



Chemical Education Article for Graduate Students

Demonstration of Non-Linear Resonance Free Energy Relationship in the S_N2 Reactions of *ortho*- Substituted Benzylamines with Benzyl Bromide

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ABSTRACT

The rates of reactions of ortho-substituted benzyl amines (BA) with benzyl bromide (BB) were measured using conductivity technique in methanol medium. The reaction followed a total second order path. The end product of the reaction is identified as di-benzyl alkyl amine (C₆H₅CH₂N(R)CH₂C₆H₅). The rates decreased with increase in resonance contribution or with increase in the σ_R^o value of electron donating substituents (X) like methoxy ($\sigma_R^o = -0.43$), Cl ($\sigma_R^o = -0.24$), at ortho position of the amine till σ_R^o value becomes -0.15 for methyl ($\sigma_R^o = -0.15$) and then the rates decreased with decrease in resonance contribution or with increase in σ_R^o value of electron withdrawing substituents (X) like H and CF₃ (σ_R^o of H = 0.00 and σ_R^o of CF₃ = 0.1). The locus of the resonance free energy relationship (RFER) has a maximum near the point for ortho-methyl benzyl amine showing that there is a sharp change in the rate determining step. A mechanism involving formation of an S_N2 type transition state between the amine nucleophiles and the benzyl bromide and its subsequent decomposition is proposed. Activation parameters were calculated and discussed.

Keywords: Non-linear resonance free energy correlation, reactions of benzyl amines, reactions of benzyl bromide, and change in rate determining step.
