ORGANIC LETTERS

2000
Vol. 2, No. 10
1357−1360

Laser Flash Photolysis of 2-Diazo-1,3-diphenyl-1,3-propanedione: An Unusual Long-Lived Triplet as a Reaction Intermediate

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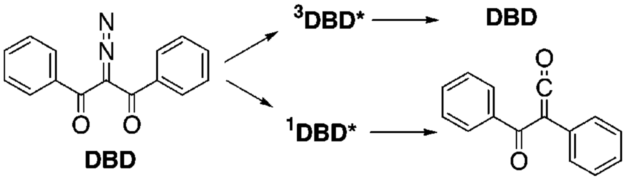
Received January 27, 2000

ABSTRACT



Laser flash photolysis of 2-diazo-1,3-diphenyl-1,3-propanedione (DBD) is presumed to involve a short-lived carbene, followed by Wolff rearrangement to a long-lived ketene. We have detected ketene ylides following photolysis of DBD in the presence of amines but not with pyridine. The triplet state of DBD lives several microseconds, an unusual observation for a diazo compound; however, the triplet is not a ketene precursor, which must result from excited singlet state fragmentation of DBD.

The photochemical behavior of diazo compounds under UV irradiation is characterized by nitrogen elimination, leading to carbenes.[1−4] In the case of α-diazocarbonyl compounds, these intermediates may then undergo Wolff rearrangement with formation of ketenes.[5−9] This reaction has also been extended to analogous diazo molecules with heteroatoms such as phosphorus, sulfur, and nitrogen. Methyleneoxophosphoranes (phosphenes),[10,11] sulfenes,[12,13] and ketene imines[14−16] have been proposed as intermediates involved in the photolysis of α-diazophosphines, α-diazosulfones, and α-diazoimines, respectively. We note that diazo compounds are commonly employed in the development of resist technology[17] due to their activity as efficient photoacid generating agents (PAGs).[18,19]

While the chemistry of carbenes and related species has been the subject of many studies, it was only with the advent of fast time-resolved techniques in the 1970s that direct kinetic studies became possible. Kinetic studies on diarylcarbenes using conventional flash photolysis by Closs and Rabinow[20] are an important milestone in this field. In the

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10.1021/ol005590k CCC: $19.00

1980s laser flash photolysis was employed to achieve a detailed understanding of carbene kinetics.[21−28] A frequent problem with this approach is the weak absorption of these intermediates in the region monitored in the laser flash photolysis experiments, typically between 300 and 700 nm. One elegant and efficient method to overcome this difficulty is to make the transient "visible" by means of a suitable species that forms a complex (e.g., ylide) with the transient and that is in turn characterized by a significant absorption in the region of interest. This "probe technique", initially introduced for the study of alkoxyl radicals and biradicals,[29−31] was adapted by Platz, Liu, and co-workers for the study of carbene reactions,[32−39] which used pyridine to trap carbenes by formation of easily detectable ylides.

In a study of the photodecomposition mechanism of α-diazonaphthoquinones, we[40] showed that pyridine, which was known to be a scavenger for carbenes, can also trap ketenes. Analogous results have been obtained in pyridine matrices, where ketene−pyridine ylides were detected by IR spectroscopy.[41,42] However, it is believed that only cyclic ketenes are able to produce UV-detectable ylides with pyridine.[43] Kresge and co-workers[44] have recently observed the formation of a pyridine ylide in aqueous solution from noncyclic ketenes. We note that the probe technique is not restricted only to the use of pyridine, since ketene ylides with various amines have been observed.[45]

In this work we report a laser flash photolytic study of 2-diazo-1,3-diphenyl-1,3-propanedione (**DBD**) with the purpose of analyzing its photochemical behavior in the presence of suitable probe molecules.

DBD was prepared from dibenzoylmethane/tosyl azide in ether according to Regitz et al.[46] Adamantanethione (tested as a possible carbene scavenger)[47] was synthesized as in earlier reports.[48]

The absorption spectra (Figure 1) of the diazo compound in acetonitrile exhibits a main peak at 254 nm (log $\epsilon = 4.4$). A weak shoulder can be observed at 370 nm (log $\epsilon = 2.2$).

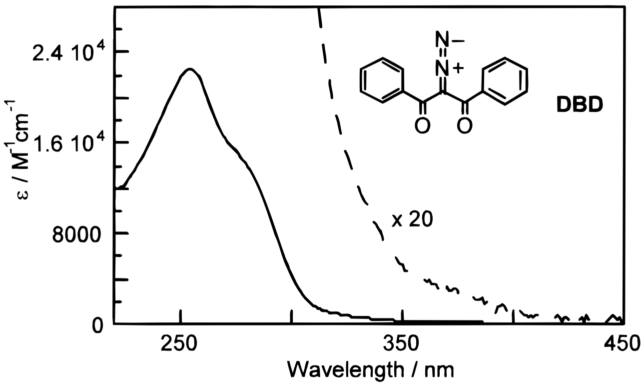

Figure 1. Ground-state absorption spectra of **DBD** and ×20 enlargement.

The transient absorption spectra[49] obtained by laser flash photolysis ($\lambda = 308$ nm) of **DBD** in an N_2-saturated acetonitrile are shown in Figure 2 at different delays after the laser pulse. They show a maximum in the UV region, at 360 nm, and a weaker broad band in the visible region. Kinetic analysis shows that two transients are present: the first one, with a lifetime of 15 μs, is responsible for the broad absorption from 340 to 700 nm and its first-order decay can be easily monitored at 420 nm (see inset of Figure 2). At 360 nm the kinetic trace can be fitted by a biexponential function which, apart from the transient mentioned above, shows another long-lived species. The lifetime of this second transient could not be measured directly, because of the weak ΔA; however its signal is stable over a 500 μs time scale (not shown). In an oxygen-saturated solution the lifetime of the first transient (420 nm) was reduced to about 100 ns, while the lifetime of the second, long-lived species (360 nm) was unchanged. The lack of any effect on transient lifetimes

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(49) For the nanosecond 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 laser 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 for laser experiments were 0.2−0.3 at the excitation 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 allow irradiation of a fresh portion of the sample by each laser shot.

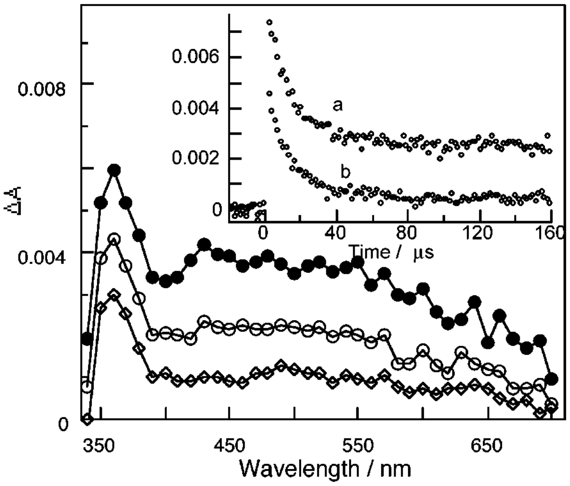

Figure 2. Transient absorption spectra obtained upon nanosecond laser flash photolysis of **DBD** in an N_2-saturated acetonitrile solution, recorded (●) 6.4 μs, (○) 17.6 μs, and (◊) 317 μs after the laser pulse. Inset: decay kinetics monitored at (a) 360 nm and (b) 420 nm; note that the weak residual observed at 420 nm is zero within the instrumental resolution.

in experiments with tetrabutylammonium chloride, a nucleophilic agent due to Cl^- anion, and tributylgermanium hydride, a hydrogen-donating radical scavenger,[50−52] allowed us to rule out the presence of cationic or radical species. Ketenes would not be expected to be quenched by oxygen in this short time scale.

To determine the nature of the transient which was affected by oxygen, we performed experiments with known triplet state quenchers: anthracene (energy of lowest triplet state: $E_T = 177$ kJ mol^{-1}),[53] 1,3-cycloxexadiene (219 kJ mol^{-1}),[53] and sorbic acid.[54] The rate constants for quenching by these species were all in the 10^9−10^{10} M^{-1} s^{-1} range (Table 1), thus indicating that the 15 μs transient may be assigned to the triplet state of the molecule. Although this represents very unusual behavior for a diazo compound,[2−4] it is consistent with the quantum yield of photoinduced N_2 extrusion from 2-diazo-1,3-diphenyl-1,3-propanedione, reported as 0.31,[55] that is, lower than for most other diazo compounds.[55] Clearly, there is a competition between nitrogen loss and formation of the triplet state.

Table 1. Effects of Different Quenchers on Lifetime of the Triplet State Observed upon Laser Flash Photolysis of **DBD** in an N_2-Saturated Solution

quencher	k_q (M^{-1} s^{-1})
oxygen	2.0×10^9
anthracene	1.2×10^{10}
1,3-cyclohexadiene	2.3×10^9
sorbic acid	2.5×10^9

As previously mentioned, a direct kinetic analysis of the long-lived transient, absorbing at >360 nm was not possible because of the weak transient absorption. A series of experiments suggests that this species is the ketene, formed via the Wolff rearrangement from the carbene. In the photolysis of α-diazonaphthoquinones,[56] a transient absorbing at 335 nm has also been assigned to the ketene.

Ketenes have been proposed as intermediates in the photolysis of 2-diazo-1,3-dicarbonyl compounds[57] and **DBD**.[58,59] Further, Lusztyk and co-workers[60] studied **DBD** in acetonitrile by means of 308 nm laser flash photolysis and observed the ketene by time-resolved IR detection. They also found that the signal assigned to the stretching of the ketene moiety is quenched by addition of various amines. To confirm that the long-lived transient observed in our laser flash photolysis experiment is the ketene, we carried out a series of experiments employing the same amines used by Lusztyk et al.[60] We note that we could not monitor any ylide formation upon addition of pyridine (up to a 2.2 M concentration). This confirms that pyridine ylide formation is usually found for compounds that form cyclic ketene, but typically not for noncyclic ketenes.[43] In contrast, when other primary and secondary amines such as diethylamine, benzylamine, *n*-butylamine, isopropylamine, and piperidine were added, easily detectable ylides could be observed, all of them characterized by a strong maxima at 310 nm. The transient absorption spectra obtained upon nanosecond laser flash photolysis of **DBD** in an N_2-saturated acetonitrile solution in the presence of 5.3×10^{-3} M diethylamine and 6×10^{-3} M piperidine are shown in Figures 3 and 4, respectively.

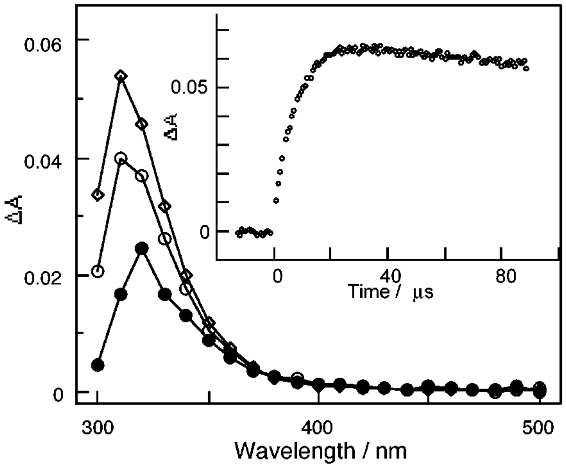

Figure 3. Transient absorption spectra obtained upon nanosecond laser flash photolysis of **DBD** in an N_2-saturated acetonitrile solution in the presence of 5.3×10^{-3} M diethylamine, recorded (●) 3.2 μs, (○) 9.6 μs, and (◊) 80 μs after the laser pulse. Inset: kinetic trace monitored at 310 nm.

The rise time for the growth of the ylide signal and its ΔA are dependent on the concentration of amine; by plotting the

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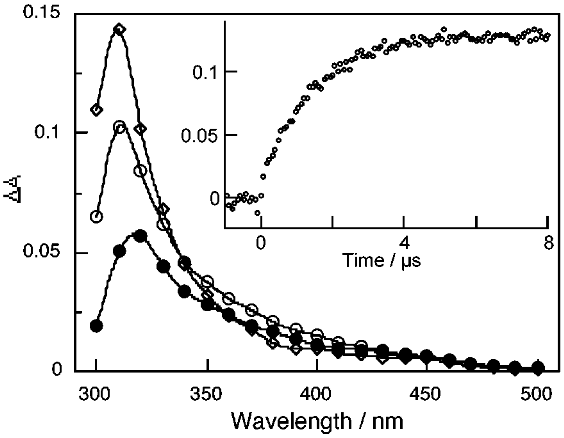


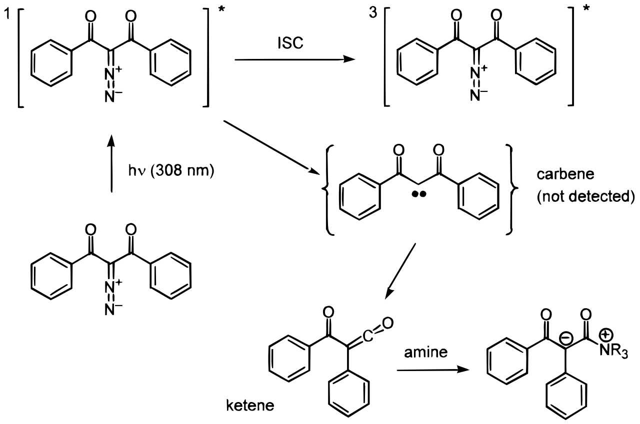
Figure 4. Transient absorption spectra obtained upon nanosecond laser flash photolysis of **DBD** in an N_2-saturated acetonitrile solution in the presence of 6×10^{-3} M piperidine, recorded (●) 0.2 μs, (○) 2 μs, and (◇) 8 μs after the laser pulse. Inset: kinetic trace monitored at 310 nm.

rate constant for the growth against the amine concentration, the rate constant for bimolecular interaction between the long-lived transient and the amine can be obtained. To avoid competitive reaction of the triplet state with the amines, 10^{-3} M 1,3-cyclohexadiene was added. Under these conditions, the decay lifetime of the triplet state was reduced to less than 100 ns. The rate constant values measured for quenching by the various amines are reported in Table 2: they are in good agreement with those obtained by Lusztyk et al. by means of time-resolved IR detection.[45,60] Another piece of information that can be typically obtained from these quenching experiments is the “natural” lifetime of the transient in absence of quencher, which can be evaluated by the intercept of the quenching plot. In our case the intercepts of the plots were usually very close to zero, suggesting a very long-lived transient. However, in some cases, for the lowest concentration of amine used, we could measure rise times of 3−6 ms, thereby indicating that the transient lifetime is at least a few milliseconds. This is consistent with the direct measurement at 360 nm, where the weak signal is stable over a 500 μs/div. time scale, and it is in agreement with the conclusion by Lusztyk and co-workers, who could only estimate for the ketene a lifetime “greater than 500 μs”. Therefore, all these results allow us to conclude that the long-lived transient with a maximum at 360 nm is the ketene, presumably formed by Wolff rearrangement of a very short-lived carbene (Scheme 1).

Table 2, Rate Constant for Ketene−Amine Ylide Formation, Observed upon Laser Flash Photolysis of **DBD** in an N_2-Saturated Solution

amine	k_q ($M^{-1}\ s^{-1}$)
pyridine	no ylide detected
diethylamine	2.4×10^7
benzylamine	1.8×10^7
n-butylamine	3.9×10^7
isopropylamine	1.0×10^7
piperidine	4.6×10^7

Scheme 1



In conclusion, the photolysis of **DBD** leads to two distinct pathways. Surprisingly, the excited singlet decays by a competition of nitrogen loss and intersystem crossing to populate the triplet state. Triplet state formation is a very unusual process for a diazo compound, as it is probably made possible by delocalization involving the carbonyl groups; there appears to be no loss of nitrogen from this species, since the long-lived ketene does not build up during triplet decay.

In addition to intersystem crossing, the singlet also forms a ketene that has been observed as a long-lived intermediate. The probe technique allowed us to monitor the absorption spectra and the kinetic behavior of the ylides formed upon interaction of this transient with various amines. The photolysis of the diazo compound is likely to occur by nitrogen extrusion from the singlet state and formation of a carbene, which rapidly undergoes Wolff rearrangement to the ketene.

Acknowledgment. J.C.S. thanks the Natural Sciences and Engineering Research Council of Canada for support and the Instituto de Tecnología Química (Valencia) where this article was written while J.C.S. was a guest under the auspices (Grant SAB1998-0121) of the Ministerio de Educación y Ciencia (Spain).

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