Kinetics and Mechanism of the Addition of Substituted Anilines to β-Nitrostyrene

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The addition of aniline to *trans*-β-nitrostyrene involved the formation of a zwitterionic intermediate in the rate-determining step followed by a rapid intramolecular proton transfer.

Mechanistic studies of nucleophilic additions to an activated carbon–carbon double bond have been a subject of many reports. However, the correlation of amine structure with the rate has received little attention. We have recently reported[5,6] the correlation analysis of the reactivity in the addition of substituted benzylamines to ethyl α-cyanocinnamate and β-nitrostyrene. Here, we report the addition of a number of monosubstituted anilines to *trans*-β-nitrostyrene (NS). Attempts have been made to correlate the rate and structure in this reaction.

The reaction was studied under pseudo-first-order conditions in acetonitrile by keeping a large excess (×10 or greater) of aniline over NS. The reaction was followed spectrophotometrically by monitoring the decrease in [NS] at 311 nm for *ca.* 80% reaction. The pseudo-first-order rate constant, k_{obs}, was evaluated from the linear ($r > 0.995$) plots of log [NS] *vs.* time. The second order rate constants, k_2, were obtained from the relation: $k_2 = k_{\text{obs}}/[\text{aniline}]$.

The product of the reaction, as characterized by its ^{1}H NMR spectrum, is 1-phenyl-1-phenylamino-2-nitroethane [$PhCH(NHPh)CH_2NO_2$]. The product was isolated in 88% yield. The overall reaction may be represented by eqn. (1).

$$ArNH_2 + PhCH{=}CH(NO_2) \rightarrow PhCH(NHAr)CH_2NO_2 \quad (1)$$

The reaction is first order with respect to both the amine and NS. The rates of addition of aniline and thirty-four monosubstituted anilines to NS were determined at different temperatures and the activation parameters were calculated.

The rate constants of the addition of *meta*- and *para*-substituted anilines do not correlate well with the pK_a values of the anilinium cations, Hammett's σ, σ^+ or σ^- values. Similarly, the rate of the *ortho*-compounds failed to show significant correlation with either the rates of the corresponding *para*-compounds or σ_0 values of Tribble and Traynham.[15] We have used the standard deviation (sd), the coefficient of determination (R^2 or r^2), Taft's[10] parameter f and Exner's[11] parameter ψ, as measures of goodness of fit.

The rate constants of the addition of *meta*- and *para*-anilines did not correlate well with Taft's dual substituent parameter (DSP) equation.[16]

The rate constants, k_2, were, therefore, analysed in terms of Charton's[17] LDR eqn. (8).

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + h \quad (8)$$

Here, σ_1 is a localized (field and/or inductive) effective parameter, σ_d is the intrinsic delocalized (resonance) electrical effect parameter when active site electronic demand is minimal and σ_e represents the sensitivity of the substituent to change in electronic demand by the active site. The latter two substituent parameters are related by eqn. (9).

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (9)$$

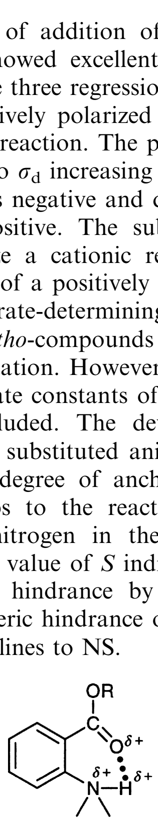
Here η, represents the electronic demand of the reaction site which is given by $\eta = R/D$, and σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For *ortho*-substituted compounds, it is necessary to account for the possibility of steric effects and Charton,[17] therefore, modified the LDR equation to LDRS eqn. (10), where V is the well known Charton's steric parameter based on Van der Waals radii.[18]

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + SV + h \quad (10)$$

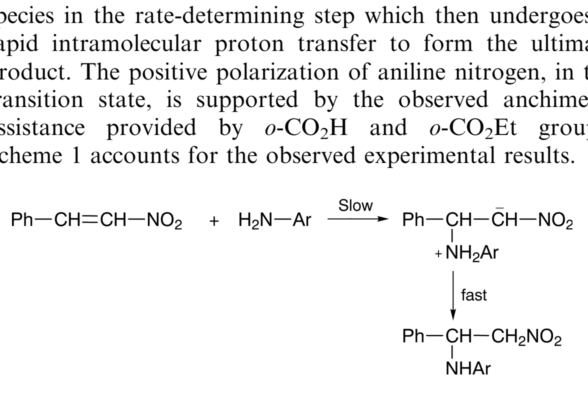
The rate constants of addition of the *meta*- and *para*-substituted anilines showed excellent correlations with the LDR equation. All the three regression coefficients are negative indicating a positively polarized nitrogen centre in the transition state of the reaction. The positive value of η adds a negative increment to σ_d increasing the donor effect of the substituent where σ_d is negative and decreasing the acceptor effect where σ_d is positive. The substituent is, therefore, better able to stabilize a cationic reaction site. This also supports the presence of a positively polarized centre in the transition state of the rate-determining step.

The rates of the *ortho*-compounds showed a poor correlation with LDRS equation. However, excellent correlations were obtained if the rate constants of *o*-CO_2H and *o*-CO_2Et compounds were excluded. The deviations noted in the *o*-CO_2H and *o*-CO_2Et substituted anilines could be attributed to the moderate degree of anchimeric assistance provided by these groups to the reaction by stabilizing the positively polarized nitrogen in the transition state (**A**). The observed negative value of S indicates that the reaction is subjected to steric hindrance by the *ortho*-substituent. This may be due to steric hindrance of the *ortho*-substituent to the approach of anilines to NS.



A

The large negative polar reaction constants point to a transition state in which the aniline nitrogen is positively polarized. This suggests the formation of a zwitterionic species in the rate-determining step which then undergoes a rapid intramolecular proton transfer to form the ultimate product. The positive polarization of aniline nitrogen, in the transition state, is supported by the observed anchimeric assistance provided by *o*-CO_2H and *o*-CO_2Et groups. Scheme 1 accounts for the observed experimental results.



Scheme 1

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Techniques used: ^{1}H NMR, spectrophotometry, correlation analysis

References: 19

Table 1: Rate constants for the addition of aniline to NS at 298 K

Table 2: Rate constants at different temperatures and activation parameters for the addition of substituted anilines to NS

Table 3: Correlation of the rates of addition of *meta*- and *para*-substituted anilines to NS with dual substituent-parameters at 298 K

Table 4: Temperature dependence of the reaction constants for the addition of substituted anilines to NS

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