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The Photo-decomposition of 1-Azidopyrene in the Benzene Solution

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1-Nitrenopyrene (Py-N) was produced by the photo-decomposition of 1-azidopyrene (Py-N_3) in the benzene solution at 77°K and at room temperature. At 77°K, Py-N was found to be stable, and its electronic absorption and ESR spectra were measured. The result shows that its ground state is triplet and the fine structure constant, D, is equal to 0.73 cm^{-1}. At room temperature, 1-nitrenopyrene was found to be converted easily into 1,1′-*trans*-azopyrene (*trans*-Py-N=N-Py) in the oxygen-free benzene solution and into 1-nitropyrene (Py-NO_2) in addition to Py-N=N-Py in the oxygen-containing benzene solution. The decay process of Py-N as a reaction intermediate and the formation processes of the reaction products were studied by the flash-photolysis technique, and from an analysis of the results, the rate constants at 23°C were determined to be 2.1×10^9 $l\text{mol}^{-1}\,\text{sec}^{-1}$ and 1.4×10^3 sec^{-1} for $2\text{Py-N}\rightarrow$*trans*-Py-N=N-Py and for $\text{Py-N}+O_2\rightarrow\text{Py-NO}_2$, respectively.

Nitrenes produced by the photo-decomposition of the corresponding azides are known to be triplet in their ground states.[1-3] Most of the measurements on the nitrenes have hitherto been made in rigid solutions at low temperature;[4-8] studies of them in fluid solutions are few in number.

The flash-photolysis experiment has demonstrated that they exist as transient intermediates in several photochemical reactions of organic azides.[9-11] In particular, Reiser *et al.*[11] studied kinetically three types of reactions of nitrenes, recombination, hydrogen abstraction from a solvent, and reaction with an azido group, taking 1-nitrenonaphthalene, 4,4′-dinitrenobiphenyl, and 1-nitrenoanthracene.

In the present paper, we studied the electronic absorption and ESR spectra of a new nitrene, 1-nitrenopyrene (hereafter to be abbreviated to Py-

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[1] G. Smolinski, L. C. Snyder, and E. Wasserman, *Rev. Mod. Phys.*, **35**, 576 (1963).

[2] G. Smolinski, E. Wasserman, and W. A. Yager, *J. Amer. Chem. Soc.*, **84**, 3220 (1962).

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

[4] A. Reiser and V. Froster, *Nature*, **208**, 682 (1965).

[5] A. Reiser, H. Wagner, and G. Bowen, *Tetrahedron Lett.*, 2635 (1966).

[6] A. Reiser, G. Bowen, and R. J. Horne, *Trans. Faraday Soc.*, **62**, 3162 (1966).

[7] A. Reiser, H. M. Wagner, R. Marley, and G. Bowen, *ibid.*, **63**, 2403 (1967).

[8] A. Reiser and R. Marley, *ibid.*, **64**, 1806 (1967).

[9] R. S. Berry, D. Cornell, and W. Lwowskii, *J. Amer. Chem. Soc.*, **85**, 1199 (1963).

[10] A. Reiser, G. C. Terry, and F. W. Wilett, *Nature*, **211**, 410 (1966).

[11] A. Reiser, F. W. Wilett, G. C. Terry, V. Williams, and R. Marley, *Trans. Faraday Soc.*, **64**, 3265 (1968).

N), and also its decay process in a benzene solution. We adopted this nitrene as a suitable research subject for the following reasons. Firstly, the photodecomposition quantum yield of the parent azide, 1-azidopyrene(Py-N_3), is very large. Secondly, since the absorption peaks characteristic of Py-N_3, Py-N, and a main final product appear at 360 nm, 415 nm, and 500 nm, respectively, we can easily distinguish the components from one another and can easily follow the reaction process.

Experimental

1-Azidopyrene was prepared by treating the 10% hydrochloric acid solution of 1-aminopyrene with aqueous sodium nitrite and srdium azide solutions below 5°C. The precipitation separated by the filtration of the solution was purified by the aid of a column chromatograph of active alumina.

Commercially-available benzene of a GR grade was purified by shaking it with concentrated sulfuric acid, water, an aqueous sodium hydroxide solution, an aqueous potassium permanganate solution containing sodium hydroxide, and water. The benzene thus treated was dehydrated by calcium chloride and thereafter by sodium metal, and finally it was distilled.

In the present study, the nitrene was prepared in both rigid and fluid benzene solutions. The rigid solution of the parent azide in benzene was illuminated by a 500 W mercury lamp at 77°K. The ESR spectrum of the nitrene thus prepared was measured by a JES ME 3X type spectrometer (X-band, 100 KHz modulation). Since the rigid benzene solution is somewhat opaque for cracking, its electronic absorption spectrum was measured by the aid of the special technique developed by Shibata.[12] Actually, the spectrum was measured by a Shimadzu MPS type spectrophotometer at the Institute of Physical and Chemical Research, an apparatus constructed especially to make possible the application of his method.

The preparation of the nitrene from a fluid benzene solution containing Py-N_3 and the measurement of its electronic absorption spectrum were made by the aid of a flash photolysis apparatus (32 Joule, duration time of 20 μsec) at the Institute of Physical and Chemical Research,[13,14] a cylindrical quartz sample cell 10 cm long and 1 cm in diameter being used. The electronic absorption spectrum was photographed at several stages before and after the flash photolysis.

The decay curve of a transient intermediate and the rise curve of the final product, Py-N=N-Py, in a benzene solution at room temperature were recorded at their peak wavelengths by the aid of an R106 photomultiplier and an oscilloscope.

Final products were separated by the aid of a column chromatography of active alumina, and each component was identified by an elemental analysis, by studying the mass spectrum, and, if possible, by comparing the electronic spectrum, the infrared spectrum, and the gas chromatogram with those of an authentic sample.

The oxygen-free solution, if necessary, was prepared by the freeze-thaw technique.

Results and Discussion

Electronic and ESR Spectra of Irradiated Py-N_3 in the Rigid Benzene Solution at 77°K. The electronic absorption and ESR spectra were measured at 77°K with the benzene solution of Py-N_3 (2.7×10^{-4} mol/*l*) irradiated by a 500W mercury lamp; the results are shown in Figs. 1 and 2, respectively.[15]

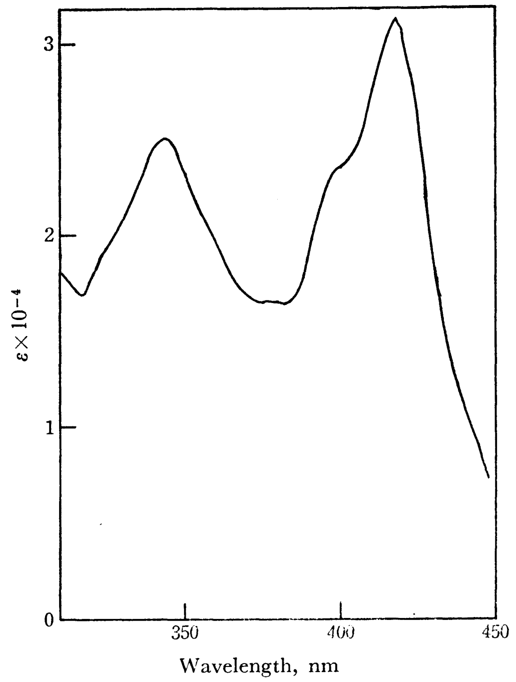

Fig. 1. The electronic absorption spectrum of Py-N in benzene at 77°K.

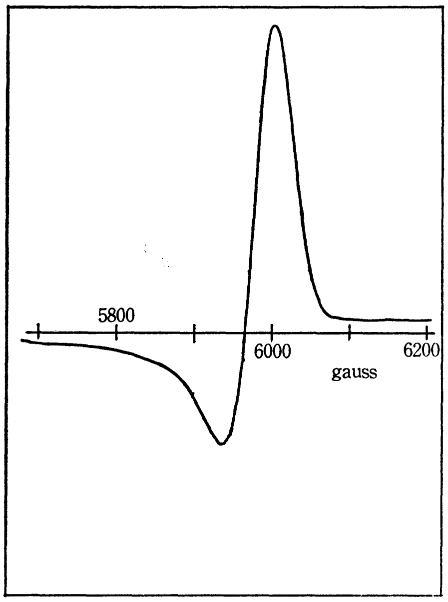

Fig. 2. The ESR spectrum of Py-N in benzene at 77°K.

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[12] K. Shibata, "Method of Biochemical Analysis," Vol. 7, ed. by D. Glick, Interscience Publishers, New York, N. Y. (1959) p. 77.

[13] A. Kira and M. Koizumi, This Bulletin, **42**, 625 (1969).

[14] A. Kira and K. Nishi, *Rep. IPCR*, **44**, 56 (1968).

[15] We observed another weak absorption band at 694 nm with a molar extinction coefficient of ~1500 in addition to the strong absorption bands shown in Fig. 1. In the present paper, however, we are concerned with only the strong bands.

The main feature of the ESR spectrum shown in Fig. 2 is that a single, rather broad line appears in a high field (5980 G). This feature is similar to that of the spectra observed for other ground-state triplet nitrenes[1,3] with quite large D and quite small E values. This means that the ESR spectrum shown in Fig. 2 and, therefore, the electronic absorption spectrum shown in Fig. 1 are due to the triplet Py-N. The D value of Py-N was found to be 0.73 cm^{-1} on the reasonable assumptions that $E=0$ and that $g=g_e=2.0023$.[16]

Flash Photolysis of Py-N_3 in Benzene. Figure 3 shows the microphotometer curves of photographs obtained by the flash photolyis of the oxygen-free benzene solution of Py-N_3 ($\sim 1\times 10^{-5}$ mol/l). Curves (a), (b), and (c) in this figure are the spectra of the solution taken before, 20 μsec after, and a few minutes after the flash excitation, respectively. Since curve (b) is identical with the spectrum of Py-N shown in Fig. 1, it is evident that Py-N is produced as a transient intermediate in the photoreaction of Py-N_3 in the oxygen-free benzene solution.

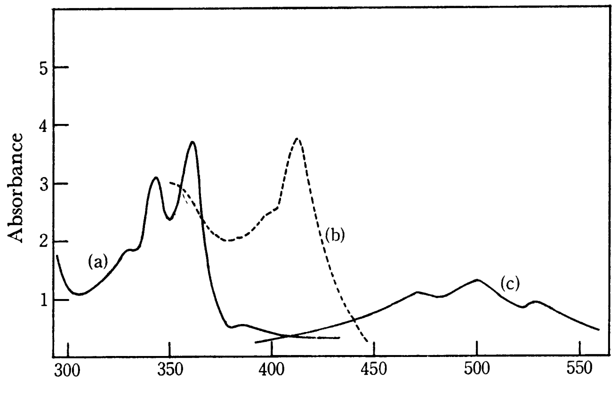

Fig. 3. The microphotometer traces of the absorption spectra measured by the aid of the flash photolysis technique with Py-N_3 in the oxygen-free benzene solution at room temperature.
(a): before a flash irradiation
(b): 20 μsec after a flash
(c): a few minutes after a flash

A final product was isolated from the solution by the aid of the active alumina-column chromatography technique. From the infrared spectrum, and also from a consideration of the electronic absorption spectrum to be described below, the final product was identified with 1,1′-*trans*-azopyrene (abbreviated hereafter to *trans*-Py-N=N-Py).

By stationary irradiation by a mercury lamp of Py-N_3 in an oxygen-free benzene solution at room temperature, we obtained two final products, dark-red and reddish-yellow crystals which were separated from each other by the aid of the active alumina-column chromatography technique in the dark.[17] The elemental analysis of the dark red sample[18] and the mass spectra[19] and infrared spectra[20] of both products show that they have the same chemical composition, Py-N=N-Py. The reddish-yellow crystal is easily converted into the dark red one by warming it from room temperature to ~100°C or by exposing it to sunlight. From these facts, it may be surmised that they are *trans*- and *cis*-Py-N=N-Py. The electronic absorption spectra observed for the dark-red and reddish-yellow samples are shown by curves (a) and (b) in Fig. 4, respectively. In view of the general feature of the electronic absorption spectra that the strongest band of the *trans*-isomer is stronger and appears in a longer-wavelength side than that of the *cis*-isomer, curve (a) in Fig. 4 is due to *trans*-Py-N=N-Py.[21] Since curve (c) in Fig. 3 is identical with this curve, the final product obtained by the flash irradiation of the oxygen-free benzene solution of Py-N_3 is identified with *trans*-Py-N=N-Py.

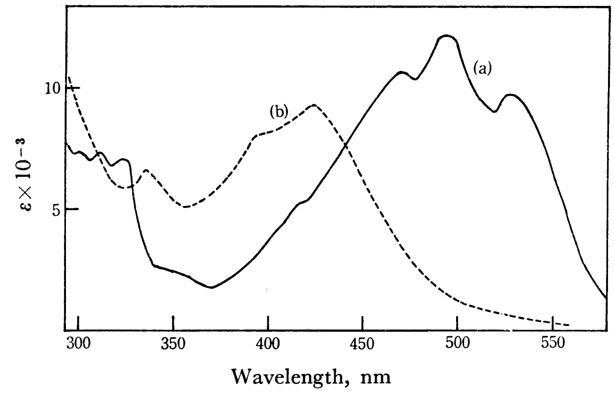

Fig. 4. The electronic absorption spectra of azopyrene.
(a): *trans*-azopyrene
(b): *cis*-azopyrene

The microphotometer curves of photographs obtained by flash photolysis measurements for Py-N_3 ($\sim 1\times 10^{-5}$ mol/l) in oxygen-containing benzene solutions are shown in Fig. 5. Curves (a), (b), and (c) in this figure are spectra observed for the solution before, 20 μsec after, and a few minutes after the flash excitation, respectively. Curve (b) in Fig. 5

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[16] Observed slight broadening in the ESR spectrum of Py-N shows that E is non-zero but is very small. The previously reported E values of nitrenes do not exceed 0.01 cm^{-1}.[3] Therefore, the D value of Py-N may be evaluated by assuming $E=0$ cm^{-1}. Wasserman *et al.* (E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964)) could reproduce well by simulation the observed ESR spectrum of methylsulfonylnitrene taking $g=2.0023$. Generally speaking, triplet states of organic molecules have the g value close to 2.0023.

[17] Toluene was used as a developing agent. After removing undecomposed Py-N_3, the dark red and reddish yellow parts of the column were cut. The products were extracted by tetrahydrofuran, recrystallized from toluene, washed by toluene and ethyl ether, and finally dried *in vacuo*. All these processes were done in the dark.

[18] Found: C, 88.31; H, 4.15; N, 6.59%. Calcd for $C_{32}H_{18}N_2$ (Py-N=N-Py) : C, 89.28; H, 4.21; N, 6.51%. A discrepancy between the found and calculated values for carbon may be due to a very small amount of water contained in the sample.

[19] Both isomers show a mass spectrum with a signal corresponding to molecular weight of 430.

[20] The N=N stretching vibrations were observed for these two isomers in nujol mull.

[21] H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press Inc., New York, N. Y. (1967), p. 504.

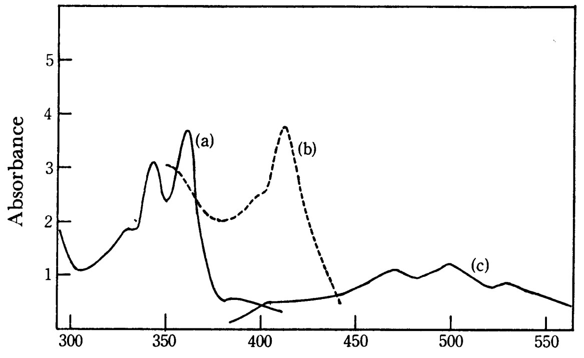

Fig. 5. The microphotometer traces of the absorption spectra measured by the aid of the flash photolysis technique with $Py\text{-}N_3$ in the oxygen-containing benzene solution at room temperature.
(a): before a flash irradiation
(b): 20 μsec after a flash
(c): a few minutes after a flash

is identical with the spectrum of Py-N given in Fig. 1. Therefore, we can conclude that Py-N is a transient intermediate in the photoreaction of $Py\text{-}N_3$ also in the oxygen-containing benzene solution.

In the case of the oxygen-containing benzene solution, we isolated two final products by the aid of column chromatography of active alumina. These procucts were identified with *trans*-Py-N=N-Py and 1-nitropyrene ($Py\text{-}NO_2$); the former was confirmed by comparing its electronic spectrum with that of *trans*-Py-N=N-Py given in Fig. 4(a), and the latter by comparing its electronic and infrared absorption spectra and its gas chromatogram with those of the authentic sample. Curve (c) in Fig. 5 consists of the absorption peaks due to *trans*-Py-N=N-Py given by curve (c) in Fig. 3 and the 400-nm peak of $Py\text{-}NO_2$.

Kinetic Study of the Reaction Process. From the identification of the transient intermediate and the final products, the following reaction mechanisms may applied to for the photoreaction of $Py\text{-}N_3$ in benzene:

for the oxygen-free benzene solution:

$$Py\text{-}N_3 \xrightarrow[\text{fast}]{h\nu} Py\text{-}N + N_2 \tag{1}$$

$$Py\text{-}N + Py\text{-}N \xrightarrow{k_2} Py\text{-}N{=}N\text{-}Py \tag{2}$$

for the oxygen-containing benzene solution:

$$Py\text{-}N_3 \xrightarrow[\text{fast}]{h\nu} Py\text{-}N + N_2 \tag{1'}$$

$$Py\text{-}N + Py\text{-}N \xrightarrow{k_2'} Py\text{-}N{=}N\text{-}Py \tag{2'}$$

$$Py\text{-}N + O_2 \xrightarrow{k_3} Py\text{-}NO_2 \tag{3}$$

From Eq. (2), the following equation can be derived for the oxygen-free benzene solution:

$$k_2t = \frac{1}{x} - \frac{1}{a} \tag{4}$$

where a and x are the concentrations of Py-N at the start of reaction (2) and at the reaction time, t, respectively, and k_2 is the rate constant for reaction (2). By replacing x and a by A_0 and A, respectively, the latter being the absorbances of Py-N observed at the start of the reaction and at the reaction time t, we can obtain the following equation:

$$k_2t = \frac{\varepsilon L}{A} - \frac{\varepsilon L}{A_0} \tag{4'}$$

Here, L is the length of the sample cell, and ε is the molar extinction coefficient of Py-N at an appropriate wavelength. In actuality, A, A_0, and ε were measured at 415 nm. The ε value at this wavelength was determined to be 3.0×10^4 from the electronic spectrum of Py-N shown in Fig. 1.

In view of the fact shown by Eq. (2) that one Py-N=N-Py molecule is produced from two Py-N entities, the following equation concerning the concentration of the final product can be obtained:

$$k_2t = \frac{\varepsilon' L}{2(A'_\infty - A')} - \frac{\varepsilon' L}{2A'_\infty} \tag{4''}$$

where A'_∞ and A' are the absorbances of *trans*-azopyrene at the final stage and at the reaction time t, respectively, and ε' is the molar extinction coefficient of *trans*-azopyrene. These quantities were measured at 470 nm, and ε' at this wavelength was determined to be 1.1×10^4 from the spectrum of the authentic sample shown in Fig. 4(a).

For the oxygen-containing benzene solution, equations similar to Eqs. (4), (4′), and (4″) hold approximately at the initial stage of the reaction. At the stage of the reaction latter than $t \sim 400$ μsec, the process shown by Eq. (3) becomes predominant. Since the concentration of oxygen in the solution is $\sim 10^{-2}$ mol/l,[22] much larger than that of Py-N ($\sim 10^{-5}$ mol/l), the following equations can be derived from Eq. (3):

$$\log x' = \log a' - k_3't' \tag{5}$$

$$k_3't' = \log A_0'' - \log A'' \tag{5'}$$

where t' is the reaction time, the origin of which is shifted by ~ 600 μsec from that of t, a', and x' are the concentrations of Py-N at $t'=0$ and at the reaction time t', respectively, and the corresponding absorbances are shown by A_0'' and A'', respectively. Furthermore, $k_3' = k_3[O_2]$, the concentration of oxygen dissolved in the solution at room temperature being represented by $[O_2]$.

For the purpose of confirming the above mechanism, the kinetic measurements were made for the reaction intermediate, Py-N, and also for the reaction products.

In the case of the photo-decomposition in an oxygen-free benzene solution, the time-dependences of the spectral intensities of Py-N at 415 nm and of Py-N=N-Py at 470 nm were measured by the photometric method until 1 msec after the flash irradiation. The result is shown in Fig. 6.

The plots of $(1/A)$ against t give a straight line, as is shown in Fig. 6(a). This means that Eq. (4′) holds well for the oxygen-free benzene solution. From the

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[22] The Chemical Society of Japan, "Kagaku Benran, Kisohen II," Maruzen, Tokyo (1966) p. 627.

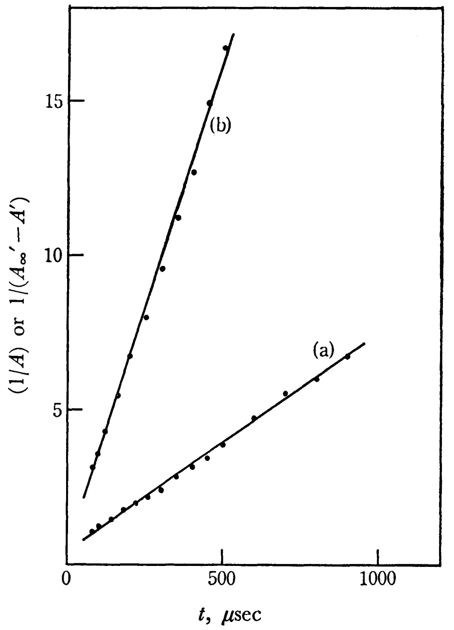

Fig. 6. The time-dependences of the absorption intensities of Py–N and Py–N=N–Py observed for the flash-irradiated Py–N_3 in the oxygen-free benzene solution at 23°C.
(a): $(1/A)$-t plots
(b): $1/(A'_\infty - A')$-t plots

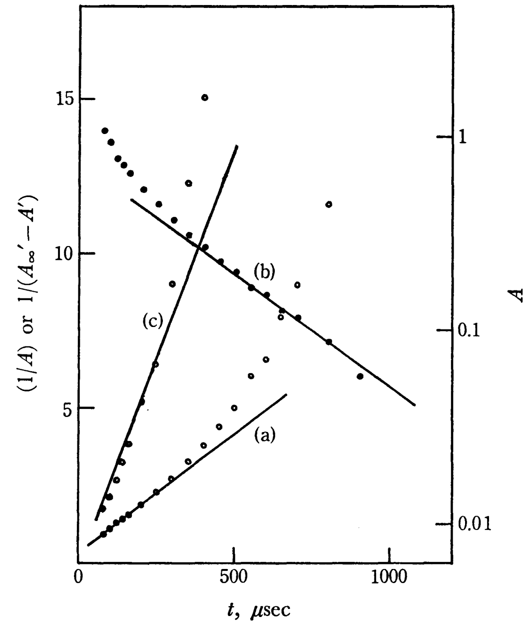

Fig. 7. The time-dependencies of the absorption intensities of Py–N and Py–N=N–Py observed for the flash-irradiated Py–N_3 in the oxygen-containing benzene solution at 23°C.
(a): $(1/A)$-t plots
(b): $\log A$-t plots
(c): $1/(A'_\infty - A')$-t plots

slope of the line, k_2 is determined to be $(2.1\pm0.2)\times 10^9 l\cdot\mathrm{mol}^{-1}\mathrm{sec}^{-1}$ at 23°C. The plots of $1/(A_\infty'-A')$ against t shown in Fig. 6(b) also give a straight line satisfying Eq. (4″), and the rate constant, k_2' is determined from its slope to be $(1.9\pm0.2)\times10^9 l\ \mathrm{mol}^{-1}\mathrm{sec}^{-1}$ at 23°C. This value obtained from the formation velocity of Py–N=N–Py coincides, within the limits of experimental error, with the rate constant obtained from the decay velocity of Py–N. The above-mentioned facts lead to the conclusion that the mechanism given by Eqs. (1) and (2) is satisfied for the photo-decomposition of Py–N_3 in an oxygen-free benzene solution.

Let us turn to the oxygen-containing benzene solution. A decrease in the absorbance, A, with the time was observed at 415 nm for Py–N in this solution; the result is shown in Fig. 7. Curves (a) and (b) in this figure show the $(1/A)$ *vs.* t and $(\log A)$ *vs.* t plots, respectively. These curves indicate that the decrease in A with time is of the second order at the earlier stage of the reaction and of the first order at the stage later than 600 μsec after the flash illumination. The former satisfies Eq. (4) with $k_2'=(2.1\pm0.2)\times10^9 l\ \mathrm{mol}^{-1}\mathrm{sec}^{-1}$ and the latter Eq. (5) with $k_3'=(1.4\pm0.2)\times10^3\ \mathrm{sec}^{-1}$.[23] According to Eq. (2′), the reaction product, *trans*-azopyrene, is formed parallel with the decay of Py–N. This formation process was also followed by measuring A' at 470 nm, and the $1/(A_\infty'-A')$ values were plotted against t; the result is shown by curve (b) in Fig. 7. This curve shows that the formation process follows Eq. (2′) with $k_2=(1.7\pm0.2)\times10^9 l\cdot\mathrm{mol}^{-1}\mathrm{sec}^{-1}$. This value agrees, within the limits of experimental error, with the value obtained from the time-dependence of A. The above facts support the reaction mechanism given by Eqs. (1′), (2′), and (3) for the photo-decomposition of Py–N_3 in the oxygen-containing benzene solution.

We should like to express our thanks to Dr. Masashi Imamura and Dr. Akira Kira, The Institute of Physical and Chemical Research, for their kindness in permitting us to use the flash-photolysis apparatus and for many valuable discussions. We are also greatly indebted to Dr. Kazuo Shibata and Dr. Teruo Ogawa, The Institute of Physical and Chemical Research, for their kindness in measuring the absorption spectra of the opaque benzene solutions at the liquid nitrogen temperature.

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[23] We also tried to obtain the rate constant for the oxygen-containing benzene solution of Py–N_3 according to another analytical method. From Eqs. (2′) and (3), we obtain

$$-\frac{dx}{dt} = k_2'x^2 + k_3'x \qquad \text{(a)}$$

From Eq. (a), the following relations can be derived

$$\frac{k_2'}{k_3'} + \frac{1}{x} = \left(\frac{k_2'}{k_3'} + \frac{1}{a}\right)e^{k_3't} \qquad \text{(b)}$$

or

$$\frac{1}{A} = \frac{1}{\varepsilon L}\left(\frac{k_2'}{k_3'} + \frac{1}{a}\right)e^{k_3't} - \frac{k_2'}{\varepsilon L k_3'} \qquad \text{(b′)}$$

Firstly we evaluated the value of k_3' according to Eq. (5′) and Fig. 7(b). Using this value of k_3', we plotted $1/A$ against $\exp(k_3't)$ and obtained a straight line, the intercept and the slope of which gave k_2'. The value was determined to be $2.15\times10^9 l\cdot\mathrm{mol}^{-1}\mathrm{sec}^{-1}$ and $2.08\times10^9 l\cdot\mathrm{mol}^{-1}\ \mathrm{sec}^{-1}$, respectively. Both agree with the values obtained from Eqs. (4′) and (4″): But we could not determine precisely a, the initial concentration of Py–N immediately after a flash, from the slope of this straight line. This is because k_2'/k_3' is much greater than $1/a$.