November, 1976] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (11), 2995—2998 (1976) 2995

The Primary Process of the Photochemical Formation of 1-Nitrenopyrene

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(Received June 18, 1976)

The primary process of the photo-decomposition of 1-azidopyrene (Py–N$_3$) was studied with the aid of nanosecond time-resolved laser photolysis. An excited singlet 1-nitrenopyrene (Py–N) was identified as an intermediate for the formation of the ground triplet nitrene. The direct photo-decomposition of 1-azidopyrene occurs through Py–N$_3$* (singlet)→Py–N* (singlet)→Py–N (triplet). The lifetime of the excited singlet nitrene was found to be 22 ns at room temperature in benzene and was found to be slightly longer at 77 K.

Organic azides decompose photochemically or thermochemically to corresponding nitrenes which are known as intermediates in various kinds of reactions; cyclization, reduction, oxidation, and dimerization.1,2) The ground states of the nitrenes produced by the photo-decomposition of the azides are known to be in the triplet state;3–5) the eliminated nitrogen molecule is in the singlet state.6) The existence of the triplet nitrenes as reaction intermediates has been confirmed by flash-photolysis experiments7–11) and also by measurements of the electronic absorption and ESR spectra of the rigid solutions at low temperature.3–5,12–16) From the spin conservation rule for the reaction, two paths are conceivable for triplet nitrene formation. One of them is the "singlet mechanism" occurring through the excited singlet nitrene (R–N*(singlet)) and the other is the "triplet mechanism" through the excited triplet azide (R–N$_3$(triplet)).

$$\begin{tikzcd}
\text{R–N}_3 \arrow[r, "h\nu"] & \text{R–N}_3^*\text{(singlet)} \arrow[r] \arrow[d] & \text{R–N}^*\text{(singlet)} + \text{N}_2 \arrow[d] \\
 & \text{R–N}_3\text{ (triplet)} \arrow[r] & \text{R–N (triplet)} + \text{N}_2 \\
 & \text{azide} & \text{nitrene}
\end{tikzcd}$$

From quenching experiment Reiser and Leyshon17) showed that phenyl azide in the excited singlet state directly decomposes to the singlet nitrene and nitrogen before it is transferred to the triplet azide by intersystem crossing. In the flash-photolysis experiment Lehman and Berry11) found that the decay time from the excited singlet state to the ground triplet state was shorter than 6 μs for some organic nitrenes, but they could not detect any singlet nitrenes. The excited singlet nitrenes spectroscopically observed so far are limited to such simple nitrenes as NH, NF, and NCN18–23) in the gaseous state.

The main purpose of the present study is to observe directly the excited singlet 1-nitrenopyrene (Py–N) by nanosecond laser photolysis and to elucidate the mechanism of the photo-decomposition of 1-azidopyrene (Py–N$_3$). The compound is suitable for this purpose since the photo-decomposition quantum yield is very large and the absorption peaks characteristic of Py–N$_3$ and the ground triplet and excited singlet Py–N can easily be distinguished from one another.

Experimental

The details of laser photolysis experiment were reported elsewhere.24) We used a coaxial type N$_2$ laser (peak power at 337.1 nm, 100 kW; pulse duration, 7 ns FWHM) as a light source for the direct excitation of samples. A monitor light (an EG and G FX-131 flash lamp) was detected with a Hamamatsu TV R666 photomultiplier and a Tektronix 465 oscilloscope.

The sensitized photo-decomposition experiment of Py–N$_3$ was carried out by using biacetyl as a triplet sensitizer. Biacetyl purified by distillation under a nitrogen atmosphere was excited with a dye laser at 423.0 nm (peak powder, 70 kW; pulse duration, 6 ns FWHM). For the excitation of dye, we constructed a travelling-wave type N$_2$ laser (peak power, 1 MW; pulse duration, 6 ns FWHM) originally designed by Godard.25) The dye laser is of a Hänsch type,26) a Bausch and Lomb grating of 600 grooves per mm and with a blaze wavelength of 500 nm being used. POPOP (1,4-bis(5-phenyl-2-oxazolyl)benzene) in a methanol–dioxane 1: 1 mixture was used as a lasing dye. The photolysis system with the dye laser is shown in Fig. 1.

1-Azidopyrene27) was purified with alumina column chromatography under red light. The effect of oxygen on the reaction was carefully investigated. We observed no oxygen effect on the primary process; therefore, the sample was used

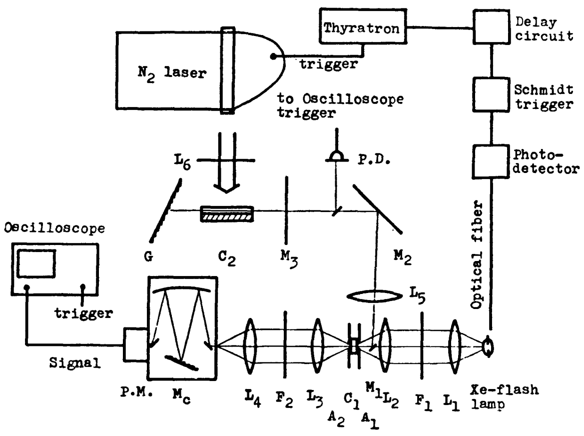

Fig. 1. Block diagram of the flash photolysis apparatus with the dye laser.
A$_{1,2}$: Apertuer, L$_6$: cylindrical lens, C$_1$: sample cell, M$_{1,2}$: 100% mirror, C$_2$: dye cell, M$_3$: 20% mirror, F$_{1,2}$: filter, M$_c$: monochromator, G: grating, P. M.: photomultiplier, L$_{1-5}$: Spherical lens, P.D.: biplanar photodiode.

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with no deaeration. Since the overall reaction was completed with a single laser shot and gave a final product, sample solutions were either flowed through a sample cell or replaced by a new one at each experiment.

Results and Discussion

Direct Photolysis of Py–N_3 with an N_2 Laser. The time-resolved absorption spectra for the direct photolysis of Py–N_3 (3.6×10^{-4}M) in benzene were measured at room temperature. The results are shown in Fig. 2. We can see that two different absorptions appear at 450 nm and at 415 nm with an isosbestic point at 425 nm and that the 415 nm band increases in intensity with the decay of the 450 nm band. The time dependence of the absorption intensities was measured at various wavelengths. The results measured at 415, 430, and 450 nm are shown as examples in Figs. 3(a), (b), and (c), respectively. The absorption maximum at 415 nm of the long-lived component increases in intensity quickly at first, gradually approaches a constant value, and hardly exhibits any decay in the observed time range of 5 μs (Fig. 3a). On the other hand, the absorption maximum at 450 nm of the short-lived component decays quickly to reach a constant value (Fig. 3c). The intensity at 430 nm near the isosbestic point is almost time-independent (Fig. 3b). The absorptions of both components overlap each other in the observed wavelength region. But, by the deconvolution of oscilloscope traces we could determine the rise-time constant for the long-lived component to be 4.5×10^7 s^{-1} and the decay-time constant for the short-lived component to be 4.4×10^7 s^{-1}. Both values agree well with each other. This leads us to the conclusion that the short-lived component is the precursor of the long-lived component.

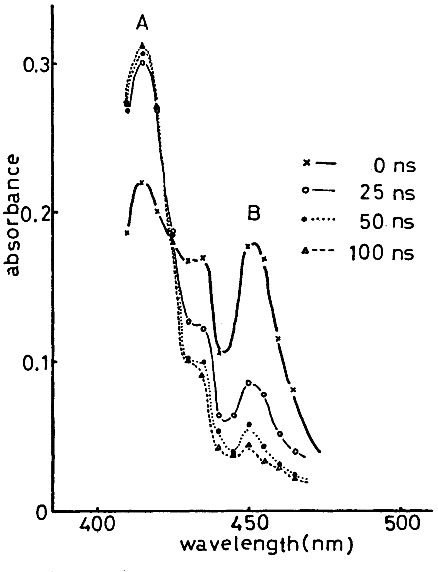

Fig. 2. Time-resolved transient absorption spectra for the direct decomposition of Py–N_3 (3.6×10^{-4} M in benzene): —×—, immediately after; —○—, 25 ns after; ···●···, 50 ns after; and ···△···, 100 ns after an N_2 laser pulse reached its maximum intensity.

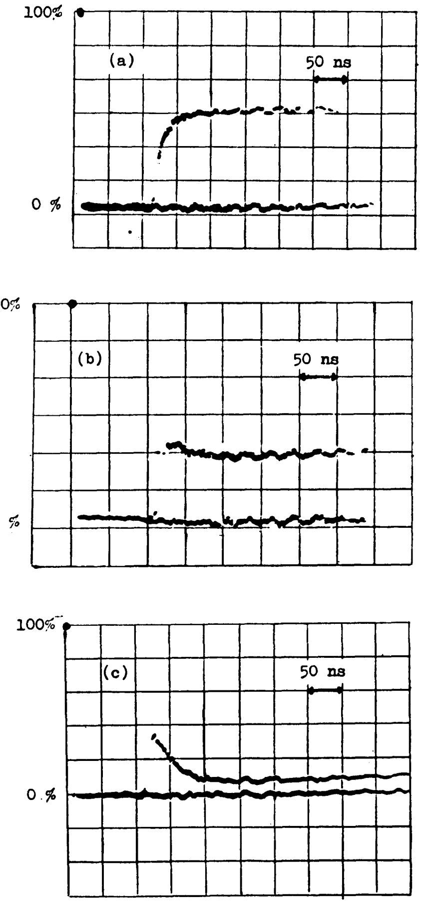

Fig. 3. Oscilloscope traces of transient absorption intensities in the direct photo-decomposition of Py–N_3 observed at (a) 415 nm, (b) 430 nm, and (c) 450 nm.

The absorption spectrum of the long-lived component is the same as that of the ground triplet Py–N observed by Yamaoka *et al.*[10] Therefore it is concluded that the ground triplet Py–N is produced through the short-lived species with the absorption maximum at 450 nm.

The molar extinction coefficient at 450 nm of the short-lived component was determined to be $\approx 2\times10^4$ cm^{-1} M^{-1} from comparison with that of the $T_1\leftarrow T_0$ absorption at 415 nm.[10] This value was estimated on the reasonable assumption that all the short-lived component molecules were transferred to T_0.

$T_1\rightarrow T_0$ Fluorescence of Nitrene. At the liquid nitrogen temperature, Py–N was produced photochemically with the N_2 laser and its emission was observed for the solution in the methylcyclohexane–isopentane 1:1 mixed solvent with the result shown in Fig. 4. The emission spectrum holds a mirror-image relationship to the $T_1\leftarrow T_0$ absorption spectrum of the ground triplet nitrene. This means that the observed emission is due to the $T_1\rightarrow T_0$ fluorescence of Py–N. The fluorescence-decay time was found to be shorter than 7 ns. Therefore the lifetime of the excited triplet states of Py–N is much shorter than the lifetime of the 450 nm species (22 ns). This clearly demonstrates that the precursor (the 450 nm species) of the ground triplet nitrene is not the excited triplet nitrene.

Quenching Experiment. In order to elucidate the role of the triplet state in the photo-decomposition of

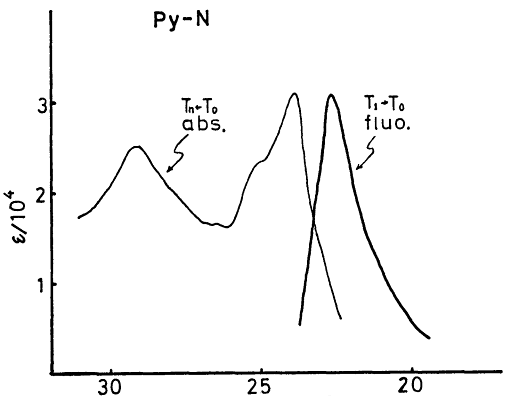

Fig. 4. The $T_1 \rightarrow T_0$ fluorescence (77 K) and absorption spectra of Py–N. The absorption spectrum is taken from Ref. 10.

Py–N_3, we examined the effect of triplet quenchers. The lowest triplet state of Py–N_3 has never been observed spectroscopically,[28] but its energy may roughly be estimated to be 56—46 kcal/mol. This is because in most of the organic azides the lowest triplet state is located 20—30 kcal/mol lower than the singlet state[29] and the singlet state energy (E_S) is 76 kcal/mol for Py–N_3. Thus, 1,3,5-cycloheptatriene ($E_T \approx 50$ kcal/mol), *trans*-stilbene ($E_T=47$ kcal/mol), and oxygen can be used as triplet quenchers for the photo-decomposition of Py–N_3. The quenching experiment using these three molecules as quenchers exhibited no definite effect. Therefore, we concluded that the main reaction path is not *via* the triplet Py–N_3 and that the singlet mechanism is applicable to the direct photo-decomposition of Py–N_3. Lewis and Saunders[30] also observed no effect of the triplet quencher upon the direct photolysis of some alkyl azides.

Sensitized Photolysis of Py–N_3 with a Dye Laser. In order to obtain further support for the singlet mechanism, we induced the N_2 elimination reaction by the selective excitation to the triplet state of Py–N_3. Biacetyl ($E_S=65.0$, $E_T=56.0$ kcal/mol) is one of the sensitizers for the triplet excitation of Py–N_3 (see Fig. 5). We selectively excited biacetyl at 423.0 nm with a dye laser. The reaction occurred and the ground triplet nitrene was produced efficiently. This was confirmed by detecting the $T_1 \leftarrow T_0$ absorption at 415 nm. The oscilloscope trace for this experiment is shown in Fig. 6(a). We can see that in the sensitized photolysis of Py–N_3 the short-lived absorption at 450 nm can not be observed (Fig. 6(b)).

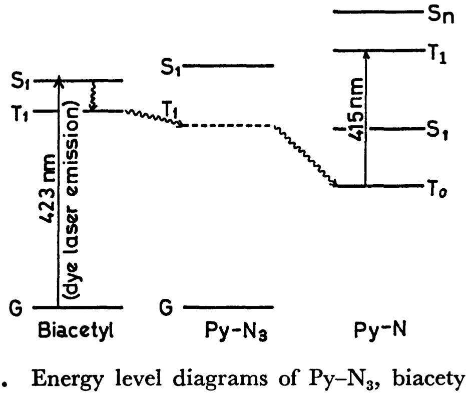

Fig. 5. Energy level diagrams of Py–N_3, biacetyl, and Py–N.

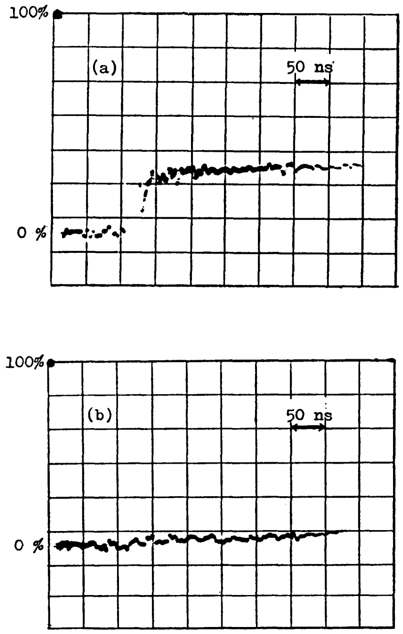

Fig. 6. Oscilloscope traces of transient absorption intensities in the sensitized decomposition of Py–N_3 (8.7×10^{-2} M in benzene) observed at (a) 415 nm and (b) 450 nm.

The present experimental results of the lifetime of the excited triplet nitrene, the effect of the triplet quenchers on the photo-decomposition, and the sensitized photolysis completely obviate the triplet mechanism for the direct photo-decomposition of Py–N_3 and support the singlet mechanism. This means that the short-lived species with the absorption at 450 nm is the excited singlet state of either Py–N_3 or Py–N. In general, the lifetime of the excited singlet state of azide can be expected to be much shorter than 7 ns (the limitation of the time resolution of the present experimental apparatus), in view of the fact that it is not fluorescent. The observed lifetime is 22 ns for the 450 nm species. This safely eliminates the possibility that the 450 nm species is the excited singlet state of Py–N_3. Thus, the absorption band at 450 nm is due to an excited singlet state of Py–N.

$S_1 \rightarrow T_0$ Fast Intersystem Crossing of Py–N. The excited singlet nitrene is relaxed by the $S_1 \rightarrow T_0$ intersystem crossing to the ground triplet nitrene with a lifetime of 22 ns. The singlet nitrene is known as a strong hydrogen abstracting agent in protic solvents. In benzene, however, we did not detect 1-aminopyrene. The excited singlet Py–N in this solvent dimerizes to form azo compounds (*cis*- and *trans*-azopyrene) after the relaxation to the ground triplet Py–N.[10] Furthermore, we observed that the lifetime becomes longer (34 ns) only slightly in a rigid solution (methylcyclohexane–isopentane=1 : 1) at 77 K. These results lead us to the conclusion that the lifetime is not determined by the chemical reaction rate but mainly by physical processes such as intersystem crossing. Lehman and Berry[11] estimated the rate of intersystem crossing for the excited singlet phenyl-

nitrene and naphthylnitrene to be faster than 6 μs but could not succeed in observing the nitrenes spectroscopically. The present experiment is the first direct observation of the excited singlet state of organic nitrene in solution.

The authors would like to express their thanks to Dr. Tsuguo Yamaoka, Chiba University, for his kindness in preparing 1-azidopyrene.

References

1) G. Lábbe, *Chem. Rev.*, **68**, 345 (1968).

2) W. Lwowski, ed., "Nitrenes," Interscience, New York, N. Y. (1970).

3) G. Smolinsky, L. G. Snyder, and E. Wasserman, *Rev. Mod. Phys.*, **35**, 576 (1963).

4) G. Smolinsky, E. Wasserman, and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3220 (1962).

5) J. A. R. Coope, J. B. Farmer, G. L. Gardner, and C. A. McDowell, *J. Chem. Phys.*, **42**, 54 (1965).

6) D. W. Cornell, R. S. Berry, and W. Lwowski, *J. Am. Chem. Soc.*, **87**, 3626 (1965).

7) R. S. Berry, D. Cornell, and W. Lwowski, *J. Am. Chem. Soc.*, **85**, 1199 (1963).

8) A. Reiser, G. C. Terry, and F. W. Willets, *Nature*, **211**, 410 (1966).

9) A. Reiser, F. W. Willets, G. C. Terry, V. Williams, and R. Marley, *Trans. Faraday Soc.*, **64**, 3265 (1968).

10) T. Yamaoka, H. Kashiwagi, and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **45**, 361 (1972).

11) P. A. Lehman and R. S. Berry, *J. Am. Chem. Soc.*, **95**, 8614 (1973).

12) A. Reiser and V. Fraser, *Nature*, **208**, 682 (1965).

13) A. Reiser, H. Wagner, and G. Bowes, *Tetrahedron Lett.*, **1966**, 2635.

14) A. Reiser, G. Bowes, and R. J. Horne, *Trans. Faraday Soc.*, **62**, 3162 (1966).

15) A. Reiser, H. M. Wagner, R. Merley, and G. Bowes, *Trans. Faraday Soc.*, **63**, 2403 (1967).

16) A. Reiser and R. Marley, *Trans. Faraday Soc.*, **64**, 1806 (1968).

17) A. Reiser and L. J. Leyshon, *J. Am. Chem. Soc.*, **93**, 4051 (1971).

18) A. E. Douglas and W. E. Jones, *Can. J. Phys.*, **44**, 2251 (1966).

19) H. W. Kroto, *J. Chem. Phys.*, **44**, 831 (1966).

20) L. J. Schone, *J. Chem. Phys.*, **45**, 2773 (1966).

21) A. Gilles, J. Masanet, and C. Vermell, *Chem. Phys. Lett.*, **25**, 346 (1974).

22) B. Gelernt, S. V. Filseth, and T. Carrington, *Chem. Phys. Lett.*, **36**, 238 (1975).

23) C. Zetzsch and F. Stuhl, *Chem. Phys. Lett.*, **33**, 375 (1975).

24) K. Yoshihara, M. Sumitani, K. Nishi, I. Yokoyama, and S. Nagakura, *Oyo Butsuri*, **43**, 335 (1974).

25) B. Godard, *IEEE J. Quant. Electron.*, **QE-10**, 147 (1974).

26) T. W. Hänsch, *Appl. Phys. Lett.*, **18**, 108 (1971).

27) 1-Azidopyrene was prepared by Dr. T. Yamaoka, Chiba University. The authors are greatly indebted to him for his kindness in giving them the sample.

28) We attempted in vain to measure $T_1 \leftarrow S_0$ absorption making use of a heavy atom solvent (ethyl iodide).

29) F. D. Lewis and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **90**, 7033 (1968).

30) F. D. Lewis and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **90**, 7031 (1968).