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An Ultrafast Study of Phenyl Azide: The Direct Observation of Phenylnitrenium Ion

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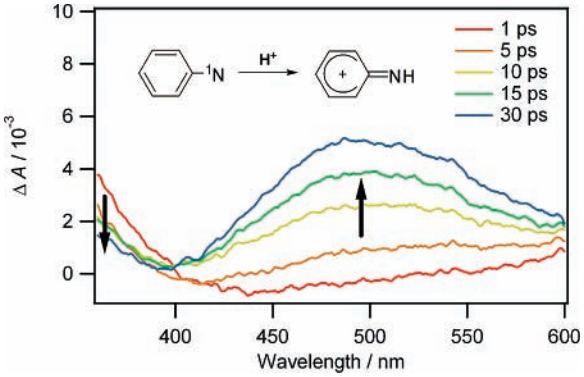
ABSTRACT



Ultrafast photolysis ($\lambda_{ex} = 308$ nm) of phenyl azide in 100% formic acid produces a broadly absorbing transient within the instrument time resolution (300 fs), which is assigned to an excited state of the azide. The azide excited state fragments within 300 fs to form singlet phenylnitrene. The decay of the nitrene ($\tau = 12.0$ ps) produces a new species with absorption centered at 500 nm, which is assigned to phenylnitrenium ion. The lifetime of phenylnitrenium ion is 110 ps in 100% formic acid. This is the first spectroscopic observation of phenylnitrenium ion.

Arylnitrenium ions are short-lived divalent reactive intermediates, which have been studied extensively due to their suspected roles in the carcinogenic activity of aryl amines.[1] In recent years, the groups of Falvey,[2] McClelland,[3] and Novak[4] have developed convenient photochemical precursors for studying the solution-phase chemistry of nitrenium ions. This has allowed the measurement of their lifetimes, the recording of their UV−vis and IR spectra, and the determination of their absolute reaction rate constants with selected nucleophiles in aqueous solution. Phenylnitrenium ion ($PhNH^+$) is the simplest arylnitrenium ion and has been investigated theoretically. Using density functional theory (DFT), Cramer et al. predicts that parent phenylnitrenium ion has a singlet ground state that is favored by 21.2 kcal/mol over the lowest energy triplet state.[5] In addition, a number of substituted arylnitrenium ions have been studied by laser flash photolysis (LFP) techniques with nanosecond

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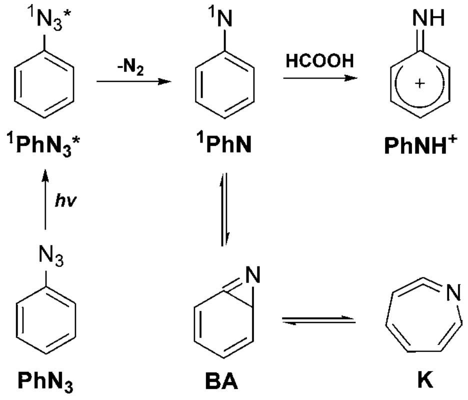
time-resolved UV−vis,[2,3] IR,[6] and Raman[7] spectroscopy. However, to our knowledge, spectroscopic features of the parent system $PhNH^+$ so far remain elusive. McClelland estimated the lifetime of $PhNH^+$ is 125−250 ps in aqueous solution based on an azide-trapping experiment.[8] The time resolution of conventional nanosecond laser flash photolysis (ns-LFP) system is not sufficient to observe such a short-lived reactive intermediate. Thus, ultrafast time-resolved spectroscopy is required to study $PhNH^+$ in solution.

Phenyl azide (PhN_3) is a convenient light-activated precursor of singlet phenylnitrene (^1PhN) which, as demonstrated by the McClelland group,[3] can be protonated to form $PhNH^+$ in acidic aqueous solution (Scheme 1). Unfortunately, upon photolysis of PhN_3 in acetonitrile or cyclohexane a polymeric tar is formed on the surface of the flow cell which prevents spectroscopic analysis. The tar is mainly formed by polymerization of the cyclic ketenimine (Scheme 1, K), which is produced by cyclization of ^1PhN ($\tau \sim 1$ ns) and subsequent rearrangement of benzazirine (BA).[9] In order to overcome tar formation, one needs to protonate ^1PhN very rapidly ($\tau < 1$ ns) and, as a result, depress the formation of K. Recently, we discovered that arylnitrenes protonate efficiently in 88% formic acid and that two very short-lived nitrenes, *o*-biphenylylnitrene and 1-naphthylnitrene, can be protonated in this solvent to form their corresponding nitrenium ions.[10] Herein, we extended this method to the parent system PhN_3 and are pleased to report the first spectroscopic observation of phenylnitrenium ion $PhNH^+$.

Scheme 1



Ultrafast photolysis[12] of phenyl azide (PhN_3) in 100% formic acid with a 300 fs pulse of 308 nm light results in the spectral changes shown in Figure 1. A broad transient absorption, centered at 520 nm, is detected at the earliest times observable (Figure 1a). Following our previous ultrafast studies on aryl azides,[13] the broad transient absorption is assigned to an excited state of phenyl azide ($^1PhN_3$*). Wirz and co-workers have reported picosecond time-resolved flash photolysis experiments performed in dichloromethane (DCM).[9b] The transient spectrum recorded 2 ps after the laser pulse has absorption maxima at 350 and 400 nm in DCM assigned to singlet phenyl nitrene and an excited-state of phenyl azide. We have repeated this experiment in acetonitrile (ACN) containing 1 M diethyl amine to scavenge ketenimine K and prevent tar formation.[14] The results are given in the Supporting Information (Figure S2). Although this experiment suffers from two-photon absorption by the solvent and related artifacts for the first picosecond after the laser pulse, it is clear that no transient abosrption forms

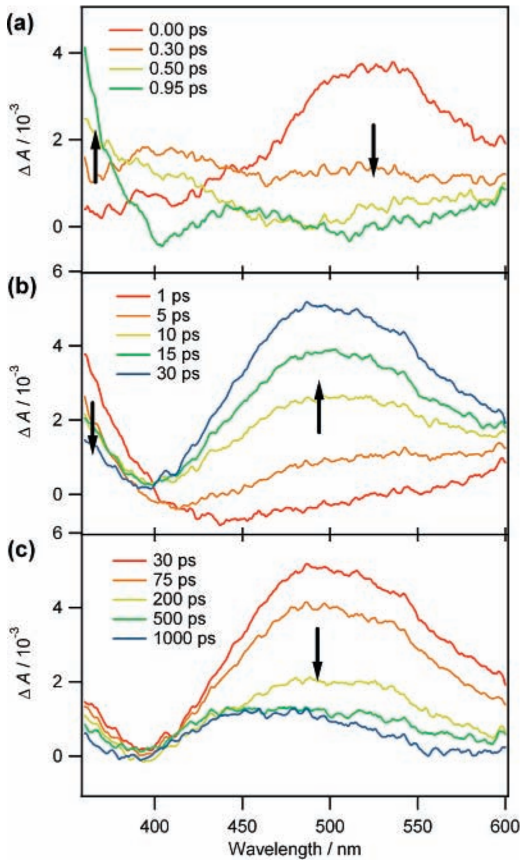


Figure 1. Transient spectra were generated by ultrafast LFP (308 nm) of phenyl azide in 100% formic acid with time windows (a) 0−0.95 ps, (b) 1−30 ps, and (c) 30−1000 ps.[11]

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(11) The contribution of solvent two photo absorption has been subtracted.

(12) The concetration of PhN_3 solution is ∼100 mM, which affords absorption ∼1 at 308 nm with 1.0 mm lightpath ($\epsilon_{308\ nm} = 91.4\ M^{-1}\ cm^{-1}$). Aggregation of PhN_3 was not observed at this concetration (Surporting Information, Figure S1). For details of ultrafast experiments, please refer to ref 13.

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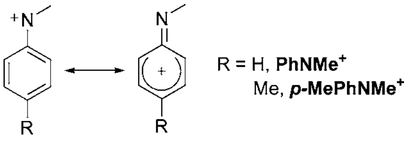
several picoseconds after pulsed laser photolysis of phenyl azide in ACN containing diethylamine. We also find that the lifetime of the excited-state of phenyl azide is ~1 ps, significantly shorter than that reported previously,[9b,15] but more similar to the lifetimes of the biphenyl and naphthyl azide excited states.[13] In 100% formic acid, $^1\mathrm{PhN}_3$* decays within our instrument response function (300 fs) and a growth below 400 nm is observed, which is assigned to singlet phenylnitrene (^{1}PhN). This assignment is consistent with the singlet nitrene spectrum reported previously.[9] Subsequently, the decay ($\tau = 12.0 \pm 1.0$ ps, Supporting Information, Figure S3) of ^{1}PhN is accompanied by the growth of transient absorption centered at 500 nm (Figure 1b). Within experimental error, the time constant of the decay recorded at 360 nm is the same as that of the growth of transient absorption monitored at 500 nm. In nonacidic solutions such as ACN,[9] the decay of ^{1}PhN is not accompanied by the formation of a transient species absorbing at 500 nm. Following our recent report on the efficient protonation of *o*-biphenylyl and 1-naphthylnitrene to form the corresponding nitrenium ions in 88% formic acid,[10] the transient absorption at 500 nm is assigned to phenylnitrenium ion (PhNH^+).[16] The lifetime of PhNH^+ is 110 ± 14 ps in 100% formic acid (Supporting Information, Figure S4), which is in excellent agreement with the value estimated by Fishbein and McClelland in aqueous solution.[8]

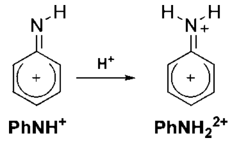
Using a pyridinium-based photochemical precursor, Falvey's group made an attempt to observe *N*-methyl-*N*-phenylnitrenium ion PhNMe^+ (Scheme 2).[17] However, the lifetime of this species was too short to detect by nanosecond time-resolved LFP methods. A methyl substituent at the para position of the phenyl ring substantially lengthens the nitrenium ion lifetime by retarding nucleophilic attack at this position. The *p*-$\mathrm{MePhNMe}^+$ nitrenium ion (Scheme 2) has a strong absorption centered at 325 nm and a weak absorption tail in the visible region centered around 470 nm.[18] TD-DFT calculations[19] predict that this nitrenium ion has two major transitions (Supporting Information, Table S1) at 296 nm ($f = 0.5713$) and 413 nm ($f = 0.0224$), in fair agreement with the experimental results. Similarly, TD-DFT calculations predict that the parent system PhNH^+ has two $\pi \rightarrow \pi^*$ transitions (Supporting Information, Tables S2 and S3) at 259 nm ($f = 0.2429$) and 450 nm ($f = 0.0284$), respectively.[20] Based on these calculations, the known spectrum of *N*-methyl-*p*-tolylnitrenium ion, and the absence of the 500 nm absorbing transient in ACN, the assignment of the 500 nm band to PhNH^+ appears secure.

Scheme 2



Protonation of a nitrenium ion to form a dication (Scheme 3) has been reported by the McClelland group.[3d] We explored the possibility of assigning the 500 nm species to the parent aniline dication $\mathrm{PhNH_2}^{2+}$. TD-DFT calculations predict that $\mathrm{PhNH_2}^{2+}$ has two transitions (Supporting Information, Table S4) at 752 nm ($f = 0.0014$) and 380 nm ($f = 0.0608$). Thus, we are reluctant to assign the 500 nm species to $\mathrm{PhNH_2}^{2+}$. The residual absorbance centered around 450 nm 1 ns after the laser pulse may be due to the formation of $\mathrm{PhNH_2}^{2+}$ (Figure 1c). In addition, the absorbance below 400 nm (Figure 1c) may be attributed to the more intense UV band for PhNH^+ or of the aniline dication, $\mathrm{PhNH_2}^{2+}$.

Scheme 3



In summary, this study has provided the first spectroscopic observation of phenylnitrenium ion. The lifetime of PhNH^+ is 110 ps in 100% formic acid at ambient temperature.

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[14] We have tried to repeat Wirz's experiment, photolysis of phenyl azide in DCM with excitation wavelength of 270 nm. However, with 270 nm of excitation, DCM always produces some artifact at all delay times we measured (up to 3 ns). The signal obtained in neat DCM is on the same order as the signal produced by photolysis of $\mathrm{PhN_3}$ in DCM. Thus we used ACN instead, which is considered as an excellent solvent for spectroscopic studies.

[15] Assuming diethyl amine reacts with diffusion control rate (~10^{10} s^{-1}), it is impossible to shorten the lifetime $^1\mathrm{PhN_3}^*$ from 100 to 1 ps.

[16] It is well-known that phenylnitrenium ion can be attacked by water molecules at the para position to form the cyclohexadiene derivative. In this study, we employed 100% formic acid, instead of 88% formic acid as in our previous studies, in order to lengthen the lifetime of PhNH^+ and increase its intensity.

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[19] TD-DFT calculations were preformed using B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level and 20 allowed electronic transitions were calculated. The full reference for Guassian 03 is given in the Supporting Information: Frisch, M. J. et al. *Gaussian 03 (Revision C.01)*; Gaussian, Inc.: Wallingford CT, 2005.

[20] Although the transitions at both 259 and 450 nm are $\pi \rightarrow \pi^*$, the oscillator strengths differ by 1 order of magnitude. This can be explained by symmetry considerations. The molecular orbitals of phenyl nitrenium ion are shown in the supporting information (Supporting Information, Table S3). In MO 22, 23, and 25, the electron densities on the hydrogen atom at the nitrenium ion center are negligible. If we ignore that hydrogen, the symmetry of the molecule will be upgraded from C_s to C_{2v}. Under C_{2v} symmetry, the orbital symmetry for MO 22, 23, and 25 will be b_2, a_2, and b_2, respectively. Thus, the transition at 259 nm (MO 22(b_2) → 25(b_2)) has a better symmetry match than the transition at 450 nm (MO 23(a_2) → 25(b_2)) and, as a result, a higher oscillator strength.

Supporting Information Available: Complete ref 16. TD DFT calculations and the calculated molecular orbitals are in Tables S1−S4. Kinetic traces for phenyl azide excited state, phenylnitrene, and phenylnitrenium ion are in Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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