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# **Kinetics of Different Electrophilic and Nucleophilic Reactions of Organic Compounds**

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**ABSTRACT:** The kinetics and mechanism of electrophilic additions to carbon-carbon multiple bond have received much attention and a very large volume of work has been reported. In contrast, nucleophilic additions to alkenes has received relatively less attention. It may be due to the fact that simple olefins do not react with nucleophilic mechanism. Nucleophilic addition reactions are best carried out on Substrats containing two or more electron- withdrawing group. Such alkenes are called activated alkenes for nucleophilic additions. A large number of activated alkenes possesses an aromatic ring at B-position. This may be helpful in stabilizing the carbanion intermediate through resonance. A perusal of the literature has shown that the effect of structure on the reactivity of an alkene has been studied in many cases, e.g. the addition of piperidine to substituted benzylidene Meldrum's acids correlate with *o'* substituent constants, with positive reaction constant. However, there seems to be no report on the correlation of reactivity and the structure of the amine except a few studies involving the primary and secondary amines. Therefore, we have under taken a study of a addition of a several monosubstituted benzylamines to two activated alkenes viz. ethyl *a*-cyanocinnamate (ECC) and B-nitrostyrene (NS).

## **I.INTRODUCTION**

The major objectives of this work 2 Bthyl *a*-cyanocinnamate (ECC) was prepared by the reported method. Its purity was checked by m.p. The preparation, purification and specification of the substituted benzylamines have already been described in the literature. Acetonitrile was purified by the usual methods. The product of the addition is Ethyl-3-benzylamino-2-cyano-3-phenylpropanoate, as confirmed by its <sup>1</sup>H NMR spectrum. The reaction was studied under pseudo-first-order conditions by keeping a large excess ( $\times 10$  or greater) of benzylamine over ECC. The solvent was asacetonitrile. The reaction was followed spectrophotometrically by monitoring the decrease in [ECC] at 300 nm for ca. 80% reaction. The pseudo-first-order rate constant,  $k_1$  was evaluated from the linear ( $r > 0.990$ ) plot of  $\log [ECC]$  versus time plots. The second order rate constants,  $k_2$ , were obtained from the relation :  $k_2 = k_1 / [amine]$ . Duplicate kinetic runs showed that obs the rate constants were reproducible to within  $\pm 3\%$ . The overall reaction may be represented as equation (1)  $ArCH_2NH_2 + Ph-CH=C(CN)COOBt \rightarrow Ph-CH_2-CH(CN)COOEt$  (1)  $NHCH_2Ar$  The reaction is first order with respect to ECC. Further, the pseudo-first-order rate constant,  $k_1$ , does not vary with the initial concentration of ECC. The rate of reaction varies linearly with the concentration of the amine. [3,4]

## **II.DISCUSSION**

Thus the reaction follows second order kinetics. The The rates of addition of benzylamine and twenty-seven monosubstituted benzylamines to ECC were determined at different temperatures and the activation parameters were calculated. The values of  $\log k_2$  at 288 K and 318 K of the twenty-eight amines are linearly related ( $r = 0.9962$ , slope = 0.7455 0.0128). The value of isokinetic temperature is 458  $\pm$  14 K. The linear correlation implies that all the amines react with the same mechanism. Further, a linear isokinetic relationship is a necessary condition for the validity of linear free

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energy relationships. Correlation Analysis of Reactivity (1) para- and meta- substituted benzylamines. - Since the rates of addition of the monosubstituted benzylamines failed to show satisfactory correlation with any single substituent-parameter equation, the rates of meta- and para- substituted benzylamines were subjected to correlation analysis in terms of dual substituent-parameter (DSP) equations of Taft and Swain et al. According to Taft et al, the inductive/field effect of substituent can be represented by a generalized scale of  $\sigma$ , but no such generalized  $\sigma_p$  can be constructed and they have proposed four different  $\sigma$ , Scales viz., OR BA  $\sigma_R$ ,  $\sigma_R$  and  $\sigma$ . [5,6] These correspond to the resonance contribution of Hammett's  $\sigma$ ,  $\sigma$ , and  $\sigma$  scales of single substituent-parameter equations respectively. However, according to Swain et al, only two parameters, F and R, are sufficient to account for the effect of substituents. F is proposed to represent the field or nonresonance contribution and R represents the resonance contribution of the substituents. [7]

### III.RESULTS

The rates of addition of meta and para compounds were separately correlated with  $\sigma$ , and four different  $\sigma$ , values in Taft's equation (2) and with the field and resonance substituent constants of Swain's equation (3). (2)  $\log k/k_0 = \rho\sigma$ , (3)  $\log k/k_0 = \rho^*F + \rho^*R$  (3) Both the meta- and para- series of substituted benzylamines meet the requirement of minimum number of substituents for analysis by DSP equations. In this set of correlation analysis, the intercept was forced through the origin. The rates of addition of the para-substituted benzylamines show excellent correlation with Taft's  $\sigma$ , and  $\sigma_R$  BA values. We have used the standard deviation (sd), coefficient multiple determination (R), and parameter f as the criteria of goodness of fit. f has been defined as = sd/ root mean square of the data (here  $\log k/k_0$ ). BA Comparison showed that f is smaller for the  $\sigma$ , scale than for the other scales by factors of ca. 4 to 10. Thus it is apparent that the rates of addition of para-substituted benzylamines to ECC correlate best with  $\sigma$ , and BA The rates of meta-substituted benzylamines show excellent correlation with  $\sigma$ , and  $\sigma$ , though the discriminating factor for the precision of fit with the other  $\sigma$  scales or with Swain's equation is not as sharp as in the case of para-substituted compounds.[8]

### IV.CONCLUSION

This agrees with the observation of Ehrenson, Brownlee and Taft that the correlation of meta-substituted compounds is generally best with  $\sigma$  and that meta-substituted compounds are less discriminating. The values of (ca. 1.11) showed that the addition of parasubstituted benzylamines is slightly more susceptible to a resonance effect than to a field effect. In the reaction of the meta- compounds, however, the value of " is ca. 0.75, indicating the greater importance of the field effect. The rates of addition of the meta - compound show an excellent correlation with  $\sigma$ , and R though the discriminating factor for precision of fit with the other  $\sigma_R$  Scales is not as sharp as in the case B of para- substituted compounds. In fact the correlation with  $\sigma$  scales meets the requirement' for a satisfactory fit [9]

### REFERENCES

1. Kuivila, H. G. *Acc. Chem. Res.* **1968**, 299. (Organotin Hydrides and Organic Free Radicals)
2. Mihailović, M. L.; Čeković, Z. *Synthesis* **1970**, 209. (Intramolecular Oxidative Cyclization of Alcohols with Lead Tetraacetate)
3. Tedder, J. M.; Walton, J. C. *Tetrahedron* **1980**, 36, 701. (The Importance of Polarity and Steric Effects in Determining the Rate and Orientation of Free Radical Addition to Olefins)
4. Tedder, J. M. *Angew. Chem. Int. Ed. Engl.* **1982**, 401. (Which Factors Determine the Reactivity and Regioselectivity of Free Radical Substitution and Addition Reactions?)
5. Giese, B. *Angew. Chem. Int. Ed. Engl.* **1983**, 22, 753. (Formation of CC Bonds by Addition of Free Radicals to Alkenes)



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6. Hart, D. J. *Science* **1984**, 223, 883. (Free-Radical Carbon–Carbon Bond Formation in Organic Synthesis)
7. Walling, C. *Tetrahedron* **1985**, 41, 3887. (Some Properties of Radical Reactions Important in Synthesis)
8. Giese, B.; Horler, H. *Tetrahedron* **1985**, 41, 4025. ( $\beta$ -Carbonyl Radicals as Three-Carbon Building Blocks for Carbon–Carbon Bond Forming Reactions)
9. Barton, D. H. R.; Zard, S. Z. *Pure Appl. Chem.* **1986**, 58, 675. (Invention of New Reactions Useful in the Chemistry of Natural Products)