

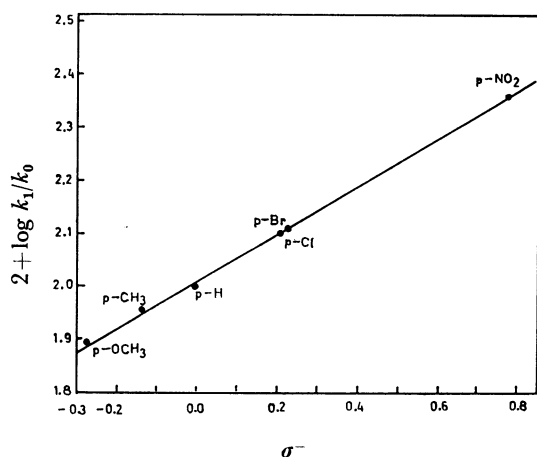


Fig. 1. Hammett plot of condensation of *p*-substituted benzaldehydes with phenacyl chloride.

There is a regular variation in the rates with the nature of the *p*-substituents. The order of reactivity being $\text{NO}_2 > \text{Cl} > \text{Br} > \text{H} > \text{CH}_3 > \text{OCH}_3$ i.e. electron-withdrawing groups increase while electron-donating groups decrease the rate. This fact is also borne out by the enthalpies of activation ($\Delta H^\ddagger$) values calculated for these reactions which are 7.8 kcal/mol for the *p*-NO₂ and 12.56 kcal/mol for the *p*-OCH₃ groups.

The sign and magnitude of the reaction constant, ρ in the Hammett equation are often evaluated to assess

the charge type of the transition state. The ρ value from the Hammett plot (Fig. 1) has been found to be $+0.446$ ($r=0.998$) by least squares method. The small value reflects a weak interaction between the substituent and the reaction site. It, however, does indicate the transition state has a negative character.

One of us (K.S.) is grateful to the Council of Scientific and Industrial Research (C.S.I.R.), New Delhi for financial assistance.

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