

Photogenerated Diarylnitrenium Ions: Laser Flash Photolysis and Product Studies on Diphenylnitrenium Ion Generated from Photolysis of 1-(*N,N*-Diphenylamino)pyridinium Ions

Ricardo J. Moran and Daniel E. Falvey*

Department of Chemistry and Biochemistry
University of Maryland
College Park, Maryland 20742

Received April 2, 1996

It has recently become possible to study nitrenium ions $[R-N-R']^{+1-3}$ using laser flash photolysis (LFP) methods. These experiments have provided valuable new information about the lifetimes of monoarylnitrenium ions in aqueous media,⁴ the roles of the singlet and triplet states in determining their chemical behavior,⁵ and the acid–base properties of primary arylnitrenium ions.^{6,7} One objective of our efforts has been to generate and characterize diphenylnitrenium ion (Ph_2N^+). This species is of interest for two reasons. First, it is the simplest example of the diarylnitrenium ions, a structural type that could not be accessed by previously reported LFP methods.⁸ Second, the isoelectronic counterparts of Ph_2N^+ , diphenylcarbene (Ph_2C),^{9–11} and diphenylcarbenium ion (Ph_2CH^+)^{12–14} have been the subject of intensive spectroscopic and kinetic research efforts over the past two decades. Similar information for Ph_2N^+ is desirable as it would permit meaningful comparisons between nitrenium ions and these other, more familiar, types of intermediates.

The currently available methods for LFP studies of nitrenium ions possess limitations either in the structures of the nitrenium ions that can be accessed and/or in the solvent media than must be employed.^{4,6,7,15} However, recently Abramovitch¹⁶ and Takeuchi¹⁷ reported generation and trapping of various nitrenium ions through the photolysis of *N*-aminopyridinium ions (e.g., **1**). This seemed an attractive alternative to the previous methods because with the pyridinium salts there is no inherent limitation to the types of nitrenium ions that can be generated. Indeed, these earlier studies reported generation and chemical trapping

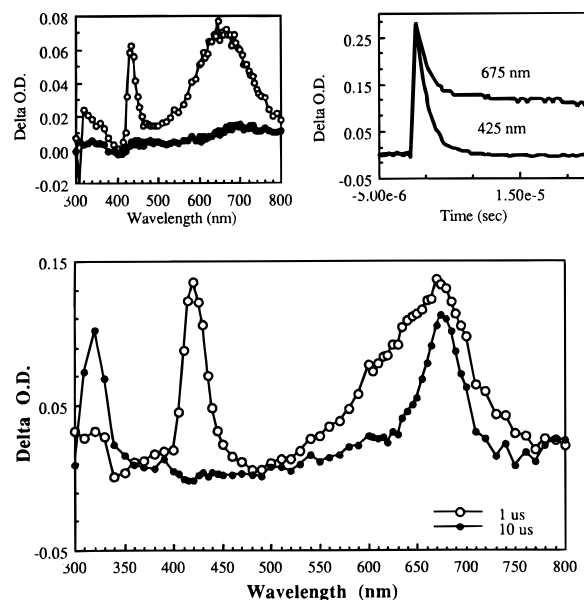


Figure 1. Transient absorption spectra obtained from pulsed laser (308 nm, 10 ns, 40–50 mJ/pulse) photolysis of *N*-(diphenylamino)pyridinium ion **1** in N_2 -purged CH_3CN containing 0.012 M CF_3CO_2H . Upper right panel shows the kinetic traces at 425 and 675 nm. Upper left panel shows the same transient spectra where the sample is 0.10 M in TMDD, the triplet state quencher. Spectra are taken at 1 μs (open symbols) and 10 μs (filled symbols) after the laser pulse.

of nitrenium ions as diverse as NH_2^+ ¹⁷ and the diacylnitrenium ion derived from phthalimide.^{16,18} Reported herein are product and LFP studies on the photochemistry of 1-(*N,N*-diphenylamino)-2,4,6-trimethylpyridinium tetrafluoroborate (**1**).

Photolysis of the pyridinium salt **1** gives stable products that would be expected from a diarylnitrenium ion intermediate. With the monoarylnitrenium ions, it had been shown that nucleophiles such as Cl^- or CH_3OH trap singlet-state nitrenium ions by attacking the aromatic ring.^{19–22} H atom donors such as 1,4-cyclohexadiene (CHD) scavenge triplet-state arylnitrenium ions through sequential H atom transfers, ultimately giving the parent amine.^{5,15} Photolysis of CH_3CN solutions containing **1**, Cl^- , and CHD gives *N*-phenyl-4-chloroaniline **3a** and its 2-chloro isomer **3b** in ca. 75% combined yield along with 11% of Ph_2NH **4**. Photolysis of **1** in neat CH_3OH also gives the expected ring adduct, *N*-phenyl-4-methoxyaniline **5** (58%), along with the triplet product, Ph_2NH (18%).

Laser flash photolysis (308 nm, 10 ns, 50 mJ) of **1** in CH_3CN containing 0.042 M CF_3CO_2H ²³ gives the transient absorption spectra shown in Figure 1. Following the excitation laser pulse, transient absorption bands at 425 and 600–700 nm are observed. The 425 nm signal decays with a first order lifetime of 1.5 μs in CH_3CN . In the high-wavelength region, there is a broad absorption band that also decays with a 1.5 μs lifetime

(18) Abramovitch, R. A.; Beckert, J. M.; Chinnasamy, P.; Xiaohua, H.; Pennington, W.; Sanjivamurthy, A. R. V. *Heterocycles* **1989**, *28*, 623–628.

(19) Gassman, P. G.; Campbell, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 3891–3896.

(20) Novak, M.; Pelecanou, M.; Roy, A. K.; Andronico, A. F.; Plourde, F.; Olefirowicz, T. M.; Curtin, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 5623–5631.

(21) Gassman, P. G.; Campbell, G. A.; Frederick, R. C. *J. Am. Chem. Soc.* **1972**, *94*, 3884–3891.

(22) Fishbein, J. C.; McClelland, R. A. *J. Chem. Soc., Perkin Trans. 2* **1995**, 663–671.

(23) In the absence of acid, the signals in the 600–700 nm region are complicated. It appears that the pyridine leaving group deprotonates Ph_2NH^+ giving a mixture of the latter and Ph_2N^+ , which also has a broad absorption in this region. The singlet nitrenium ion signal at 425 nm is not noticeably affected by the acid. A more complete analysis of this issue will be presented in the full paper.

(1) Abramovitch, R. A.; Jeyaraman, R. In *Azides and Nitrenes: Reactivity and Utility*; Scriven, E. F. V., Ed.; Academic: Orlando, FL, 1984; pp 297–357.

(2) Simonova, T. P.; Nefedov, V. D.; Toropova, M. A.; Kirillov, N. F. *Russ. Chem. Rev.* **1992**, *61*, 584–599.

(3) Heller, H. E.; Hughes, E. D.; Ingold, C. K. *Nature* **1951**, *168*, 909–910.

(4) Davidse, P. A.; Kahley, M. J.; McClelland, R. A.; Novak, M. *J. Am. Chem. Soc.* **1994**, *116*, 4513–4514.

(5) Srivastava, S.; Falvey, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 10186–10193.

(6) McClelland, R. A.; Kahley, M. J.; Davidse, P. A.; Hadzialic, G. J. *J. Am. Chem. Soc.* **1996**, *118*, 4794–4803.

(7) McClelland, R. A.; Davidse, P. A.; Hadzialic, G. J. *J. Am. Chem. Soc.* **1995**, *117*, 4173–4174.

(8) Certain highly stabilized diarylnitrenium ions have been detected as intermediates in the electrochemical oxidation of substituted diarylamine. For example: Serve, D. *J. Am. Chem. Soc.* **1975**, *97*, 432–434.

(9) Eisenthal, K. B.; Turro, N. J.; Sitzmann, E. V.; Gould, I. R.; Hefferon, G.; Langan, J.; Cha, Y. *Tetrahedron* **1985**, *41*, 1543–1545.

(10) Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, *22*, 311–361.

(11) Platz, M. S.; Maloney, V. M. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; M. S. Platz, Ed.; Plenum: New York, 1990; pp 239–352.

(12) Dorfman, L.; Sujdak, R. J.; Bockrath, B. *Acc. Chem. Res.* **1976**, *9*, 352–357.

(13) Belt, S. T.; Bohne, C.; Charette, G.; Sugamori, S. E.; Scaiano, J. C. *J. Am. Chem. Soc.* **1993**, *115*, 2200–2205.

(14) Bartl, J.; Steenken, S.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 7710–7716.

(15) Anderson, G. B.; Yang, L. L.-N.; Falvey, D. E. *J. Am. Chem. Soc.* **1993**, *115*, 7254–7262.

(16) Abramovitch, R. A.; Shi, Q. *Heterocycles* **1994**, *37*, 1463–1466.

(17) Takeuchi, H.; Hayakawa, S.; Tanahashi, T.; Kobayashi, A.; Adachi, T.; Higuchi, D. *J. Chem. Soc., Perkin Trans. 2* **1991**, 847–855.

Table 1. Second-Order Rate Constants (k_{nuc}) Obtained from Decay of Transient Absorptions at 425 nm Produced by Laser Flash Photolysis of **1a** in CH_3CN with Added Nucleophiles

nucleophile	k_{nuc} ($\text{M}^{-1}\text{s}^{-1}$)
Cl^- ^a	1.0×10^{10}
MeOH	5.2×10^6
EtOH	4.9×10^6
H_2O	6.1×10^5

^a The Cl^- source is $\text{nBu}_4\text{NCl} \cdot \text{H}_2\text{O}$.

to give longer-lived bands at 680 and 325 nm. The long-lived peaks are assigned to the diphenylamine cation radical ($\text{Ph}_2\text{NH}^{\bullet+}$) by comparison to literature spectra.^{24–26} Further confirmation of this assignment was achieved through independent generation of $\text{Ph}_2\text{NH}^{\bullet+}$ by photolysis of Ph_2NH in the presence of 1,4-dicyanobenzene, a single electron acceptor (see supporting information).

The short-lived species that absorbs at 425 and at 660 nm is assigned to the singlet diphenylnitrenium ion, $^1(\text{Ph}_2\text{N}^+)$ on the basis of the following observations.

(1) Photolysis of **1** gives stable products that are consistent with formation of a singlet arylnitrenium ion intermediate. Significantly, high yields of ring adducts (**3** and **5**) are observed when the photolysis is done in the presence of nucleophiles.

(2) The short-lived transient species is quenched by nucleophiles. The decay rate constants at 425 nm (k_{obs}) were measured at various nucleophile concentrations. A pseudo-first-order analysis provides the second-order rate constants (k_{nuc}) presented in Table 1. The k_{nuc} values of 10^5 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ fall in the range expected for a nitrenium ion. Moreover, the order of reactivity $\text{Cl}^- > \text{MeOH} > \text{EtOH} > \text{H}_2\text{O}$ follows that observed for arylcarbenium ions^{14,27} and monoarylnitrenium ions.²⁸

(3) Competitive trapping experiments provide relative rate constants that agree with those from LFP. Pyridinium ion **1** was irradiated in the presence of both MeOH and EtOH. The ratio of adducts was determined by ^1H NMR. After correcting for the concentrations of the traps, a ratio of $k_{\text{MeOH}}/k_{\text{EtOH}} = 1.26$ was determined. This is in reasonable agreement with the LFP ratio of $k_{\text{MeOH}}/k_{\text{EtOH}} = 1.05$ considering the uncertainties associated with NMR peak integration.

(4) The lifetime of the transient species is unaffected by the addition of O_2 , a quencher of excited triplet states.²⁹ This excludes the possibility that the transient is due to the excited triplet state of the pyridinium ion. Also, the transient spectra are not solvent-specific. Essentially the same spectra are detected in CH_2Cl_2 and in CH_3CN . This argues against assignment to a nitrile ylide such as have been observed with carbenes in CH_3CN .³⁰

(5) Finally, the lifetime of the short-lived species is unaffected by the addition of an H-atom donor, $(\text{Me}_3\text{Si})_3\text{SiH}$. The triplet state of Ph_2N^+ is ruled out for this reason.⁵ It also should be noted that electronic structure calculations generally predict singlet ground states for simple arylnitrenium ions.^{31–34} In contrast, the diarylcarbenes are typically ground state triplets.^{9–11}

(24) Weir, D.; Scaiano, J. C.; Schuster, D. I. *Can. J. Chem.* **1988**, *66*, 2595–2600.

(25) Scheerer, R.; Grätzel, M. *J. Am. Chem. Soc.* **1977**, *99*, 865–871.

(26) Shida, T.; Hamill, W. H. *J. Chem. Phys.* **1966**, *44*, 2369–2374.

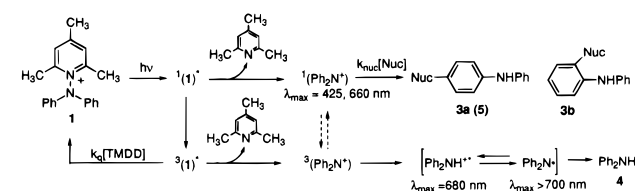
(27) Mayr, H.; Patz, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 938–957.

(28) Robbins, R. J.; Yang, L. L.-N.; Anderson, G. B.; Falvey, D. E. *J. Am. Chem. Soc.* **1995**, *117*, 6544–6552.

(29) Rosenthal, I. In *Singlet Oxygen*; Frimel, A. H., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. I, pp 13–35.

(30) Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198–202.

(31) Cramer, C. J.; Dulles, F. J.; Falvey, D. E. *J. Am. Chem. Soc.* **1994**, *116*, 9787–9788.

Scheme 1

We attribute the appearance of $\text{Ph}_2\text{NH}^{\bullet+}$ to a parallel triplet pathway illustrated in Scheme 1. The excited singlet state of the pyridinium precursor (**1**) partitions between heterolytic bond scission, yielding $^1(\text{Ph}_2\text{N}^+)$, and intersystem crossing, giving the excited triplet state of the precursor (**3**). The latter cleaves to give the triplet state nitrenium ion ($^3\text{Ph}_2\text{N}^+$) which in turn rapidly abstracts a H-atom (presumably from the solvent¹⁵) to give the cation radical $\text{Ph}_2\text{NH}^{\bullet+}$.⁵ This mechanism is supported by a triplet quenching experiment. Addition of TMDD (0.1 M), a triplet quencher,³⁵ to the LFP solutions suppresses the appearance of the $\text{Ph}_2\text{NH}^{\bullet+}$ band at 680 nm. This is illustrated in the upper left panel of Figure 1. In contrast, the lifetimes and positions of the bands assigned to $^1(\text{Ph}_2\text{N}^+)$ are unaffected by TMDD.

The reactivity of Ph_2N^+ toward alcohols is almost three orders of magnitude lower than that of the corresponding diarylcarbenium ion, Ph_2CH^+ .¹⁴ A similar effect has been noted by McClelland and Novak⁴ when *N*-acetyl-2-fluorenylnitrenium ion is compared to a carbenium ion analog. The lower reactivity of the nitrenium ions can be attributed to the different sites of attack. Nucleophiles attack the ring carbons of arylnitrenium ions, resulting in decreased aromaticity. In contrast, nucleophiles attack the exocyclic atom of arylcarbenium ions resulting in increased aromaticity (because the π -electron localization in the aromatic ring is increased in the transition state).

In summary, Ph_2N^+ has been generated through the photolysis of 1-(*N,N*-diphenylamino)-2,4,6-trimethylpyridinium ion **1**. Both its absorption spectrum and its rates of nucleophilic trapping have been characterized using LFP. In principle any type of nitrenium ion should be accessible through *N*-aminopyridinium ion photolysis.^{16,17,36,37} However, the practical limitations have yet to be explored. Future studies will examine the dynamics of singlet-triplet state interconversion for Ph_2N^+ as well as the applications of *N*-aminopyridinium ion photochemistry to the study of previously inaccessible classes of nitrenium ions.

Acknowledgment. We thank Profs. Rudolph A. Abramovitch and Christopher J. Cramer for helpful suggestions. This work was supported by the National Science Foundation. This paper is dedicated to Professor Gary B. Schuster on the occasion of his 50th birthday.

Supporting Information Available: Table of the product studies under various conditions and transient spectra of independently generated $\text{Ph}_2\text{NH}^{\bullet+}$ and from photolysis of **1** under neutral conditions (2 pages). See any current masthead page for ordering and Internet access instructions.

JA961086S

(32) Li, Y.; Abramovitch, R. A.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 2911–2914.

(33) Ford, G. P.; Scribner, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 4281–4291.

(34) Ford, G. P.; Herman, P. S. *J. Mol. Struct. (THEOCHEM)* **1991**, *236*, 269–282.

(35) Ullman, E. F.; Singh, P. *J. Am. Chem. Soc.* **1972**, *94*, 5077–5078.

(36) Abramovitch, R. A.; Evertz, K.; Huttner, G.; Gibson, H. H.; Weems, H. G. *J. Chem. Soc., Chem. Commun.* **1988**, 325–327.

(37) Takeuchi, H.; Higuchi, D.; Adachi, T. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1525–1529.