ORGANIC LETTERS

2006
Vol. 8, No. 8
1637−1640

Ultrafast Study of the Photochemistry of 2-Azidonitrobenzene

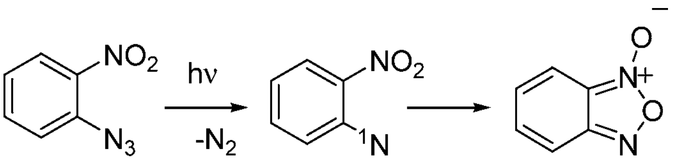
Ryan D. McCulla,[†] Gotard Burdzinski,[‡] and Matthew S. Platz*,[†]

Department of Chemistry, The Ohio State University, 1118 Newman-Wolfrom,
100 West 18th Avenue, Columbus, Ohio 43210, and Quantum Electronics Laboratory,
Faculty of Physics, Adam Mickiewicz University, 85 Umultowska,
Poznan 61−614, Poland

platz.1@osu.edu

Received January 27, 2006

ABSTRACT



1 **1N** **2**

Ultrafast time-resolved studies of the photochemistry of 2-azidonitrobenzene demonstrate that the lifetimes of excited singlet 2-azidonitrobenzene and 2-nitrophenylnitrene are 500 fs and 8.3 ps, respectively, in solution at ambient temperature. The singlet nitrene is a discrete intermediate but is too short lived to undergo bimolecular reactions.

Photolysis of 2-substituted aryl azides often produces cyclized products in excellent yields.[1] Singlet aryl nitrenes are thought to be intermediates in these transformations, but if they exist, they are generally too short lived for bimolecular chemical trapping reactions or for direct observation by nanosecond time-resolved spectroscopy. For example, thermolysis or photolysis of 2-azidonitrobenzene **1** leads cleanly to benzofuroxan **2** and the hypothetical nitrene intermediate **1N** has never been intercepted by an external trap.[2] In fact, recent computational studies[2f] support earlier assertions made from experiment[2d,e] that the pyrolysis of **1** produces **2** by a concerted one-step mechanism.[3] The photolysis of **1** yields **2**, but we conclude this occurs through a stepwise mechanism.

The putative nitrene intermediate, 2-nitrophenylnitrene **1N**, has been studied in its triplet ground state by spectroscopy of ^{3}**1N** inmobilized in a cryogenic matrix.[4] The formation of 1,2-dinitrosobenzene has also been observed by matrix spectroscopy.[4] However, we are not aware of any prior studies of **1N** employing time-resolved techniques in solution. This has prompted an analysis of the photochemistry of **1** using UV−vis transient absorption spectroscopy with nanosecond, picosecond, and femtosecond time resolution. Herein, we report that the singlet nitrene is a discrete intermediate, but its lifetime is too short to allow its capture in bimolecular reactions.

The azide, 2-azidonitrobenzene **1**, was prepared as previously reported.[5] The photochemistry of **1** has been reported in the literature and revealed that the exclusive stable product of these reactions was benzofuroxan **2**.[2] To confirm these findings, characterization by HPLC[6] of the photoproducts resulting from the irradiation of **1** (1.6 mM) in acetonitrile

---

[†] The Ohio State University.
[‡] Adam Mickiewicz University.

(1) Smith, P. A. S. *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: New York, 1984; p 95.

(2) (a) Purvis, R.; Smalley, R. K.; Suschitzky, H.; Alkhader, M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 249. (b) Tsunoda, T.; Yamaoka, T.; Ikari, K. *Kogyo Kagaku Zasshi* **1969**, *72*, 156. (c) Efimov, S. P.; Smirnov, V. A.; Pochinok, A. V. *Khim. Vys. Ener.* **1983**, *17*, 445. (d) Dyall, L. K. *Aust. J. Chem.* **1975**, *28*, 2147. (e) Dyall, L. K.; Kemp, J. E. *J. Chem. Soc. B* **1968**, *9*, 976. (f) Rahut, G.; Eckert, F. *J. Phys. Chem. A* **1999**, *103*, 9086.

(3) Dyall, L. K. *Aust. J. Chem.* **1975**, *28*, 8, 2147.

(4) (a) Takayama, T.; Kawano, M.; Uekusa, H.; Ohashi, Y.; Sugawara, T. *Helv. Chim. Acta* **2003**, *86*, 1352. (b) Murata, S.; Tomioka, H. *Chem. Lett.* **1992**, 57. (c) Dunkin, I. R.; Lynch, M. A.; Boulton, A. J.; Henderson, N. *J. Chem. Soc., Chem. Commun.* **1991**, 1178.

(5) Kauer, J. C.; Carboni, R. A. *J. Am. Chem. Soc.* **1967**, *89*, 2633.

10.1021/ol0602452 CCC: $33.50

by low-pressure mercury lamps shows that the only photoproduct is **2** at both low (<5%) and high (>90%) conversion of starting material in agreement with previous reports.

Transient UV−vis absorption spectra were obtained at different times after the laser pulse using two separate laser flash photolysis systems. Ultrafast processes were monitored on a femtosecond UV−vis transient absorption spectrometer, which will be described in an upcoming full paper. Longer time-scale events were accessed using a nanosecond UV−vis transient absorption spectrometer operating in kinetic (PMT) or spectral (ICCD) mode.[7]

Transient UV−vis absorption spectra were first obtained using the nanosecond time-resolved laser flash photolysis instrument. A deoxygenated solution of **1** in acetonitrile (0.14 mM) was excited at 308 nm. A fast growth signal, monitored at 360 nm, appeared within the laser pulse and showed no decay over the entire observation window of 50 μs. Transient absorption spectra recorded 100 ns after the laser pulse reveal a broad absorption centered at 355 nm. This absorption spectrum was attributed to benzofuroxan **2** because of a high correlation with the steady-state UV spectrum of **2**, as shown in Figure 1. Consistent with this assignment was the observation that the signal was not quenched by the addition of diethylamine, which traps azirines, ketenimines, and singlet nitrenes but has very limited reactivity with **2**.[8]

To provide temporal information on the fast growth process, the femtosecond transient absorption technique was utilized. Femtosecond time-resolved transient absorption spectra were recorded within a time window from −1 ps to 1 ns following 273 nm excitation of **1** in acetonitrile. Figure 2 shows the data obtained in the 360 to 660 nm spectral range over a time range between 0.2 and 50 ps. A transient absorption band was observed promptly with a maximum at 420 nm. The transient absorption shifts to 360 nm over 50 ps. A kinetic trace recorded at 420 nm has two time constants of 400 fs and 8.3 ps as shown in Figure 3 (top). We have recently reported that the excited states of 2- and 4-azidobiphenyl have lifetimes of 450 and 100 fs, respectively.[9] For this reason, the time constant of 400 fs is assigned to the decay of the excited singlet state of azide **1**. The 8.3 ps process is attributed to the disappearance of an intermediate whose identity will be discussed shortly.

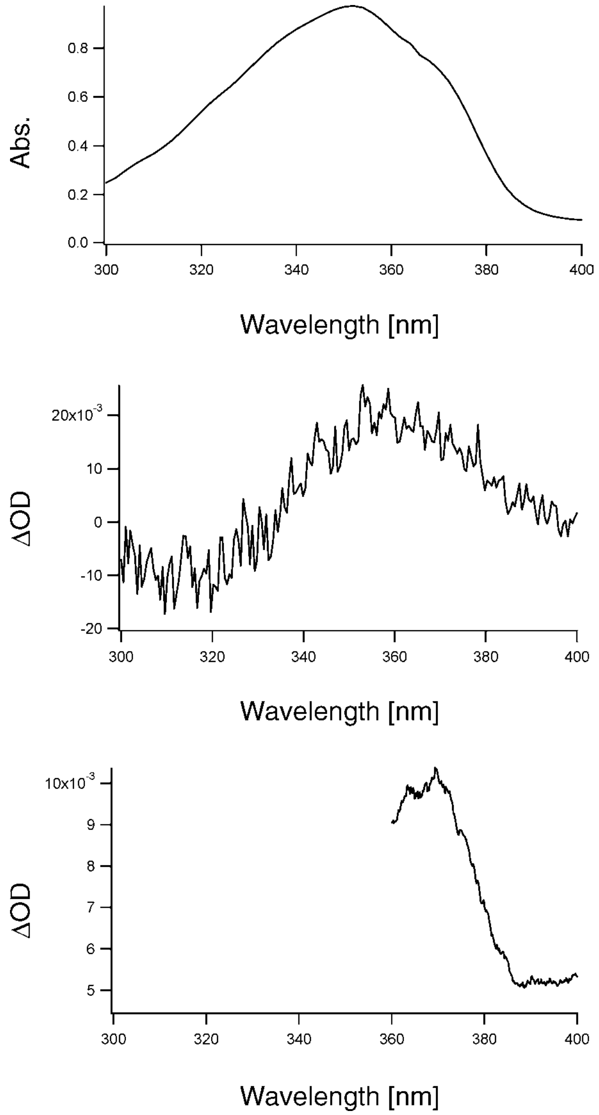


Figure 1. (top) Steady-state UV spectrum of **2**. (middle) Transient spectrum produced by nanosecond LFP (308 nm) of **1** in deoxygenated acetonitrile solution recorded 100 ns after the laser pulse. (bottom) The transient spectrum observed 1 ns after the femtosecond laser photolysis (273 nm) of **1** in acetonitrile.

In an attempt to better deconvolute the time constants, a kinetic trace was recorded at 520 nm. Once again, a single exponential fit of the decay trace was not possible. A greater proportion of the signal at 520 nm can now be attributed to the shorter time constant, relative to 420 nm, and the fit of the kinetic data at 520 nm is shown in Figure 3 (bottom). The shorter time constant is now 620 fs, when the longer time constant was fixed at 8.3 ps, which is again assigned to the excited singlet state of the azide. Thus, a reasonable estimate of the excited singlet azide lifetime is ~500 fs. The excited singlet biphenyl azides absorb broadly (400−550 nm) in the visible region.[9] Thus, transient absorption of the singlet excited state of 2-azidonitrobenzene at 420 nm seems reasonable.

The identity of the intermediate that gives rise to the longer time constant of 8.3 ps was investigated by time-dependent density functional (TD-DFT) calculations using the Gaussian03 suite of programs.[10] The geometries of the triplet, open-shell singlet, and closed-shell singlet of **1N** were optimized at the UB3LYP/6-311+G(d,p) level of theory. The triplet was found to be the ground state being 12.5 kcal/mol lower in energy than the open-shell singlet which was the lowest energy singlet by 20.4 kcal/mol. The UV−vis spectra of the

---

(6) A Beckman−Coulter System Gold HPLC, fitted with a 126 Sovlent Module and a 168 Detector, was used for HPLC chromatographs. An elutant mixture of 4:1 hexane/ethyl acetate through an IBM silca column was used for all chromatographic separations.

(7) (a) Gritsan, N. P.; Zhai, H. B.; Yuzawa, T.; Karweik, D.; Brooke, J.; Platz, M. S. *J. Phys. Chem.* **1997**, *101*, 2833.

(8) Latham, D. W. S.; Meth-Cohn, O.; Suschitzky, H. *Tetrahedron Lett.* **1972**, 5365.

(9) Burdzinski, G. T.; Gustafson, T. L.; Hackett, J. C.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 13764.

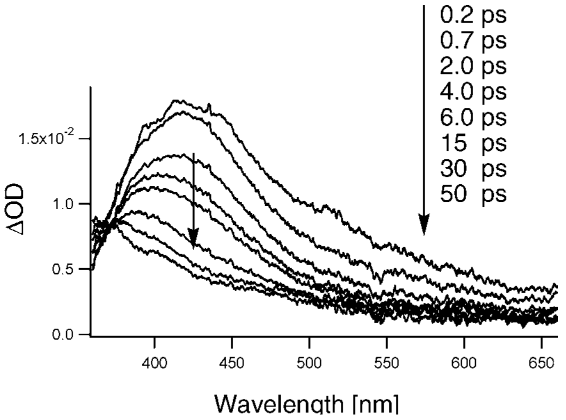


Figure 2. Transient absorption spectra recorded from 0.2 to 50 ps after the photoexcitation (273 nm) of **1** in acetonitrile.

three states were estimated using TD-DFT calculations at the same level of theory. In the experimental spectral window, the strongest predicted transitions will be at 376, 393, and 444 nm for the triplet, the closed-shell singlet, and the open-shell singlet nitrene, respectively. Singlet aryl nitrenes often have absorption bands with maxima ranging from 320 to 410 nm.[11] Ortho-substituted aryl nitrenes have bands that are red-shifted compared to the isomeric meta- and para-substituted aryl nitrenes, and nitro-substituted aromatics have even further red-shifted absorption bands (e.g., nitrobenzene which has λ_{max} of 252 nm compared to 180 nm for benzene).[12] Considering the computational results and the related experimental data, it seems reasonable to expect that the singlet **1N** absorption maximum will be between 380 and 450 nm.

The excited singlet azide and singlet nitrene are expected to contribute to the kinetic trace measured at 420 nm, and this is consistent with the observed biexponential decay. Therefore, the intermediate associated with the 8.3 ps time constant is assigned to the open-shell singlet of **1N**. This conclusion is fortified by the observation that singlet 2-biphenylnitrene, which can undergo an intramolecular ring closure to form carbazole, has a similar lifetime in solution of 16 ps.[9] The lifetime of nitrene **1N** is 8.3 ps, which corresponds to a decay (ring closure) rate constant of 1.2 × 10^{11} s^{-1}. This rate constant is at least an order of magnitude faster than the diffusion controlled rate constant for bimolecular reactions in the least viscous solvents. Thus, this nitrene cannot be efficiently intercepted by a bimolecular trapping reaction.

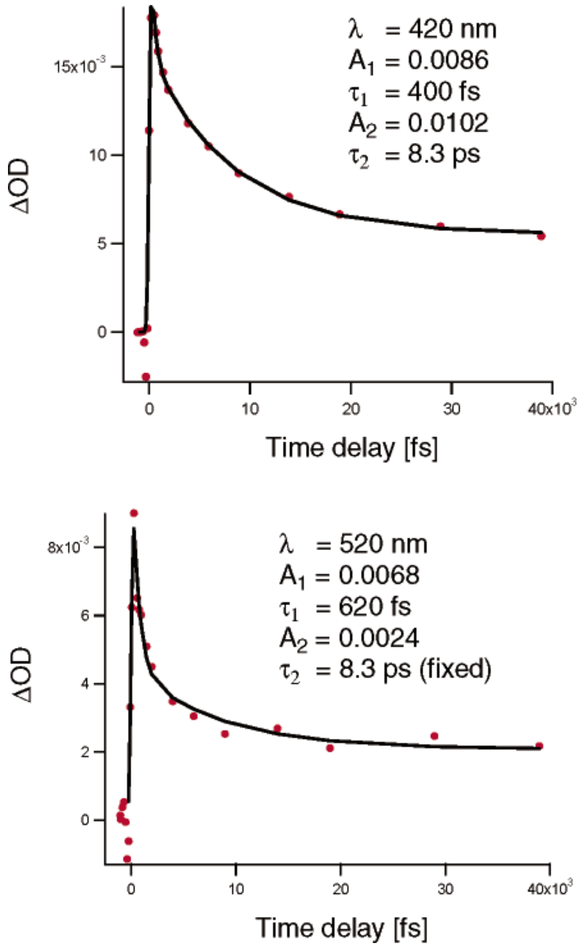


Figure 3. Time-resolved transient absorption measurements in acetonitrile after photoexcitation (273 nm) of **1**. (top) Transient absorption decay recorded at 420 nm. (bottom) Transient absorption decay recorded at 520 nm. The solid curves are nonlinear least-squares fits to the experimental points (instrument response function of 350 fs).

It should be noted that singlet 4-biphenylnitrene[9] and a dichloro derivative[13] both undergo vibrational cooling in acetonitrile with a time constant of 11 ps. Population loss of singlet 2-nitrophenylnitrene proceeds on the same time scale as vibrational cooling, and thus, we may actually be monitoring the decay of vibrationally excited rather than thermally relaxed singlet 2-nitrophenylnitrene.

We conclude that the transient spectrum recorded 200 fs after the laser pulse is due to a mixture of the azide singlet

---

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

(11) (a) Tsao, M.; Gritsan, N.; James, T. R.; Platz, M. S.; Hrovat, D. A.; Thatcher Borden, W. *J. Am. Chem. Soc.* **2003**, *125*, 9343. (b) Gritsan, N. P.; Platz, M. S. *Adv. Phys. Org. Chem.* **2001**, *36*, 255.

(12) (a) Romand, J.; Vodar, B. *Compt. Rend.* **1951**, *233*, 930−932. (b) Grammaticakis, P. *Bull. Soc. Chim. Fr.* **1950**, *17*, 158−166.

(13) Gritsan, N. P.; Polshakov, D. A.; Tsao, M. L.; Platz, M. S. *Photochem. Photobio. Sci.* **2005**, *4*, 23.

excited state (major) and the singlet nitrene (minor). The spectrum recorded 2 ps after the laser pulse is due in very large part to the singlet nitrene (Figure 2) with a small contribution from benzofuroxan **2** below 400 nm. The transient absorption recorded 1 ns after the laser pulse is shown in Figure 1, and although the available spectral window truncates much of the absorption band, the observed spectrum does correlate with that of heterocycle **2**. The lack of absorption past 400 nm indicates that the nitrene has completely reacted within 1 ns, presumably, to form benzofuroxan **2**.

In summary, femtosecond time-resolved data on the photolysis of **1** are reported. The photolysis of **1** yields **2** in the following stepwise mechanism. The photoexcited singlet state of the azide, which has a lifetime of 500 fs, extrudes nitrogen to form singlet nitrene **1N**. The lifetime of **1N** is 8.3 ps, and **1N** cleanly undergoes ring closure to form **2**.

Acknowledgment. Support of this work by the National Science Foundation, the Ohio State University Center for Chemical and Biophysical Dynamics, and the Ohio Supercomputing Center is gratefully acknowledged.

Supporting Information Available: Optimized geometries, energies, zero-point corrections, and TD-DFT UV spectra of the triplet, closed-shell singlet, and open-shell singlet of **1N** can be found in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0602452