transient. Due to the lack of any effect on transient lifetimes in experiments with tetrabutylammonium chloride, a nucleophilic agent due to Cl^- anion, tributylgermanium hydride, a hydrogen-donating radical scavenger, and anthracene, a triplet state quencher makes the involvement of cations, radicals, and triplet states unlikely.

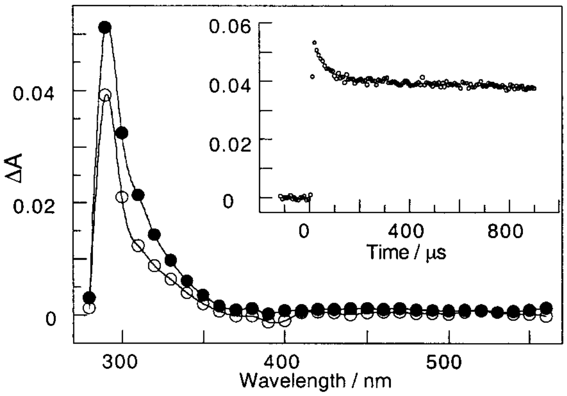

Figure 1. Transient absorption spectra obtained upon nanosecond LFP of DSD in N_2-saturated acetonitrile solution, recorded (●) 16 μs and (○) 800 μs after the laser pulse. Inset: decay kinetics monitored at 290 nm.

DSD undergoes nitrogen loss upon photoexcitation, presumably with formation of a carbene followed by Wolff rearrangement to form the sulfene. Conceivably, the two transients observed in the LFP experiments could be assigned to these species. To determine the nature of these transients, we performed one of the "classic" experiments in the detection of carbenes (and sometimes ketenes); their trapping with pyridine. The transient absorption spectra obtained upon nanosecond LFP of DSD in N_2-saturated acetonitrile solution in the presence of 0.15 M pyridine shows an intense absorption extending from 300 to 600 nm and a well-defined maximum at 440 nm (Figure 2). This spectrum could be

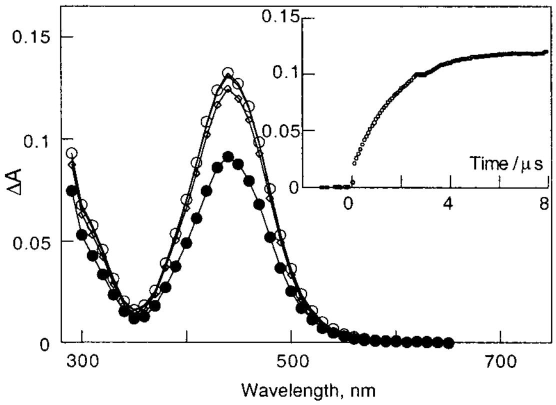

Figure 2. Transient absorption spectra obtained upon nanosecond LFP of DSD in N_2-saturated acetonitrile solution in the presence of 0.15 M pyridine, recorded (●) 1.8 μs, (◊) 6.2 μs, and (○) 16.7 μs after the laser pulse. Inset: kinetic trace monitored at 440 nm.

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(28) For the laser flash photolysis work, a Lumonics EX-530 excimer laser (Xe/HCl, 308 nm, ~6 ns pulse width, 50−100 mJ/pulse) was used for excitation. The system is controlled by a Power Macintosh computer running LabVIEW 4.1 software. A Tektronix 2440 digital oscilloscope captures the signal from the photomultiplier tube. Further details on a similar system have been provided elsewhere (Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747. Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396). The optical densities of the samples were 0.2−0.3 at the laser wavelength. A flow system (a 7 × 7 mm Suprasil quartz flow cell, connected with a 100 mL reservoir with Teflon tubing) was used in order to ensure irradiation of a fresh portion of the sample by each laser shot.

tentatively assigned either to a carbene−pyridine or a sulfene−pyridine ylide.

While the first type of complex is well documented,[18−20,29−31] the generation and subsequent characterization of a sulfene−pyridine ylide under LFP conditions has never been reported, although these species have been known for many years.[17] The rise time for ylide formation (see inset of Figure 2) is dependent on the pyridine concentration and allows for the determination of a rate constant by plotting the first-order rise rate constant vs pyridine concentration; $k_q = 3.9 \times 10^6$ M^{-1} s^{-1}. Additionally, the intercept yields the lifetime in the absence of pyridine for the transient responsible for ylide formation. The value we found, 4 ms, is in fairly good agreement with the direct measurement, 11 ms, considering the large error associated with the extrapolation of very long lifetimes. Therefore, the long-lived transient absorbing at 290 nm is the same one responsible for the ylide formation with pyridine.

To establish the nature of this transient, we monitored the effects of various quenchers on the unimolecular rate constant for the pyridine ylide growth. This method has already been applied in the study of carbenes[9,18,19,29] and ketenes.[24] In our experiments we used a fixed concentration of pyridine (2×10^{-4} M) as a transient probe. Under these conditions the rise time for pyridine ylide formation was ∼2 ms. The effects of oxygen (10^{-2} M) and adamantanethione (up to 10^{-3} M) on the kinetics of pyridine ylide growth were analyzed, since both are efficient scavengers of triplet carbenes.[9,19,32−38] The lack of an effect upon addition of either reagent excludes a triplet carbene as the transient responsible for ylide formation. This is also consistent with the long lifetime observed (11 ms) for the ylide precursor.

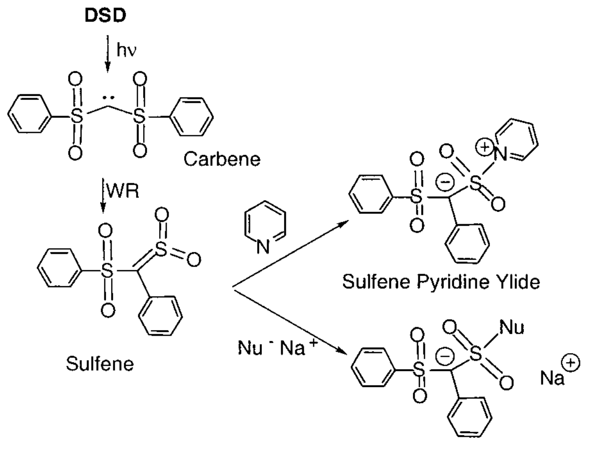
The effects of acetone (up to 0.1 M) and methanol (2.25 M) on the kinetics of pyridine ylide growth were analyzed, since both are good singlet carbene scavengers.[39−43] Again, the lack of an effect excludes a singlet carbene as the transient responsible for ylide formation.

At this point, the possibility that the ylide might be formed by interaction of pyridine with a sulfene must be considered. Although sulfenes have been proposed as intermediates involved in several reactions[17,44] their subsequent reactions are still under investigation. The intermediacy of sulfenes is usually inferred by identifying the products of nuclephile trapping.[13−15,45−47] Although there are many literature reports, we could not find any LFP study focused on the sulfene trapping step. Thus, we decided to use the probe technique (photolysis in the presence of 2×10^{-4} M pyridine, rise time for pyridine ylide formation, 2 ms) to monitor the effects of different sulfene quenchers on sulfene−pyridine ylide rise time: the results are summarized in Table 1. In these experiments there is a competition for the sulfene between nucleophile and the pyridine, which reduces the yield of sulfene−pyridine ylide as well as its rise time (Scheme 1).

Table 1. Bimolecular Rate Constants (k_{app}) for Interaction of Various Nucleophiles with the Sulfene Obtained upon LFP (308 nm) of DSD in N_2-Saturated Solution, in the Presence of 2×10^{-4} M Pyridine as a Probe

nucleophile	k_{app} (M^{-1} s^{-1})
sodium acetate	1.1×10^7
sodium azide	2.4×10^7
sodium thiocyanate	5.0×10^5
sodium hydroxide	nonlinear quenching plot
sodium cyanide	$<10^3$, see text
methanol	$<10^3$
water	$<10^3$

Scheme 1



For many of the nucleophiles studied, the shortening in the rise time of the sulfene−pyridine ylide was accompanied by a disproportionately large decrease in the signal due to the sulfene−pyridine ylide. The UV/vis spectra of DSD

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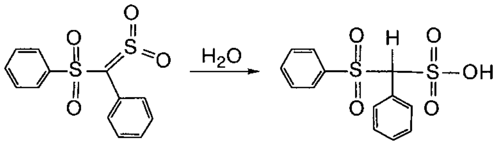
solutions containing sodium acetate and sodium cyanide showed the presence of a band ($\lambda \sim 300$ nm) not present in solutions containing nucleophile or DSD alone. Both of these observations can be rationalized via an interaction between the nucleophile and ground state DSD. Given the relative concentrations of nucleophile (<1 mM) and DSD (>10 mM), such an interaction may significantly deplete the amount of nucleophile available for reaction with the sulfene. In fact, for sodium cyanide there was no observable quenching of the sulfene despite its very high nucleophilicity.[48] This is likely due to a (dark) reaction of sodium cyanide with DSD prior to laser excitation. This effect is also apparent with results obtained with sodium acetate, where reversible complexation may be involved. Attempts to use 355 nm for excitation, where lower concentrations of DSD are required—due to the high extinction coefficient at this wavelength—led to inconclusive results presumably as a result of the failure to control the thermal reactions already mentioned. The rate constants observed for all of the ionic species should be interpreted as lower limits of the actual rate constant, since some nucleophile may have been consumed in dark reactions. Attempts were also made to use the nonionic nucleophiles water and methanol as sulfene scavengers. Only a small effect was observed with the concentrations employed (16 and 2.25 M, respectively). Despite the lack of an observable interaction on the time scale of the laser experiment, the products resulting from the attack of water[14,15] and methanol[13] on sulfenes have been detected in product studies. In fact, product studies we performed on DSD showed that one of the main products formed upon photolysis in acetonitrile/water is the expected sulfonic acid formed via reaction of the sulfene with water (Scheme 2). Similar products have been observed in the photolysis of other α-diazosulfones.[16]

Scheme 2



Therefore, all these results allowed us to conclude that the long-lived transient observed at 290 nm upon laser flash photolysis of DSD is due to a sulfene intermediate formed by Wolff rearrangement.

The second transient observed upon LFP of DSD in N_2-saturated acetonitrile lives 50 μs and can also be monitored at 290 nm. The experiments already performed do not support the presence of radicals, triplet states, cations, and the triplet carbene, due to the lack of effect by selective scavengers. However, the possibilility of the transient being a singlet carbene cannot be entirely eliminated despite its lack of reactivity with the typical scavengers of singlet carbenes. This doubt arises from the fact that the reactivity of the singlet carbene of DSD may be altered dramatically relative to typical singlet carbenes by the presence of the electron-withdrawing sulfonyl substituents. The role of electronic effects in the stability of carbenes is well established.[49]

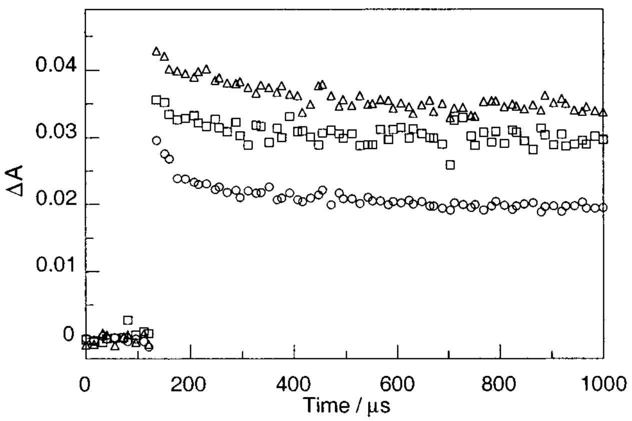


Figure 3. Kinetic decay traces obtained upon nanosecond LFP of DSD in N_2-saturated (○) CH_3CN, (□) benzene, and (△) dioxane solutions; monitored at 300 nm and recorded 50 μs after the laser pulse.

Nitrile ylides, formed from reaction of acetonitrile with a carbene, are species which have been observed in the photolysis of other diazo compounds.[50−55] To test if this transient could be a nitrile ylide, the transient absorption spectra of DSD in dioxane and benzene solution under N_2 were recorded. A very similar transient was observed in these solvents. Monitoring at 300 nm, the short-lived transient shows a lifetime (Figure 3) of ∼200 μs in dioxane and ∼44 μs in benzene, thus ruling out a nitrile ylide as a possible intermediate. The exact nature of this species remains under investigation.

In conclusion, the photolysis of diphenylsulfonyldiazomethane (DSD) occurs through nitrogen extrusion, presumably involves a carbene, which undergoes rapid Wolff rerrangement to a sulfene. The probe technique allowed us to monitor the absorption spectra and the kinetic behavior of a sulfene−pyridine ylide. It was characterized by quenching studies employing different nucleophiles. The presence of carbene intermediates could not be detected in our LFP experiments, even using the shortest time scale available.

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