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Laser Flash Photolysis of 3-(4-Biphenylyl)-2H-azirine. Direct Detection of Nitrile Ylide

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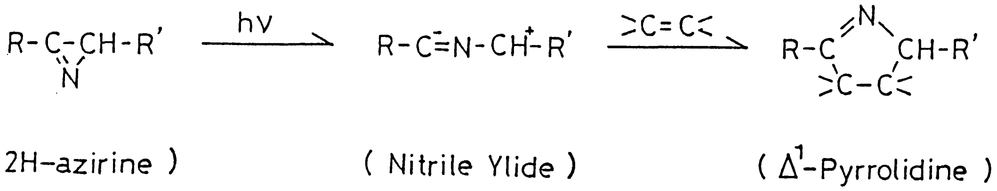
Laser flash photolysis of 3-(4-biphenylyl)-2H-azirine (AZ) has been investigated in cyclohexane. Two kinds of transient species; that is, a triplet state (T_1) of AZ and a nitrile ylide (NY) were detected. Both transient species have λ_{max} at 410 nm and the decay rates were 6.7×10^5 s^{-1} (T_1) and 8×10 s^{-1}(NY), respectively. Reaction rate constants of NY with propanone and acrylonitrile were also determined.

Reactions of nitrile ylide have been of increasing interest in connection with the synthesis of various heterocyclic compounds.1) This species is one of 1,3-dipoles and is very reactive toward a wide variety of dipolarophiles such as olefins, ketones, and esters to form five-membered heterocyclic rings. Padwa2) and Schmid3) have shown individually that 2H-azirines undergo easily ring opening on photoirradiation to afford nitrile ylides which react with olefin to give pyrrolidines (Eq. 1).

Nitrile Ylide thus formed was detected by the irradiation of arylazirine in a rigid matrix at 77 K by Schmid and coworkers.4) However, the reaction dynamics of nitrile ylides were not clarified because of the experimental limitations for the stational photoirradiation at low temperature. In the present work, we studied the laser flash photolysis of 3-(4-biphenylyl)-2H-azirine (AZ, R = 4-biphenyl, R′ = H)5)



(1)

to elucidate the reaction mechanism of the nitrile ylide on the basis of the direct measurement.

Laser flash photolysis of AZ was carried out in argon saturated cyclohexane (1.0×10^{-3} mol dm^{-3}) by using a Xe-Cl excimer laser apparatus (λ: 308 nm, pulsewidth: 15 ns). Figure 1 shows transient absorption spectra recorded at various times after the flash and decay traces monitored at 410 nm. The traces indicate the presence of two kinds of transient species with different lifetimes which are indicated as A (short-lived) and B (long-lived) in Fig. 1. The decay behavior of these species follows first-order kinetics and the rate constants for A and B are 6.7×10^{5} s^{-1} and 8×10 s^{-1}, respectively. The absorption spectrum of A which is presumed by the difference spectrum as shown by a dotted line in Fig. 1 was similar to that of B (spectra 2 and 3), and both have the same absorption maximum around 410 nm. In the presence of oxygen, A was quenched whereas B was not affected.

The photolysis of AZ was carried out in the presence of propanone as a triplet sensitizer. The results are shown in Figs. 2 and 3. The rise of transient species with a λ_{max} at 410 nm was observed at propanone concentrations higher than 0.2 mol

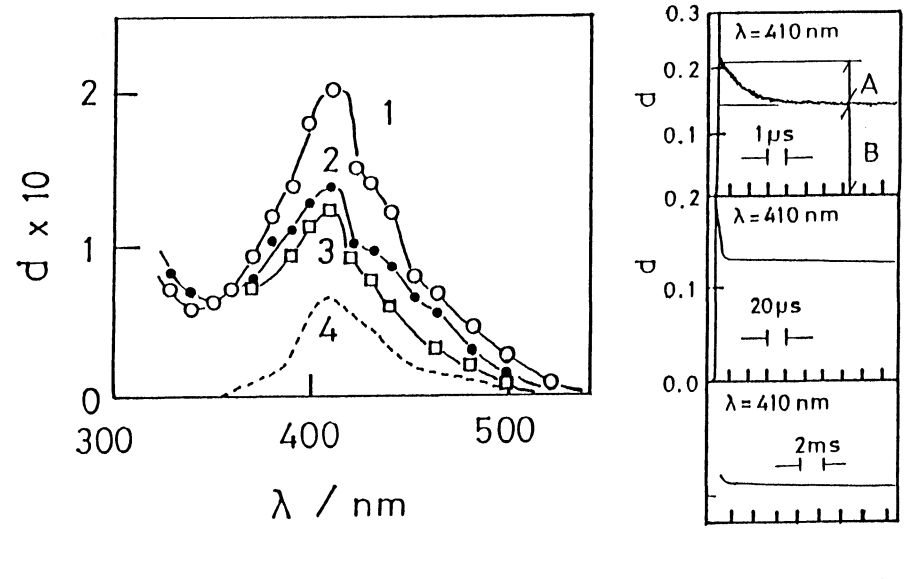


Fig. 1. Transient absorption spectra and the decay traces. Recorded at 0.1 (1), 6 (2), and 160 μs (3) after the flash. Dotted line shows the difference spectrum (1 - 2). [AZ] = 1.0×10^{-3} mol dm^{-3} in cyclohexane.

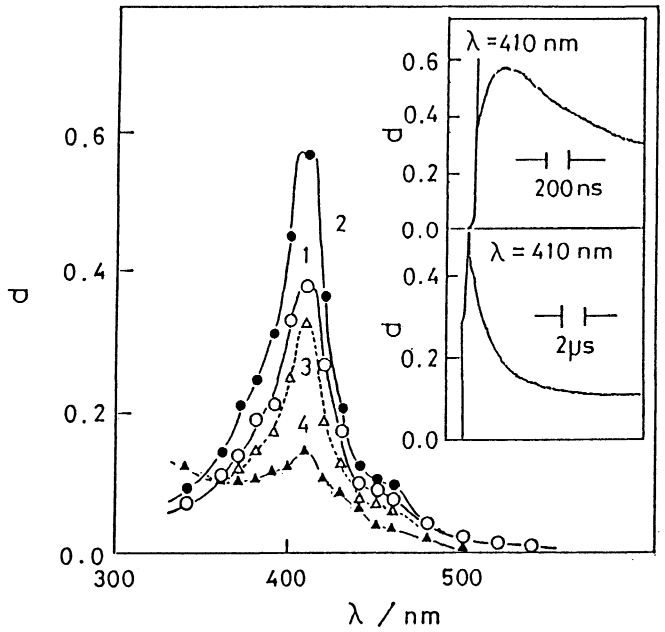


Fig. 2. Transient absorption spectra and digitizer traces measured in the laser flash photolysis of AZ in the presence of propanone. Recorded at 0.1 (1), 0.35 (2), 1.65 (3), and 6 μs (4) after the flash. [AZ] = 1.0x10^{-3} mol dm^{-3}, [Propanone] = 0.5 mol dm^{-3} in cyclohexane.

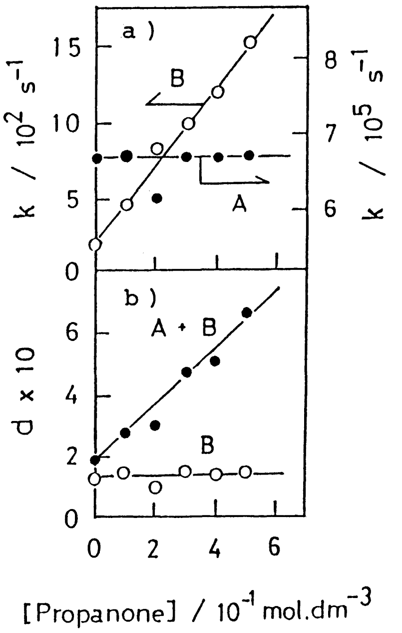


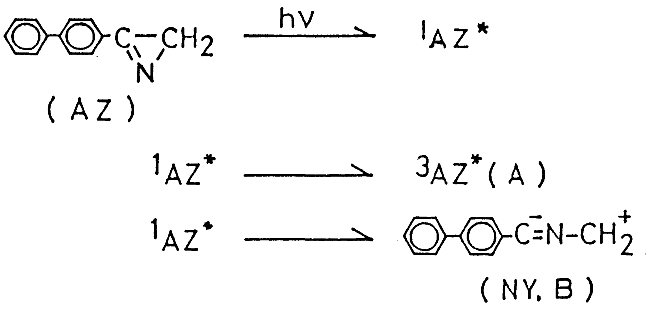
Fig. 3. Effect of propanone on the transient species [decay rate (a) and absorbance (b); short-lived (A) and long-lived species (B)].

dm^{-3}. The decay behavior of this band indicates the presence of two transient species with λ_{max} at 410 nm which correspond to the species A and B. The yield of A increased with increasing the concentration of propanone, while the yield of B was not affected by the propanone concentration. The decay rate of B, which was determined at ms time region, increased with increasing the propanone concentration. Based on the linear plot in Fig. 3a, the rate constant of the reaction between B and propanone was obtained; 2.5 x 10^3 dm^3 mol^{-1} s^{-1}.

On the basis of the triplet sensitization and chemical reactivities toward oxygen and propanone described above, the species A and B can be assigned to a triplet state of AZ and a nitrile ylide (NY), respectively. NY is known to react with propanone$^{6)}$ and an electrondeficient olefin such as acrylonitrile (AN).$^{7)}$ The photolysis of AZ was, therefore, carried out in the presence of AN. The decay rate of B increased with increasing the concentration of AN, although the initial absorbance of B (λ_{max} = 410 nm) was not affected (Fig. 4). The rate constant was determined to be 2.3 x 10^6 dm^3 mol^{-1} s^{-1}.

In conclusion, the present results indicate that the excited singlet state of

AZ decays rapidly into NY or the triplet state of AZ. The lifetime of the triplet AZ is 1.5 μs. NY undergoes 1,3-dipolar addition with propanone and AN with the rate constants of 2.5×10^3 dm^3 mol^{-1} s^{-1} and 2.3×10^6 dm^3 mol^{-1} s^{-1}, respectively; as shown in Scheme 1.



Scheme 1.

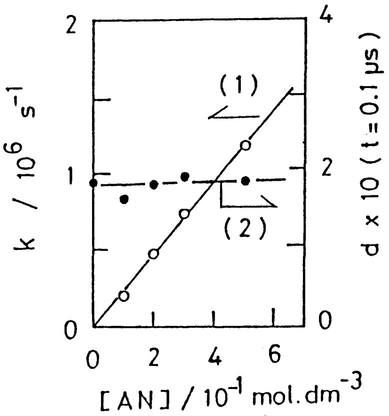


Fig. 4. Effect of AN on the trasient species [decay rate of the long-lived species, B (1) and the absorbance at t = 0.1 μs (2)].

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5) Pale yellow crystals; mp 73.5-74.2°C; Elementary analysis, Found: C, 86.87%; H, 5.74%; N, 7.21%. Calcd for $C_{14}H_{11}N$: C, 87.01%; H, 5.84%, N, 7.15%; ^1H-NMR ($CDCl_3$, TMS) δ (ppm) 1.81 (2H, s), 7-8 (biphenyl, m); UV (cyclohexane) λ (nm) 268.8 (1.99×10^5 dm^2 mol^{-1}).

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