CHEMISTRY LETTERS, pp. 1121 - 1124, 1984. © The Chemical Society of Japan 1984

KrF LASER PHOTOLYSIS AND RADIOLYSIS OF 4-VINYLPYRIDINE

Satoshi MATSUNUMA,† Tadahiro ISHII,† Takashi HANDA,† and Shigeyoshi ARAI*

The Institute of Physical and Chemical Research,
Hirosawa, Wako, Saitama 351
†Department of Applied Chemistry, Science University of Tokyo,
Kagurazaka, Shinjuku-ku, Tokyo 162

The irradiation of alcoholic solutions of 4-vinylpyridine (VP) with KrF laser pulses produced a transient absorption with a large peak at 335 nm and a small one at 500 nm. The absorption is attributed to a hydrogen-adduct of VP. The radiation chemical results obtained with VP are consistent with the assignment.

Rare gas halide excimer lasers are light sources fit for photolyses of fundamental compounds, because the lasers provide short and high-power pulses in the UV region. Therefore, excimer laser flash photolysis has been increasingly applied to photochemical studies of a variety of fundamental chemical compounds. Although luminescences of pyridine and its derivatives have been examined extensively,[1,2] there is only a limited knowledge of their photochemical processes. We have carried out KrF laser photolyses of pyridine derivatives in methanol and methylcyclohexane solutions and observed transient absorptions for 4-vinylpyridine (VP). This paper reports photochemical processes of VP, together with the results obtained with the pulse radiolysis and low-temperature γ-radiolysis of the same compounds.

The apparatus and procedures for KrF laser flash photolysis are essentially the same as the previous paper.[3] The light source was a Tachisto TAC II system 100 excimer laser, which generated the 248-nm light pulse with a duration of about 20 ns and a maximum power of 200 mJ. The source of analyzing light was a Ushio 500 W xenon lamp. The laser and analyzing light beams passed through a rectangular quartz cell in the same direction (optical path length, 1 cm; cell volume, 5 cm^3). A glass bulb was connected to the cell for evacuation of solutions. Signals from a photomultiplier were stored in a Kawasaki Electronica KR-3250 transient memory and displayed on a X-Y recorder as a function of time. The apparatus and procedures for pulse radiolysis have been described previously.[4] The electron beam pulse used had a duration of 0.5 μs. The γ-irradiated matrix isolation experiment at low temperatures was performed in a conventional method.[5] The optical cell made of Suprasil quartz had a path length of 0.1 cm. 4-Vinylpyridine obtained from Tokyo Kasei Co. was distilled on pellets of sodium hydroxide under reduced

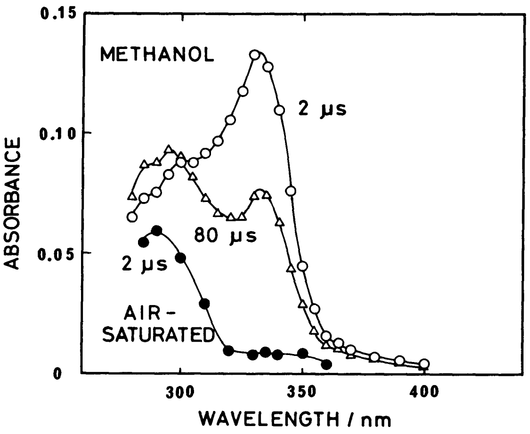

Fig. 1. Transient spectra obtained with KrF laser photolysis of methanol solution of 2 X 10^{-4} mol dm^{-3} VP in the absence or presence (solid circles) of air.

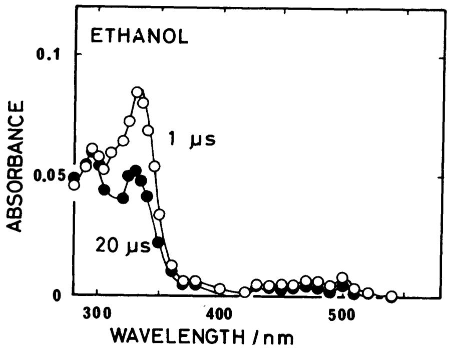

Fig. 2. Transient spectra obtained with KrF laser photolysis of deaerated ethanol solution of 0.9 X 10^{-4} mol dm^{-3} VP.

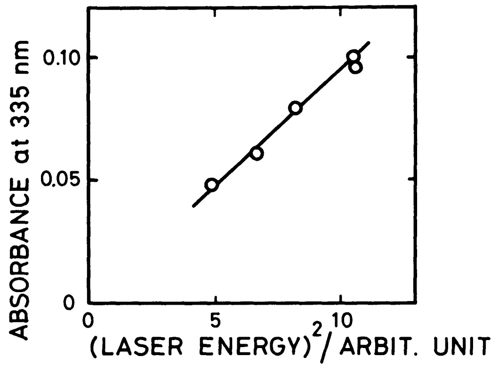

Fig. 3. Laser energy dependence of absorbance at 335 nm. Solution, 0.9 X 10^{-4} mol dm^{-3} VP in methanol.

pressure. Methanol and ethanol (the highest grade) purchased from Wako Junyaku Co. were used without purification. Tetrahydrofuran (THF) and 2-methyltetrahydrofuran (MTHF) from Wako Junyaku Co. were fractionally distilled and stored in contact with Na and K alloy.

Figures 1 and 2 present the transient absorption spectra obtained with KrF laser photolysis of VP in methanol and ethanol solutions, respectively. Two absorbing species with different lifetimes were observed in both solutions; one has a sharp band at 335 nm and the other a band around 295 nm. The former disappeared more rapidly as compared with the latter. The addition of air to the solutions completely removed the absorption at 335 nm, leaving the absorption at 295 nm almost unchanged. The weak absorption was observed around 500 nm in both solutions; the decay behavior was the same as that of the absorption at 335 nm. Figure 3 shows the laser energy dependence of the initial absorbance monitored at 335 nm. The linear relation between absorbance and square of laser energy suggests that the absorbing species is produced via a two-photon process.

The pulse radiolysis of ethanol and THF solutions of VP yielded essentially the same transient spectra as the photolysis of alcoholic solutions, as shown in Fig. 4. In order to obtain information of primary products, the γ-irradiated matrix isolation experiment was carried out for MTHF and EPA (mixed solvent of diethylether, isopentane, and ethanol) solutions of VP at 77 K and elevated temperatures. The results are presented in Fig. 5. The spectrum with maxima at 370, 385, 525, and 550 nm for the MTHF solution at 77 K is attributed to the anion radical of VP produced in electron attachment.6) However, the spectrum observed after warming the solution has the main peak at 340 nm and small ones at 475 and 505 nm, being almost identical with those obtained with the photolysis of alcoholic solutions. In the EPA

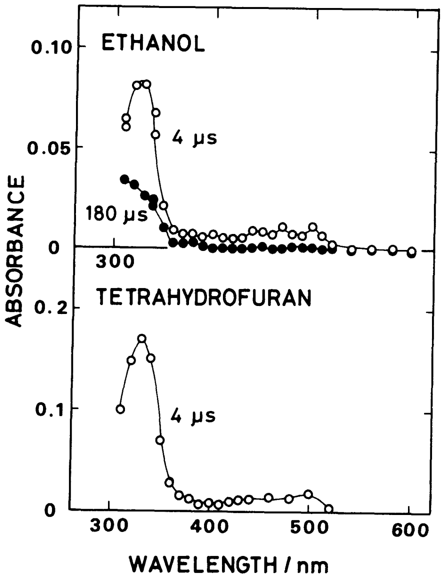

Fig. 4. Transient spectra obtained with pulse radiolysis of ethanol and THF solutions of about 5 X 10^{-4} mol dm^{-3} VP. Pulse duration, 0.5 μs.

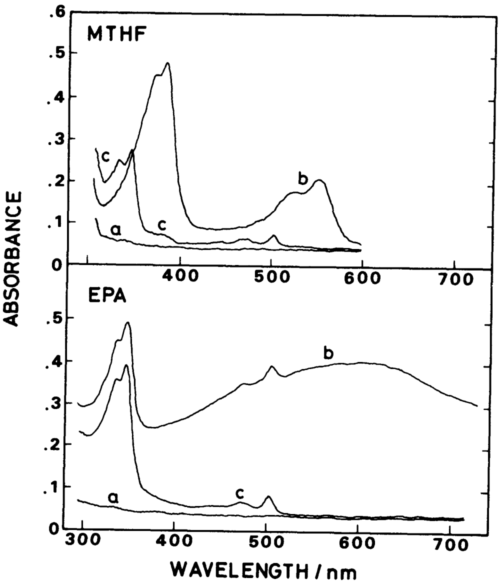

Fig. 5. Absorption spectra for γ-irradiated MTHF and EPA solutions of about 1 X 10^{-2} mol dm^{-3} VP at 77 K. Spectrum a, before irradiation; b, after irradiation; c in MTHF, after warming; c in EPA, after photobleaching with visible light.

solution at 77 K, the broad absorption due to the trapped electron is supperposed on the spectrum observed after warming the MTHF solution. The illumination of the EPA solution with visible light bleached the absorption due to the trapped electron, as shown in Fig. 5.

In the present experiment, we observed the transient absorbing species with an intense band at 335 nm and weak ones at 475 and 505 nm in both photolysis and pulse radiolysis. The same species was also produced in γ-radiolysis of the EPA solution at 77 K and in the warming process of the γ-irradiated MTHF solution.

It is well-known that γ-radiolysis of glassy MTHF solutions of aromatic compounds at 77 K results in the formation of solute anion radicals via electron attachment.5) The spectrum obtained with the γ-irradiated MTHF solution of VP is in good agreement with the previous observation and attributed to the anion radical of VP.6) Upon warming the MTHF solution, a new absorbing species with bands at 335, 475, and 505 nm is produced in parallel with the disappearance of the anion radical. In γ-irradiated MTHF solutions at 77 K, protonated MTHF is expected to exist as a counter ion of the anion radical.7) The ion recombination between these ions takes place, when the solvent rigidity is decreased by warming, giving a neutral hydrogen-adduct as a product. Thus, the new absorption can be assigned to the hydrogen-adduct of VP. The transient absorptions observed in pulse radiolysis of ethanol and THF solutions also correspond to the hydrogen-adduct. In the ethanol solution, the adduct arises from the rapid protonation reaction of the anion radical with ethanol, where the anion radical is produced by the reaction of the solvated electron with VP.8) In the THF solution, ion recombination proceeds very rapidly at room temperature, although the anion radical of VP is produced at an earlier stage. The counter ion is, of course, protonated THF. The absorptions due to the hydrogen-adduct and the trapped electron can be seen in the spectrum for the γ-irradiated EPA solution at 77 K, while that of the anion radical is lacking. This fact suggests that the anion radical reacts with ethanol in the EPA solution at a low temperature such as 77 K.

Since the ionization potential of VP in solutions may be considerably lower than that of pyridine, i.e., 9.23 eV in the gas phase,[9)] the two-photon process induced by KrF laser pulses results in ionization of VP in alcohols. The ejected electron, which forms instantaneously the solvated electron in alcohols, adds to VP and the resulting anion radical immediately changes into a hydrogen-adduct by its protonation reaction with a solvent molecule. The cation radical of VP produced in the photo-ionization probably abstracts a hydrogen atom from an alcohol molecule, giving a stable pyridinum ion. The long-lived species with a band at 295 nm remains unidentified in this study. In the hydrogen-adduct, the proton can add to either the nitrogen atom in the ring or the β-carbon atom in the vinyl group. The nitrogen atom might be favored in the protonation, because the anion radical of VP has the highest electron density at the position of nitrogen.[10)] However, the observed spectrum resembles the spectrum of an α-methylbenzyl radical closely in shape.[11)] The position of the proton addition is not conclusive at this moment.

References

1) I. Yamazaki and H. Baba, J. Chem. Phys., 66, 5826 (1977).
2) I. Yamazaki, K. Sushida, and H. Baba, J. Chem. Phys., 71, 381 (1979).
3) K. Kasama, A. Takematsu, and S. Arai, J. Phys. Chem., 86, 2420 (1982).
4) A. Kira, S. Arai, and M. Imamura, J. Chem. Phys., 54, 4890 (1971).
5) W. H. Hamill, "Radical Ions," ed by E. T. Kaiser and L. Kevan, John Wiley, New York (1968), p. 321.
6) C. David, P. Janssen, and G. Geuskens, Spectrochim. Acta, Part A, 27, 367 (1971).
7) M. Hoshino, S. Arai, and M. Imamura, Radiat. Phys. Chem., 15, 377 (1980).
8) S. Arai and L. M. Dorfman, J. Chem. Phys., 41, 2190 (1964).
9) K. Watanabe, J. Chem. Phys., 26, 542 (1957).
10) N. K. Ray and K. K. Sharma, Theoret. Chim. Acta, 22, 403 (1971).
11) S. Noda, Y. Fujii, and H. Yoshida, Bull. Chem. Soc. Jpn., 50, 2226 (1977).

(Received April 18, 1984)