Title	Solvolysis of pyridoxal hydrochloride in alcohols
Sub Title	
Author	永田, 佳子(Nagata, Yoshiko) 与田, 玲子(Yoda, Reiko) 松島, 美一(Matsushima, Yoshikazu)
Publisher	共立薬科大学
Publication year	1993
Jtitle	共立薬科大学研究年報 (The annual report of the Kyoritsu College of Pharmacy). No.38 (1993.) ,p.55- 55
Abstract	
Notes	抄録
Genre	Technical Report
URL	https://koara.lib.keio.ac.jp/xoonips/modules/xoonips/detail.php?koara_id=AN00062898-00000038-0055

Solvolysis of Pyridoxal Hydrochloride in Alcohols*

Yoshiko NAGATA, Reiko YODA and Yoshikazu MATSUSHIMA

永田佳子，与田玲子，松島美一

Pyridoxal phosphate, a biologically active form of vitamin B_6, is an essential cofactor to many enzymes which catalyze amino acid reactions. The catalytic activities have been shown to be duplicated by pyridoxal in the absence of specific apo-protein. Studies on these nonenzymatic model reactions have greatly improved our understanding of its catalytic role.

According to the established formulation of a general mechanism that explains the role of pyridoxal in the catalysis of both model and enzymatic reactions, the initial step of the reactions is formation of the Schiff base (aldimine) between pyridoxal and an amino acid. In aqueous solution, the formation of the aldimine of pyridoxal is incomplete even in the presence of one hundred fold excess of an amino acid. On the other hand, in alcoholic media the formation is almost complete at equimolar concentration. Many model reactions were carried out in alcoholic media, since these systems were considered to mimic the enzymes better.

We reported a kinetic study on the formation of the aldimine in methanol in 1968. Freshly prepared methanol solution of pyridoxal was used in the study. On standing of the solution, however, the reproducibility of the kinetic data invariably became poor without any appreciable change in the absorption spectrum of the solution. The formation of pyridoxal acetal with the solvent was suspected but was not proved. Recent developments of HPLC and other analytical means offered facile methods to solve the problem.

HPLC, ^{1}H-NMR, MS and product analysis showed that pyridoxal hydrochloride was solvolyzed in methanol to form pyridoxal monomethylacetal. The reaction followed first order kinetics with the rate constant of 1.45×10^{-4} s^{-1} at 40 °C. The rate was not appreciably enhanced in the presence of an excess amount of HCl. The reaction was greatly retarded by addition of an equimolar amount of KOH. The results showed that the pyridinium-phenol species of pyridoxal hemiacetal is reactive. The reaction is responsible for the "aging" of alcoholic solutions of pyridoxal, which has caused poor reproducibility of the kinetic data for the formation of Schiff bases with amino acids.

* 本報告は *Chem. Pharm. Bull.*, **41**, 1019—1022 (1993) に発表