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STUDIES ON THE HYDRATION AND HEMIACETAL FORMATION OF PYRIDINECARBALDEHYDES

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The equilibrium constants and the rates of hydration and hemiacetal formation of pi-deficient aza-aromatic aldehydes were determined by NMR and UV spectrometry. At their equilibria, the hydrate and the hemiacetal forms are remarkably favored with the aldehydes carrying a formyl group ortho or para to the ring nitrogen atom, which is interpreted as the pi-electronic destabilization caused by the direct interaction between the two electron-withdrawing groups (ring nitrogen and carbonyl groups).

Table The eqilibrium and rate constants of pyridinecarbaldehydes.

	K(304K)	k(304K)
2-Pyridinecarbaldehyde + CH_3OH		
in DMSO-d_6	1.45×10^{-1}	1.07×10^{-5}
in acetonitrile	1.05×10^{-1}	1.58×10^{-5}
4-Pyridinecarbaldehyde + CH_3OH		
in DMSO-d_6	5.07×10^{-1}	1.01×10^{-4}
in acetonitrile		6.35×10^{-4}(UV)
3-Pyridinecarbaldehyde + CH_3OH		
in DMSO-d_6	5.87×10^{-2}	5.80×10^{-6}
4-Pyridinecarbaldehyde + H_2O		
in DMSO-d_6	3.16×10^{-2}	
in acetonitrile	1.32×10^{-2}	1.50×10^{-3}(UV)

In some strongly donable aprotic solvents such as dimethyl sulfoxide and pyridine, both the hydration and hemiacetal formation are remarkably favored, but the rates in these solvents are not accelerated considerably. The behavior is interpreted as the stabilization of the produced geminal diols by the hydrogen bond formation.
The activation of the reactant hydroxylic compounds also plays an important role in the solvent effect.