ABSTRACT

This thesis presents rate data for the hydrolysis of *o*-, *m*- and *p*-substituted benzamides and phenylacetamides in both acid and base at 65.6°C and 86°C. Chemical shift data for the side chain protons of similarly substituted phenylacetamides and benzhydrazides, the latter serving as model compounds for the benzamides, are also presented.

The hydrolysis rates of the *m*- and *p*-substituted amides in both acid and base were well correlated by the Hammett σ constants. The significance of the ρ values obtained (in the phenylacetamide and benzamide series) is discussed in terms of the relative kinetic importance of steps one and two of the accepted simple two-step mechanism for amide hydrolysis.

The *ortho* rates are shown to be dependent on both inductive and steric effects and suggestions are made as to the nature of the steric and inductive effects that are operating.

The chemical shifts of the $-CH_2$, $-NH$ and $-NH_2$ protons of the *m*- and *p*-substituted phenylacetamides and benzhydrazides all gave excellent correlations with the

Hammett σ constants. It is concluded that the effect of non-*ortho* ring substituents on the side chain in these amide systems, both in the ground state and in chemical reactions, is mainly an inductive one.

The -NH proton chemical shifts of the *o*-benzhydrazides are shown to be dependent on purely electrical effects while the $-NH_2$ chemical shifts are dependent on inductive and steric effects. This finding, strange at first glance, is explained.

The methylene proton chemical shifts of the *o*-phenylacetamides seem to be dependent on both electrical and steric factors.