Photochemical Reactions of Nicotinic Acid in Aqueous and Ethanol Solutions

Fumikatsu TAKEUCHI, Takako FUJIMORI and Akira SUGIMORI

Department of Chemistry, Faculty of Science and Technology, Sophia University, Kioi-cho, Chiyoda-ku, Tokyo

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In a previous paper, photodecarboxylation of pyridinecarboxylic acids was reported.[1] The present paper deals with pH dependence of the photoreaction of nicotinic acid in aqueous and ethanol solutions.

Nicotinic acid was irradiated with a low pressure mercury lamp at room temperature in 5×10^{-4}M solution. The acidity of the solution was adjusted with acetate or phosphate buffer. Before irradiation nitrogen was bubbled to eliminate oxygen in the solution. Photo-products were separated by anion exchange chromatography (column; Dowex-1 formate, eluent; formic acid) and identified by elementary analysis, IR, NMR and comparison with authentic specimens synthesized.

Nicotinic acid shows manifold photoreactivity depending on solvent and acidity. In Scheme 1 are summarized photoreactions of nicotinic acid. In Fig. 1 is shown pH dependence of the photoreaction in aqueous solutions, together with pH dependence of λ_{max} of UV spectra of nicotinic acid.

The cationic form of nicotinic acid undergoes photo-hydroxylation at 2-position.[2] The anionic form is photoreactive in lower pH region to give 2-(3-pyridyl-)pyridine-5-carboxylic acid (decarboxylative bipyridyl formation), while this form is stable in alkaline solution.

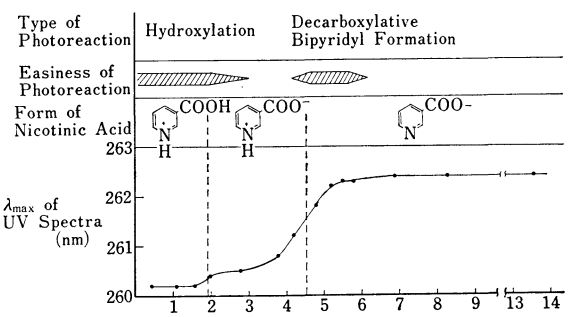
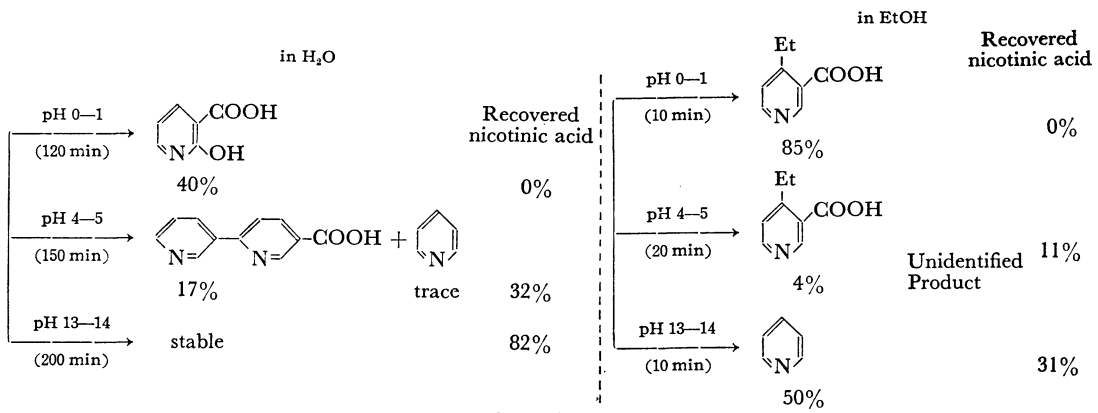


Fig. 1. pH dependence of the photoreaction and λ_{max} of nicotinic acid in aqueous solutions.

The photoreactivity of nicotinic acid in ethanol solutions differs from that in aqueous solutions. Nicotinic acid in ethanol undergoes photo-ethylation in acidic media and photo-decarboxylation in alkaline media. Since the photoreactions in ethanol were not affected by the addition of 1,3-pentadiene, the photoreactions in ethanol would proceed from excited singlet state.



Scheme 1

1) C. Azuma and A. Sugimori, *Kogyo Kagaku Zasshi*, **72**, 239 (1969).

2) Photo-induced hydroxylation of pyridine nucleus was reported with *N*-methylnicotinamide, but the reaction was not observed with *N*-methylnicotinic acid. S. Y. Wang, *Biochemistry*, **7**, 3740 (1968).

3) Photo-induced alkylation of *N*-heteroaromatic compounds in alcoholic solutions was reported with quinoline, phenanthridine, pyrimidine and pyridine. F. R. Stermitz, C. C. Wei and W. H. Huang, *Chem. Commun.*, **1968**, 482; F. R. Stermitz, C. C. Wei and C. M. O'Donnel, *J. Amer. Chem. Soc.*, **92**, 2745 (1970); F. R. Stermitz, R. R. Seiber and D. E. Nicodem, *J. Org. Chem.*, **33**, 1395 (1968); M. Ochiai, E. Mizuta, Y. Asahi and K. Morita, *Tetrahedron*, **24**, 5861 (1968); E. F. Travecedo and V. I. Sternberg, *Chem. Commun.*, **1970**, 609.