

MATRIX INFRARED STUDY OF THE PHOTOLYSIS PRODUCTS OF 2,3-PYRIDINE DICARBOXYLIC ANHYDRIDE (2,3-PDA): A SEARCH FOR 2,3-DIDEHYDROPYRIDINE

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Abstract. Photolysis of 2,3-PDA (1) in N₂ or Ar matrices leads to loss of CO₂ preferentially at C2 and formation of (2), whose end product is (3). In contrast to mild photolysis of 3,4-PDA, which yields 3,4-DHP, this mechanism precludes the intermediacy of 2,3-DHP (6) in the photolysis of 2,3-PDA.

Didehydropyridines (DHPs, commonly called pyridynes) have been the most studied of all known didehydroheteroarenes (or hetarynes).¹ They have been proposed as likely intermediates in many organic reactions, principally those involving cycloaddition, cine-substitution, or tele-substitution.

Among the six possible DHP isomers, 3,4-DHP is the most firmly established.¹ We recently have reported the infrared spectrum of 3,4-DHP generated *via* mild photolysis ($\lambda > 340$ nm) of 3,4-PDA in N₂ or Ar matrices at 13 K.² The C≡C stretching frequency was observed at 2085 cm⁻¹ along with ten additional peaks in the range 450 - 1600 cm⁻¹. Subsequent irradiation with $\lambda > 210$ nm light immediately decomposed 3,4-DHP into HCN (2101 cm⁻¹) and diacetylene (2181 cm⁻¹), or acetylene (744 cm⁻¹) and cyanoacetylene (2236 cm⁻¹) as a result of alternative two-bond scissions. The IR bands assigned to 3,4-DHP disappeared upon annealing at 55 K. However, we found no evidence of 2,3-DHP from the photolysis of 2,3-PDA; the matrix IR spectra of the photolyzed products contained three groups of new bands whose growth and decay patterns are strongly dependent on the photolysis wavelengths and irradiation time.

Table 1. IR bands resulting from the photolysis of 2,3-PDA in an N₂ matrix at 13 K.

product	irradiation λ (nm)	observed frequencies (cm ⁻¹)
X	$\lambda > 340, 300$	2185, 2095
Y	$\lambda > 300$	2154, 1015, 876
Z	$\lambda > 340, 300, 210$	3322, 3317, 3110, 2968, 2257, 2235, 2130, 2118, 2109, 1628, 1038, 896, 763, 730

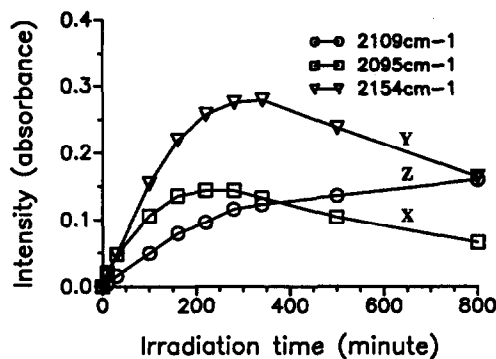


Figure 1. Three types of growth-curve when 2,3-PDA is irradiated with $\lambda > 300$ nm.

When matrix isolated 2,3-PDA was irradiated (200 W Hg-Xe arc lamp) with $\lambda > 300$ nm light for 14 hours, growth-curves for each newly appearing band revealed that at least three products have been formed in the matrix. As shown in Figure 1, compound Z grows continuously and remains as the most stable product. Compound Y grows faster than compound Z, but after a certain period of time (~330 min) it slowly begins to decay. The third type of compound, X, is very similar to Y, but begins to decay earlier (~210 min). The bands of X, Y and Z are listed in Table 1.

As summarized in Table 1 and Figure 2, compounds X, Y and Z are also distinguished by their photochemical behavior. Spectra (a), (b) and (c) in Figure 2 were obtained respectively from the photolysis of 2,3-PDA in an N_2 matrix with $\lambda > 340$ nm filter for 10 hours, subsequently 2 hours with $\lambda > 300$ nm filter, and 1.5 hours more with $\lambda > 210$ nm filter. Similar spectra were observed when samples were separately irradiated over these wavelength regions. While the bands due to Z appear in all spectra, those due to Y are evident only in spectrum (b); bands due to X appear in both spectra (a) and (b). The bands of X and Y are stable upon annealing, but completely vanish upon shorter wavelength irradiation. Compound Y does not interconvert to X photochemically. However, it is not certain whether compound Y is independently formed from 2,3-PDA or from compound X.

Compound Z is readily identifiable as β -ethynylacrylonitrile, (3) in Scheme 1. Compound X, which has a characteristic $=C=C=O$ band at 2095 cm^{-1} and $-N\equiv C$ absorption at 2185 cm^{-1} , may be attributable to (2).^{3,4} Compound Y is not easy to identify, but (5) is the most plausible structure. Thus, photolysis of 2,3-PDA preferentially cleaves CO_2 at C2 and forms intermediate (2), whose final product is β -ethynylacrylonitrile. It is unlikely that 2,3-DHP is involved in the formation of (3) from 2,3-PDA as was claimed by Dunkin and MacDonald⁵ and by Cava *et al.*⁶ This result suggests that if a chosen precursor of the heterayne loses its substituent

to form the first radical center adjacent to the heteroatom, the ring-opening process takes place before the necessary second radical center can form.

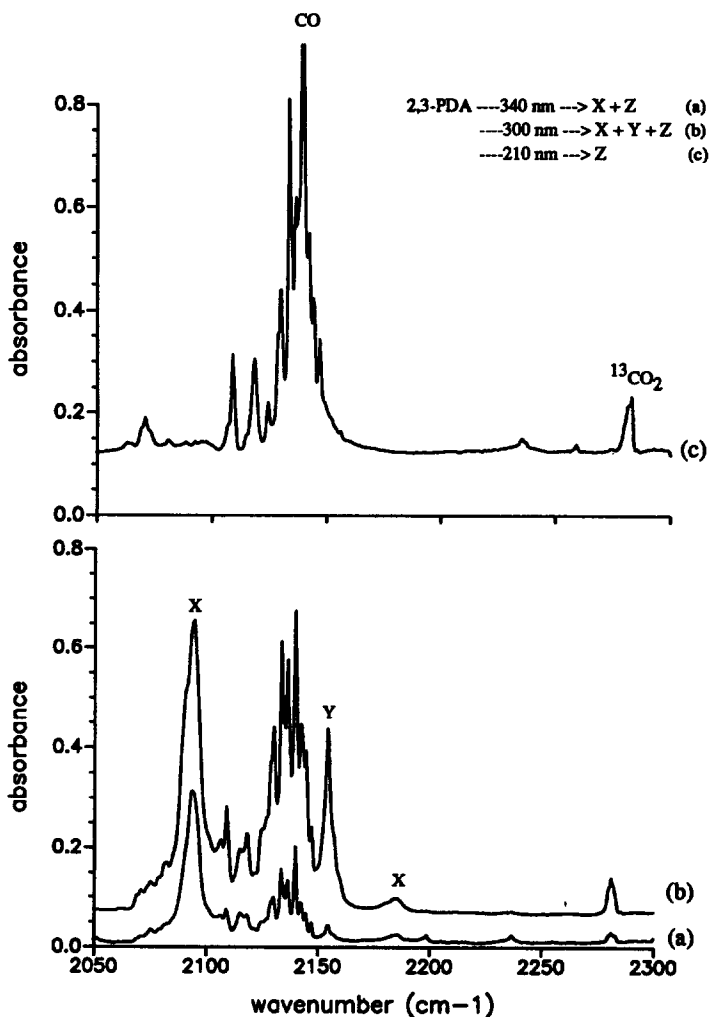
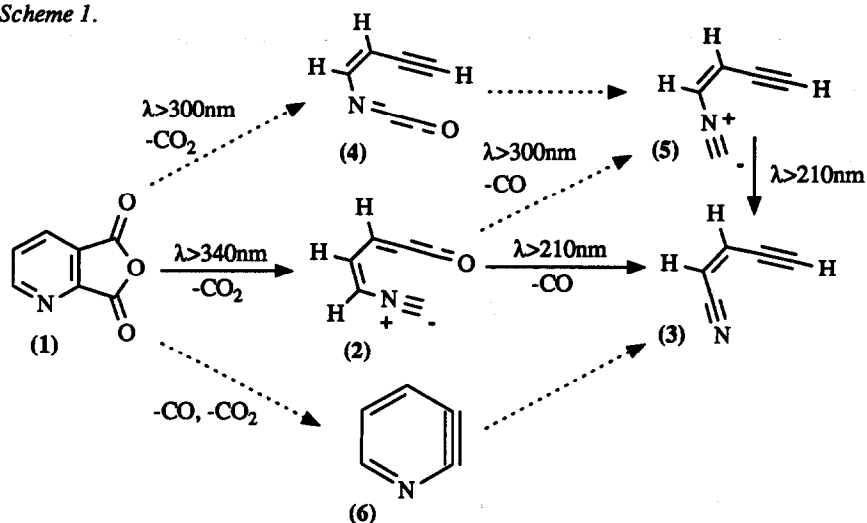


Figure 2. IR spectra (Bomem DA3 FTIR, 1 cm^{-1} resolution) in the $2050 - 2300\text{ cm}^{-1}$ region of the photolysis products from 2,3-PDA in an N_2 matrix at 13 K; (a) 10 hr. photolysis through water and $\lambda > 340\text{ nm}$ filter; (b) 2 hr. photolysis after (a) with $\lambda > 300\text{ nm}$ filter; (c) subsequent 1.5 hr. photolysis through $\lambda > 210\text{ nm}$ filter.

Scheme 1.



Recent *ab-initio* studies on the six DHP isomers at the GVB level with a 3-21G basis set predict that the 2,3-DHP singlet ground state lies 7.4 kcal/mole higher in energy than 3,4-DHP and is the second most stable among the six DHPs.⁷ The harmonic C≡C stretching frequency of 2,3-DHP, if it is ever formed in a matrix isolation experiment, is predicted by the same calculation to be observed about 40 cm⁻¹ below that of 3,4-DHP.

References

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