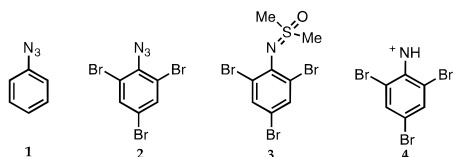# Transient Absorption Spectra and Reaction Kinetics of Singlet Phenylnitrene and Its 2,4,6-Tribromo Derivative in Solution

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Time-resolved techniques have provided lifetimes for a representative selection of carbenes in both the singlet and the triplet state, but this is not so for nitrenes.[1] In particular, neither singlet nor triplet phenylnitrene has been detected in solution. The lifetime of singlet phenylnitrene at room temperature in solution is limited by ring expansion to 1-azacyclohepta-1,2,4,6-tetraene and was estimated as $10^{10\pm1}$ s^{-1} on the basis of several assumptions.[2] Platz and co-workers have since provided convincing evidence that denitrogenation and ring expansion proceed stepwise upon photolysis of phenyl azide (**1**).[3] The stage was set to identify singlet phenylnitrene by flash photolysis. We report transient absorption spectra determined by pump-probe spectroscopy of phenyl azide (**1**), 2,4,6-tribromophenyl azide (**2**), and 2,4,6-tribromophenyl sulfoximine (**3**).[4]

Solutions (ca. 10^{-3} M) were circulated in a flow system, pumped at 248 nm (4 mJ, 0.7 ps half-width, 12 Hz), and probed by a delayed continuum pulse (310−700 nm) of the same duration.[5] Transient absorption spectra were recorded at ca. 50 different time delays ranging from 2 ps to 1.8 ns relative to the excitation pulse. Delays of up to 17 ns were produced by passing the probe beam over an extended delay line, but these spectra were not used to determine kinetics. The transient absorbance data were subjected to global analysis, i.e., factor analysis followed by nonlinear least-squares fitting of appropriate kinetic models.[5,6]

The transient absorbance changes produced by flash photolysis of phenyl azide (**1**) in dichloromethane are shown in Figure 1. Experiments with other solvents were hampered by the deposition of polymeric tars on the windows of the flow cell. The final spectrum (1.8 ns delay) is the same as that observed by nanosecond flash photolysis[2] of **1** and has been unambiguously assigned to the product of ring expansion, 1-azacyclohepta-1,2,4,6-tetraene.[7] Prior to the discussion of these observations the tribromo derivatives **2** and **3** are considered.

Ortho-substituents retard ring expansion and substantial evidence for an enhanced lifetime of *ortho*-disubstituted singlet phenylnitrenes has been accumulated.[2,8] Bromination should, at the same time, accelerate intersystem crossing (isc) due to the heavy-atom effect. The lifetime of singlet phenylnitrene is limited by ring expansion, isc competes effectively only at temperatures below 200 K.[2] 2,4,6-Tribromophenyl azide (**2**) is known to react predominantly[9] *via* the triplet nitrene that dimerizes to the corresponding azo compound.[2] The transient spectra obtained by picosecond pump-probe spectroscopy of **2** in dichloromethane clearly required three spectral components in the factor analysis and a biexponential rate law in the kinetic fitting procedure (Figure 2). The resulting rate constants $k_1 = 6.0 \pm 1.9 \times 10^{10}$ s^{-1} and $k_2 = 9.4 \pm 0.3 \times 10^8$ s^{-1} gave a good fit to the amplitude coefficients (Figure 2, inset).

The two time-resolved processes are attributed to formation of singlet 2,4,6-tribromophenylnitrene from the excited singlet state of **2**, followed by isc of the singlet nitrene (Figure 2, spectrum at 50 ps delay) to the triplet nitrene. The characteristic final spectrum (Figure 2, spectrum at 17 ns delay) is clearly that of triplet 2,4,6-tribromophenylnitrene which has been identified previously.[2] The assignment of the first two transient intermediates rests on two observations: (*i*) Proton transfer in 1:1 aqueous acetonitrile produced the nitrenium ion **4**, $\lambda_{max} = 420$ and 600 nm.[10,11] The rate of formation and the yield of **4** increased upon addition of perchloric acid, $(\tau_{obsd})^{-1} = k_0 + k_{H^+}[H^+]$ with $k_{H^+} = 3.5 \pm 0.1 \times 10^9$ M^{-1} s^{-1}, and the decay rate of the singlet nitrene increased accordingly. (*ii*) Pump-probe spectroscopy of sulfoximine **3** gave the same, albeit weaker, transient absorption changes and the same rate constant as azide **2** for the second process (isc of singlet nitrene). The spectra taken immediately after the pump pulse were, however, different (broad absorption, $\lambda_{max} = 340$ and 400 nm, tailing to > 500 nm) from those obtained with **2**, and the first process had a different rate constant, $k_1 = 4.5 \pm 0.4 \times 10^{10}$ s^{-1}. These observations indicate that the primary transient absorptions detected by pump-probe spectroscopy of **2** (Figure 2, spectrum at 2 ps delay) and **3** are due to the excited singlet states of these compounds.

We now return to parent phenyl azide (**1**). Factor analysis of the data matrix obtained by pump-probe spectroscopy indicated that three components were sufficient to reproduce the observed spectra within experimental accuracy. Fitting of a single exponential rate law to the reduced data set gave a first-order rate constant of $4.6 \pm 0.6 \times 10^9$ s^{-1} for the overall spectral changes. In the preceding paper,[12] Gritsan, Yuzawa, and Platz report kinetic flash photolysis of **1** in pentane at temperatures below 0 °C and thereby provide a direct measurement of the lifetime of singlet phenylnitrene. At first sight our results appear to be inconsistent with the data reported by these authors: we observe time-resolved absorbance decay predominantly at wavelengths >370 nm (Figure 1), whereas they report decay at 350 nm and a slight rise at longer wavelengths. This suggests that, as in the case of **2**, the transient spectra observed with **1** might represent two sequential processes and that only

(1) Platz, M. S. *Acc. Chem. Res.* **1995**, *28*, 487−492.

(2) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783−3790.

(3) Marcinek, A.; Leyva, E.; Whitt, D.; Platz, M. S. *J. Am. Chem. Soc.* **1993**, *115*, 8609−8612.

(4) Azide **2** (0.4 g) was heated to 175 °C for 1.5 h in DMSO. The product **3** was purified by chromatography: mp 98−100 °C; H-NMR (CDCl$_3$): δ 7.68 (s, 2H), 3.22 (s, 6H).

(5) Details of the experimental set-up and of the data analysis were described: Hasler, E.; Hörmann, A.; Persy, G.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1993**, *115*, 5400−5409.

(6) Bonneau, R.; Wirz, J.; Zuberbühler, A. D. *Pure Appl. Chem.* **1997**, in the press.

(7) Schrock, A. K.; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228−5234. Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092−8098.

(8) (a) Poe, R.; Grayzar, J.; Young, M. J. T.; Leyva, E.; Schnapp, K.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 3209−3211. (b) Poe, R.; Schnapp, K.; Young, M. J. T.; Grayzar, J.; Platz, M. S. *J. Am. Chem. Soc.* **1992**, *114*, 5054−5067. (c) Marcinek, A.; Platz, M. S. *J. Phys. Chem.* **1993**, *97*, 12674−12677. (d) Marcinek, A.; Platz, M. S.; Chan, S. Y.; Floresca, R.; Rajagopalan, K.; Golinski, M.; Watt, D. *J. Phys. Chem.* **1994**, *98*, 412−419. (e) Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 3347−3350. (f) Gritsan, N. P.; Zhai, H. B.; Yuzawa, T.; Karweik, D.; Brooke, J.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 2833−2840.

(9) A small amount of polymer is formed, presumably via ring expansion of the singlet nitrene.

(10) The lifetime of 2,4,6-tribromophenylnitrenium ion is 200 ns; 2,6-dibromo-1,4-benzoquinone was the main product isolated after photolysis in aqueous acid. Details will be reported elsewhere.

(11) For a review on protonation of singlet aryl nitrenes, see: McClelland, R. A. *Tetrahedron* **1996**, *52*, 6823−6858. See, also: McClelland, R. A.; Kahley, M. J.; Davidse, P. A.; Hadzialic, G. *J. Am. Chem. Soc.* **1996**, *118*, 4794−4803. Michalak, J.; Zhai, H. B.; Platz, M. S. *J. Phys. Chem.* **1996**, *100*, 14028−14036.

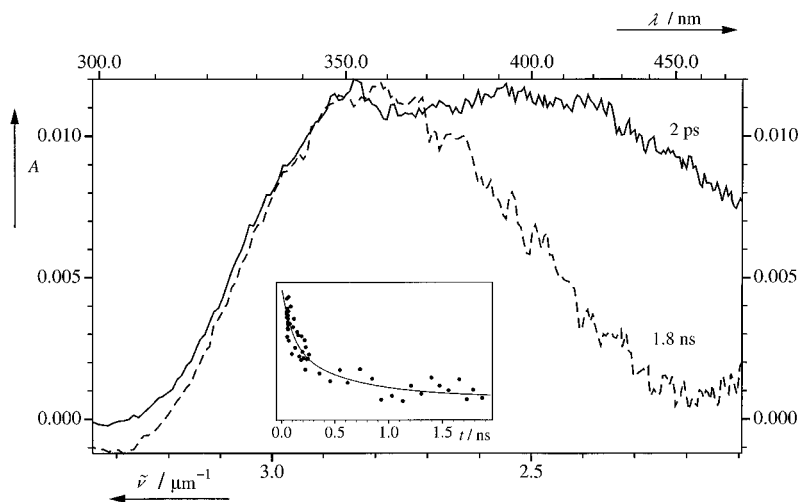　© 1997 American Chemical Society

Figure 1. Pump-probe absorption spectra of **1** in dichloromethane. The points shown in the inset are the loading coefficients (arbitrary scale) of the first eigenspectrum determined by factor analysis of the complete set of pump-probe spectra. The full line is the best fit of a biexponential rate law to the complete set of data (global analysis, ref 5).
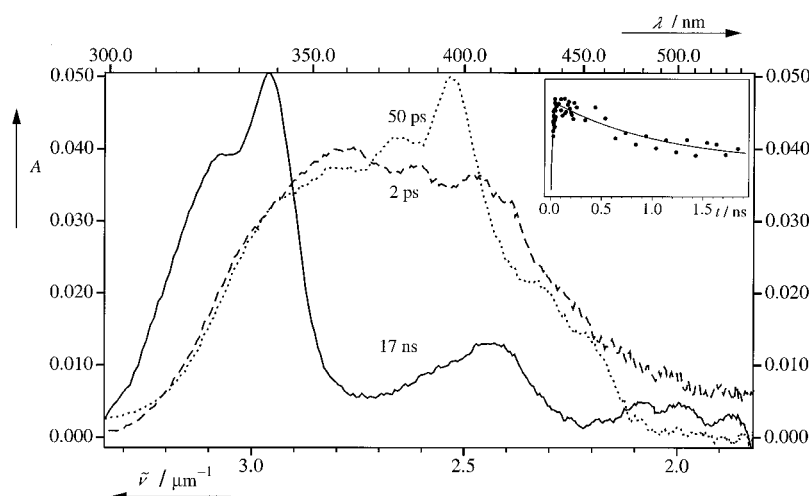

Figure 2. Pump-probe absorption spectra of **2** in dichloromethane. Inset: see caption to Figure 1.

Table 1. Rates of Formation (k_1) and Decay (k_2) of Singlet Arylnitrenes in Dichloromethane

arylnitrene	$k_1/(10^9 \text{ s}^{-1})$	$k_2/(10^9 \text{ s}^{-1})$	λ_{max}/nm
phenylnitrene	10 ± 3	ca. $1.7^{a)}$	350
2,4,6-tribromophenylnitrene	60 ± 2	0.94 ± 0.03	395

^{a} The kinetic data determined at temperatures below ambient by Gritsan et al.[12] are considered to be more accurate.

the slower one was resolved by Gritsan et al. Indeed, the peak at about 350 nm in our spectra decays discernibly more slowly than the broad absorption above 400 nm. Fitting of a biexponential function to the data (inset of Figure 1) gave $k_1 = 1.0 \pm 0.3 \times 10^{10} \text{ s}^{-1}$ and $k_2 = 1.7 \pm 1.1 \times 10^9 \text{ s}^{-1}$. The short-lived spectral component exhibits a broad absorption in the range of 370−470 nm, the longer-lived one shows a relatively narrow peak at 350 nm. While our data are consistent with a biexponential model function representing two independent processes, the large standard errors of the rate constants show that spectral changes are too small and the rate constants of the two processes too similar to warrant the use of such a model on purely statistical grounds.

In order to obtain conclusive evidence that the spectra observed at room temperature represent a congested view of two or more processes overlapping in time, we repeated the

measurements at −20 °C. These data confirm the above interpretation: the two processes are resolved, and the slower spectral changes are consistent with those reported by Gritsan et al. Thus, we assign the component exhibiting an absorption peak at 350 nm to singlet phenylnitrene. Tribromination shifts the absorption maximum to 395 nm. Similar band shifts of about 40 nm were found in the spectra of the triplet nitrenes derived from **1** and **2**.[2]

The absorption maxima and the rates of formation and decay of singlet phenylnitrenes are collected in Table 1. The transient spectra determined with **1** at room temperature are congested due to overlap between the formation and decay processes. The observed rates of formation represent a lower limit for the rate of nitrogen elimination from singlet excited azide, since the initial absorbance changes may correspond to the decay of the excited azide, internal conversion of electronically−excited singlet nitrene, thermalization of a vibrationally excited singlet nitrene, or a combination of these processes. Ring expansion is the dominant decay process of phenylnitrene in solution at room temperature. The lifetime of 2,4,6-tribromophenylnitrene is mainly limited by isc, but protonation to form the nitrenium ion is competitive in aqueous solution.

(12) Gritsan, N. P.; Yuzawa, T.; Platz, M. S. *J. Am. Chem. Soc.* **1997**, *119*, 5059−5060.

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