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Article

Kinetic Study on Aminolysis of 4Ãƒ Â¢Ã‚€Ã‚•Pyridyl Benzoate and *O*Ãƒ Â¢Ã‚€Ã‚•4Ãƒ Â¢Ã‚€Ã‚•Pyridyl Thionobenzoate in Acetonitrile: Factors Influencing Reactivity and Reaction Mechanism

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Abstract

A kinetic study on nucleophilic substitution reactions of 4ÃƒÂ¢Ã‚Â€Ã‚Â•pyridyl benzoate (**2a**) and *O*ÃƒÂ¢Ã‚Â€Ã‚Â•4ÃƒÂ¢Ã‚Â€Ã‚Â•pyridyl thionobenzoate (**2b**) with a series of cyclic secondary amines in acetonitrile at 25.0ÃƒÂ Ã‚Â°C is reported. Plots of pseudoÃƒÂ¢Ã‚Â€Ã‚Â•firstÃƒÂ¢Ã‚Â€Ã‚Â•order rate constant (k_{obsd}) vs. [amine] are linear and pass through the origin for the reactions of **2a** but curve upward for those of **2b**. The upward curvature observed for the reactions of **2b** is typical for reactions that proceed through a stepwise mechanism with a zwitterionic intermediate $T^{ÃƒÂ±}$, which decomposes to the products via uncatalyzed and catalyzed routes competitively. The reaction of **2a** has been suggested to proceed through a stepwise mechanism with $T^{ÃƒÂ±}$, in which expulsion of the leaving group occurs in the rateÃƒÂ¢Ã‚Â€Ã‚Â•determining step on the basis of a linear BrÃƒÂ¸nstedÃƒÂ¢Ã‚Â€Ã‚Â•type plot with $ÃƒÂ²_{nuc}$ = 0.77. The catalyzed reaction of **2b** from $T^{ÃƒÂ±}$ has been proposed to proceed through a concerted mechanism with a sixÃƒÂ¢Ã‚Â€Ã‚Â•membered cyclic transition state rather than via a stepwise pathway with an anionic intermediate $T^{ÃƒÂ¢Ã‚Â€Ã‚Â²}$. Factors influencing reactivity and reaction mechanism are discussed in detail.

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