ABSTRACT

This thesis presents kinetic investigation into the formation and acylation of ureas.

PART A

The reactivity of various m- and p-substituted anilines towards phenyl isocyanate is found to increase with increasing basicity. With ortho-substituted anilines, there is a considerable reduction in reactivity but electronic effects are still important. Although an accurate first-order loss in amine is observed for many m- and p-substituted anilines a linear relationship is found to exist between k_{obs} and $[Amine]_{initial}$, implying a second-order dependence in amine. This is confirmed for the reaction with α-naphthyl isocyanate. The mechanism is interpreted in terms of a slow proton transfer within the amine-isocyanate complex. A bifunctional mechanism is postulated to be operative for the various substituted benzoic acids, diphenylureas, cyclic unhindered ureas, phenylacylureas, acetanilides and benzamides used as catalysts.

$$RNH_2 + RNCO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Complex \xrightarrow[BH]{\text{slow } k_2} Product + BH$$

Whereas the inequality $k_{-1} >> k_2$ [Amine] for the isocyanate-amine system appears to hold for a wide range of solvents, for the isothiocyanate-amine system, k_{-1} and k_2 [Amine] appear to be more finely balanced such that a change in solvent results in a change in amine dependence.

PART B

The reactions of various substituted phenylureas with 3:4-dichloro-

phenyl isocyanate and acetic anhydride in acetonitrile and acetic acid respectively are found to be first-order in each component. Reasonable Hammett correlations are obtained with the various m- and p-substituted phenyl ureas used. In contrast, the "ortho effect" is quite different for the two systems. For the isocyanate-urea system, ortho substituents result in reduction in reactivity. However, electronic effects are still important and correlation is obtained with σ_o values. With the anhydride-urea system, there is no definite correlation with electronic effects - o-methoxy- and o-iodophenylurea being more reactive than the other ureas used. This "enhanced" reactivity is discussed in terms of an "external field" effect.