Direct Observation of Singlet Phenylnitrene and Measurement of Its Rate of Rearrangement

Nina P. Gritsan,*,[†,‡] Tetsuro Yuzawa,[†] and
Matthew S. Platz*,[†]

Newman and Wolfrom Laboratory of Chemistry
The Ohio State University, 100 West 18th Avenue
Columbus, Ohio 43210
Institute of Chemical Kinetics and Combustion
630090 Novosibirsk, Russia

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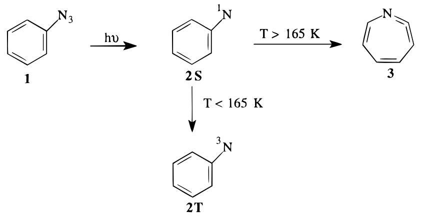
Aromatic azides are widely used in industry as photoresists[1] and in biochemistry as photoaffinity labeling reagents.[2] Their photochemistry has been called "wonderfully complex" but has recently been unraveled.[3]

Photolysis of phenylazide (**1**) releases singlet phenylnitrene (**2S**) which in solution phase ($T > 165$ K) rapidly rearranges to 1,2-azacycloheptatetraene **3**.[3] At temperatures below ≈165 K, **2S** preferentially relaxes to triplet phenylnitrene **2T** instead.[4,5]



In 1984 we assumed[4a] that ring expansion of **2S** had a normal pre-exponential factor of 10^{12-14} s^{-1} and that intersystem crossing (ISC) of **2S** had zero activation energy (E_a) and a rate similar to that of aryl carbenes (10^{9-10} s^{-1}).[8] On this basis it was possible to deduce that E_a for rearrangement was 2−4 kcal/mol and that the lifetime of **2S** was 10−100 ps at 298 K.[4a] In subsequent years triplet phenyl nitrene **2T** and cyclic ketenimine **3** were thoroughly characterized by matrix UV−vis and IR spectroscopy,[9] and **3** was studied in solution by time resolved UV−vis and IR techniques.[10]

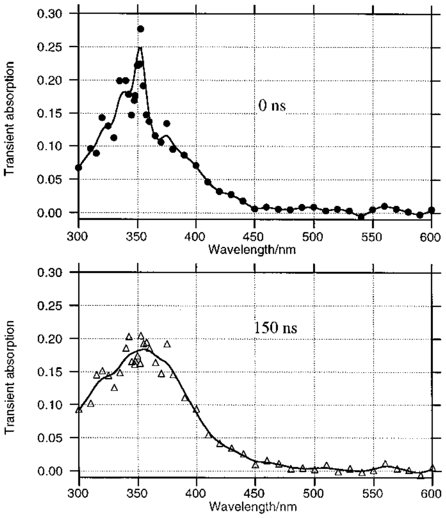


Figure 1. Transient spectrum observed (top) immediately following the laser pulse and (bottom) 150 ns later. The sample was phenyl azide **1** in pentane at 233 K using 266 nm, 10 mJ, 150 ps/pulse excitation.

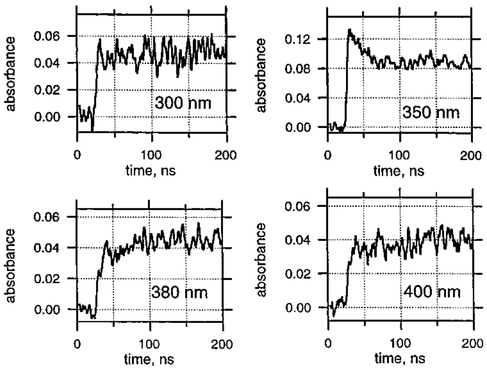


Figure 2. The variation in optical density as a function of time, at different wavelengths, following excitation (266 nm) of phenyl azide at 225 K.

Herein we are pleased to report the first spectroscopic detection of singlet phenylnitrene,[11] absolute measurement of its lifetime in solution, and the Arrhenius parameters describing its rearrangement.[5] We find that the barrier to rearrangement is larger than previously deduced because ISC is much slower than originally anticipated.

Phenyl azide **1** was studied by laser flash photolysis (LFP, Nd-YAG, 150 ps, 266 nm, 10 mJ) in pentane. At room temperature a transient absorbing at 350 nm is observed. The formation and decay of this species, at ambient temperature, is faster than the time resolution of the spectrometer (1 −2 ns). At lower temperatures (<280 K) the formation of the transient remains "instantaneous", but its decay can be resolved. At low temperatures the decay of the 350 nm absorbing transient is accompanied by the formation of ketenimine **3** which absorbs broadly above 300 nm[9,10] (Figures 1 and 2).

The decay of the 350 nm transient was monitored as a function of temperature. Its decay was well fit to an exponential function to yield an observed rate constant. An Arrhenius treatment of these rate constants is given in Figure 3 and yields $E_a = 6.2 \pm 0.4$ kcal/mol and $A = 10^{13.6\pm0.4}$ s^{-1} in pentane.

LFP of phenylisocyanate, in pentane, also produced a rapidly decaying transient which absorbed at 350 nm. Its decay is

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[†] The Ohio State University.

[‡] Institute of Chemical Kinetics and Combustion.

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(11) There are only a few previous reports of the direct detection of singlet aryl nitrenes. The lifetimes of singlet 4-(dimethyamino)phenylnitrene has been reported (Kobayashi, T.; Ohtuni, H.; Suzuki, K.; Yamaoka, T. *J. Phys. Chem.* **1985**, *89*, 776) as has that of 1-pyrenylnitrene (Sumitani, M.; Nagakura, S.; Yoshihara, K. *Bull. Chem. Soc. Jpn.* **1976**, *97*, 12674).

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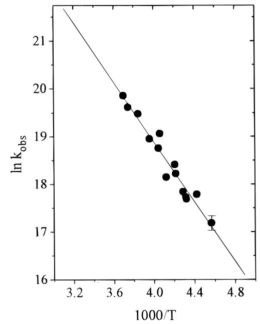
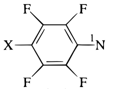


Figure 3. Temperature dependence of the rate constant of the rearrangement of singlet phenylnitrene in pentane. Fitting for the data below 0° yields $k_{obs} = 10^{13.6\pm0.4}$ exp $(-(6200 \pm 400)/RT)$. The decay is measured over a temperature range in which rearrangement is the only significant decay route of singlet nitrene **2S**.[4]

associated with Arrhenius parameters $A = 10^{13.4\pm1.0}$ s^{-1} and $E_a = 6 \pm 1$ kcal/mol. The transient signal observed with phenylisocyanate is weaker than that obtained from phenylazide, hence the experimental error in the Arrhenius parameters is somewhat larger. There is no doubt, however, that the same species is formed from both precursors. Thus, the 350 nm absorbing transient cannot be an excited state of the precursor but is instead a reactive intermediate which is attributed to singlet phenylnitrene **2S**. Nitrene **2S** is expected to be in its lowest electronic state because it is unlikely that an excited state of this species will have a lifetime of many ns in solution and must overcome an enthalpic barrier to relax.

This spectroscopic assignment follows closely on our work with perfluorinated singlet nitrenes **4a,b**.[12]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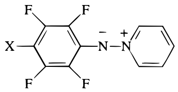
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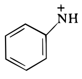
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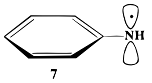
	4a X = F	**4b** X = C_6F_5
λ max	330 nm	350 nm
τ (294 K , pentane)	32 ± 3 ns	254 ± 5 ns

Fluorination is known to lengthen the lifetime of singlet aryl nitrenes which allows their facile capture with a variety of reagents.[13] Trapping with pyridine produces isolable ylides **5a,b** which have intense absorptions near 390−400 nm. Thus, in these cases it is possible to correlate the decay of the singlet nitrene with the formation of an ylide[12] or with the formation of ketenimine.

Singlet phenylnitrene **2S** is known to react with an external trap, the proton.[14] Indeed, H_2SO_4 shortens the lifetime of **2S** in acetonitrile at 243 K. However, we cannot obtain the absolute rate constant of this process because of the very short lifetime of **2S** in acetonitrile and the overlapping absorption of the reaction product, phenylnitrenium ion **6**.[14]

The assignment of the 350 nm transient to singlet nitrene **2S** is further supported by the Arrhenius parameters and the position of the absorption band itself. The Arrhenius parameters correctly model the known temperature dependence of the photochemistry of phenylazide.[4a] Previous work demonstrated that the rate of ISC (**2S** → **2T**) becomes equal to that of nitrene rearrangement at 165 K. The deduced rate of rearrangement, 2.5×10^5 s^{-1}, at 165 K is comparable to the temperature independent rate of ISC determined for **4a**,**b** ($2.2 \times 10^6-10^7$ s^{-1}).[12,15] Furthermore, the Arrhenius parameters predict that the lifetime of **2S** in pentane at 298 K will be 0.1−1.0 ns in good agreement with the findings of Wirz et al.[18,19] and of theory.[5]

Finally, we note that a λ_{max} of 350 nm of **2S** is unsurprising for several reasons. Singlet phenylnitrene is predicted[7] to have an open shell configuration as does the corresponding triplet. Thus, these two species should have comparable electronic spectra. Indeed, this is the case with **4a**,**b**[12] both of which absorb near 350 nm. The spectrum of triplet phenylnitrene **2T** has been analyzed.[4a,20] In the UV region between 300 and 400 nm triplet phenyl nitrene has several π, π^* transitions related to those of anilino radical **7**[21] but has, in addition, a characteristic transition on nitrogen in which an electron is promoted from the nonbonding doubly occupied sp orbital into a singly occupied p orbital of the nitrene nitrogen. This transition is related to the well-known degenerate $A^3\ \Pi_i - X^3\ \Sigma^-$ transition of ^3NH at 336 nm and the spectra of triplet methylnitrene **8** and triplet 1-norbornylnitrene **9** which have λ_{max} values of 315 and 298 nm, respectively.[23,24]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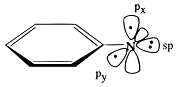

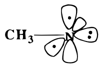
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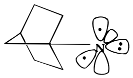
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Additional studies of the rearrangement of various substituted singlet aryl nitrenes are in progress and will be reported in due course.

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