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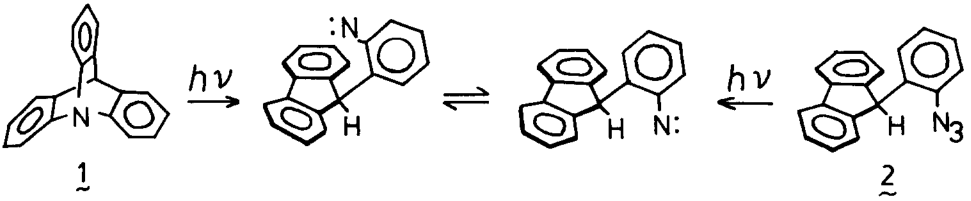
TIME-RESOLVED ABSORPTION SPECTROSCOPIC STUDIES ON THE REACTION OF CONFORMATIONALLY FIXED o-(9-FLUORENYL)PHENYLNITRENES

Shigeru Murata, Tadashi Sugawara, Nobuaki Nakashima, Keitaro Yoshihara,
and Hiizu Iwamura*
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Laser-flash photolysis studies have been carried out on a solution of ap- and sp-9-(2-azido-4,6-dimethylphenyl)fluorenes (3) in methanol-ether at 25°C. The rates of formation of azanorcaradiene (5) from ap-nitrene (4)ap, and of 9-methoxyfluorene (7) from o-quinoid intermediate (6) were determined. The deuterium isotope effect on the migration of the hydrogen is discussed.

Previously we had shown that chemical and spectroscopic behavior of o-(9-fluorenyl)phenylnitrenes generated from photorearrangement of 1-azatriptycene (1) and from photodecomposition of o-(9-fluorenyl)phenylazide (2) differed in some detail, and postulated that the difference should be ascribed to the different conformations of the nitrenes.[1,2] We were able to verify the working hypothesis by means of generation of the nitrenes with fixed conformations independently from the corresponding azides (3)ap and (3)sp.[3] During photolysis at 77 K in an EPA glass, 3ap showed the increase of an absorption at 340 nm, due to azanorcaradiene (5). On the other hand, a broad absorption was obtained at 554 nm from 3sp under these conditions. The latter absorption was assigned to o-quinoid species (6) formed by the migration of the hydrogen atom at the 9-position of the fluorene ring to the nitrenic center.[3] As an extension of these studies to the photoreactions of 3ap and 3sp in fluid solutions, we wish to report here the absolute rates of formation and decay of these intermediate species determined by the time-resolved absorption technique.

An undegassed methanol-ether (92:8) solution (4.8×10^{-5} M) of 3ap was irradiated by an excimer laser (351 nm, 12 ns, <50 mJ) at 25°C. When monitored at



340 nm, an absorption of A = 0.20 was detected at 100 ns after the laser pulse, and increased according to first-order kinetics. The rate constant of the increase of the absorption at 340 nm was obtained as 7.1 (± 0.2) x 10^5 sec^{-1}, which was assigned to the rate of formation of the azanorcaradiene (5), k_{add}. We already reported that the formation of azanorcaradiene by the photolysis of 1 had the rate constant in the order of 10^6 sec^{-1}.[2] The rate obtained here is close to this value, but slightly smaller. It probably is due to decrease of electrophilicity of the nitrene generated from 3ap because of the substitution of methyl groups.

Next we monitored the reaction at 550 nm where o-quinoid intermediate (6) was expected to absorb. No absorption was observed even after 2 μs. The result indicates that under photoirradiation at 25°C the isomerization process from 3ap and 4ap to the corresponding sp rotamers should be too slow to compete with the formation of the azanorcaradiene (5).

Turning now to the photolysis of 3sp under similar conditions, we note that an absorption (A = 0.12) at 550 nm was observed right after the laser pulse (shorter than 20 ns), and did not changed even after 4.5 μs. These results show the o-quinoid species (6) was formed at a rate faster than 10^8 sec^{-1} and disappeared at a rate slower than 2 x 10^5 sec^{-1}. The decomposition rate was measured by the use of a steady light source as a monitor light, and it was found to be 2.6 (± 0.2) x 10^3 sec^{-1}. We obtained 9-methoxy-9-(2-amino-4,6-dimethylphenyl)fluorene (7)[4] from the photoirradiation of 3sp in methanol-ether in a parallel experiment by low-pressure mercury lamp. So the value obtained here was assigned to the pseudo first-order rate constant for the reaction of o-quinoid species (6) with methanol to give 7.

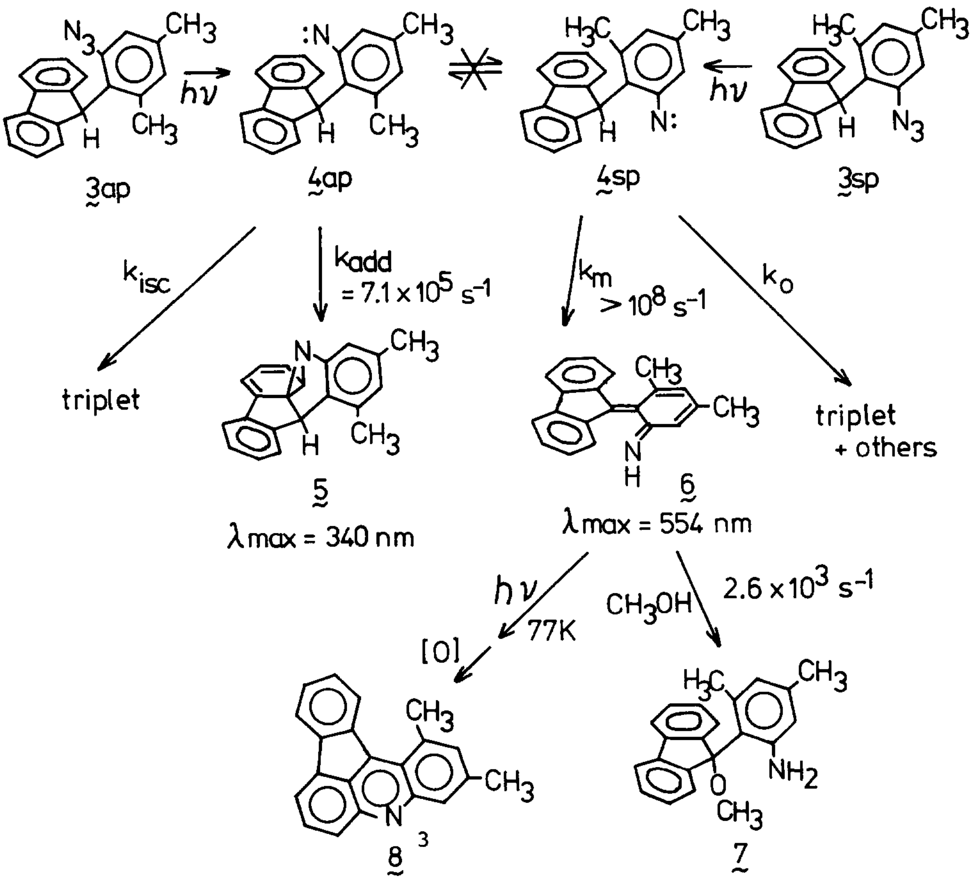
It is not so surprising that the rate of formation of 6 was too fast to be measured by the use of the pulsed laser on a nanosecond time scale. We already reported that at cryogenic temperature the 1,4-migration of the hydrogen at 9-position of fluorene in 4sp was exclusive and intersystem crossing to triplet 4sp could not compete.[3] No ESR signal of triplet nitrene was found in the photolysis of 3sp.

The 9-deuterio derivative (3')sp, which provided an ESR signal owing to retardation of the migration rate by the deuterium isotope effect,[3] was irradiated under these conditions. The rate constant was still too fast to be measured. The failure is not unreasonable since the deuterium isotope effect could not be so large at 25°C as at cryogenic temperature (vide infra).

However in spite of the same concentration of the material, the absorbance at 550 nm obtained by irradiation of 3'sp was 0.082, which was 68 % of 3sp. Assuming that the concentration of o-quinoid species (6) is proportional to the fraction among the whole reaction paths, this result is expressed in terms of following equation.

$$\frac{k_m^D}{k_m^D + k_o} \cdot \frac{k_m^H + k_o}{k_m^H} = 0.68$$

In this equation, k_m^H and k_m^D show the rates of 1,4-migration of 3sp and 3'sp, respectively, and k_o means the total rate of other reaction rates, which seem not to be affected by the change of atom at 9-position. In another experiment, we obtained that $k_m^H / (k_m^H + k_o)$ was 0.44 from the product distributions of the photoreactions of 3sp in methanol-ether (12:1) in the presence of sodium methoxide.[5] Using this value, we obtained the deuterium isotope effect of 1,4-migration at 25°C as $k_m^H / k_m^D = 1.84$.[6]



A normal primary isotope effect was obtained in a fluid solution at 25°C. On the other hand the remarkable effect observed at cryogenic temperature should be understood as a tunneling mechanism. At any rate a large difference in reactivity of ap and sp azides was demonstrated even at 25°C and absolute rate constants of some processes were determined.[7]

References and Notes

1) T.Sugawara, H.Iwamura, J. Am. Chem. Soc., 102, 7134 (1980).
2) T.Sugawara, N.Nakashima, K.Yoshihara, H.Iwamura, J. Am. Chem. Soc., 105, 858 (1983).
3) S.Murata, T.Sugawara, H.Iwamura, J. Am. Chem. Soc., 105, 3723 (1983).
4) Spectroscopic data of 7 are as follows. Colorless oil: MS, m/e 315 (M^+, 67), 283 ($M^+ - CH_3OH$, 86), 282 (100); ^1H NMR ($CDCl_3$) δ 1.16(s,3H), 2.15 (s,3H), 2.77(s,3H), 6.12(s,1H), 6.45(s,1H), 7.2 - 7.7(m,8H); IR (Nujol) 3470, 3360, 1065 cm^{-1}.
5) The experimental details will be described in a full paper.
6) Recently an unusually large deuterium isotope effect was reported for hydrogen transfer from solvent to some radicals even at 65°C. (P.S.Engel, W.Chae, S.A.Baughman, G.E.Marschke, E.S.Lewis, J.W.Timberlake, A.E. Luedtke, J. Am. Chem. Soc., 105, 5030 (1983).)
7) The product analyses of these nitrenes in fluid solutions are under way in our laboratry. The absolute rates obtained here would be employed for understanding the reaction mechanisms.

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