Available online at www.joac.info

ISSN: 2278-1862

Journal of Applicable Chemistry

2015, 4 (6):1579-1583

(International Peer Reviewed Journal)

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

V. Jagannadham[1*], R. Ravi[1] and R. Sanjeev[2]

1. Department of Chemistry, Osmania University, Hyderabad-500007, INDIA
2. Department of Chemistry, Ashoka Institute of Engineering and Technology, Hyderabad-508252, INDIA

Email: jagannadham1950@yahoo.com

Accepted on 9th November 2015

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 ($C_6H_5CH_2N(R)CH_2C_6H_5$)*. The rates decreased with increase in resonance contribution or with increase in the* σ_R^o *value of electron donating substituents (X) like methoxy* (σ_R^o = -0.43)*, Cl* (σ_R^o = -0.24)*, at ortho position of the amine till* σ_R^o *value becomes -0.15 for methyl* (σ_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* CF_3 (σ_R^o *of H = 0.00 and* σ_R^o *of* CF_3= 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.

INTRODUCTION

Though the Hammett and Taft equations are nearly more than seventy five years old, the interest even today in their application for predicting the organic reaction mechanisms is still continuing. Ever since the Hammett [1] and Taft [2,3] equations were developed, there were several hundreds of reactions with *meta*- and *para*- substituted benzene derivatives in the literature, for which the Hammett and Taft reaction (ρ) constants were reported. There were some reactions which deviate from linearity of Hammett ρσ plot and documented in detail by Schreck [4]. There were several reports on non-linear Hammett relationships. An example of nonlinear Hammett ρσ plot is that reported by Crowell et.al. [5] in the reaction of aromatic aldehydes with n-butyl amine. The products are substituted benzylidene-n-butyl amines. This was interpreted in terms of the change in the rate determining step from reversible addition of amine to aldehyde to the subsequent dehydration step which is favored by electron donating substituents. Hancock et al had tried to explain the V-shaped Hammett locus based on the same explanations of change in mechanisms of Wolf-Kishner reaction of hydrazones [6] and U-shaped Hammett locus for the rates of solvolysis and thiosulfate reactions of α-chloro toluenes [7] for two sets of electron donating and electron withdrawing of substituents. One of the recent examples in this direction is the reactions of alkaline hydrolysis of O-aryl thionobenzoates [8]. Another notable example of this kind is from our laboratory in the reactions of N-substituted benzylamines with benzyl bromides [9].

DISCUSSION

The conductivity of the reaction mixture increases with time as the reaction produces HBr as one of the end products.

Under the conditions [*o*-BA] > > [BB], the plot of log (C_∞ - C_t) versus time (eq. 1) was linear until three half-lives with correlation coefficient of 0.999, indicating the order in [BB] was unity.

$$\log (C\infty - Ct) = \log (C\infty - Co) - (k/2.303) \bullet t \qquad (1)$$

Here C_∞, C_o and C_t are the conductivities of the reaction mixture at infinite time, initial and at regular intervals of time respectively. From slopes of such plots, the pseudo first order rate constants (k_{obsd}/min) were calculated for all the *o*-substituted benzylamines. The plot of log (k_{obsd}/min) versus log [BA] was again found to be linear with a correlation coefficient of 0.995 indicating the order in [BA] was unity.

The pseudo-first-order rate constants (k_{obsd}) for all reactions obeyed eq. (2) in methanol. The clean second-order rate constants, *k* was obtained as the slope of the plot of k_{obsd} against [benzylamine]. The second-order rate constants (*k*) are summarized in table 1.

$$k_{obsd} = k\,[\text{benzylamine}] \qquad (2)$$

Therefore the simple rate equation of the reaction would be:

$$\text{Rate} = k\,[\text{benzylamine}]\,[\text{benzyl bromide}]$$

where '*k'* is the second order rate constant. Under otherwise similar conditions the solvolysis reaction of benzyl bromide in the absence of benzylamine was checked and the rate was found to be 10 times less than the rate of the second order reaction. Hence the rates of background reaction of benzyl bromide were neglected in these studies.

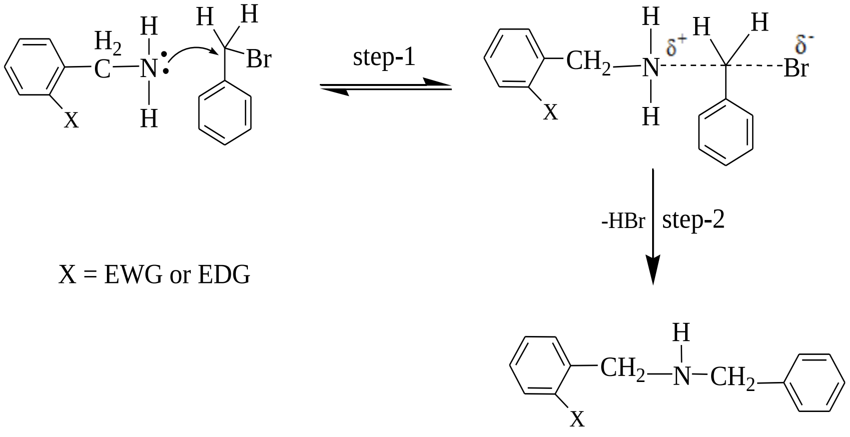
Table-1: Effect of temperature and substituent on *k* and activation parameters in *ortho*-substituted benzylamines - benzyl bromide reaction

[BA]= 0.1 mol dm^{-3}, [BB] = 0.01 mol dm^{-3}, Solvent: methanol, Temp = 298-313K

X in BA	σ^0_R	*k* x 10^2 (dm^3 mol^{-1} min^{-1})				Ea k J mol^{-1}	ΔH$^\neq$ k J mol^{-1}	-ΔS$^\neq$ J (mol K)$^{-1}$
		298K	303K	308K	313K			
2-CH_3O	-0.43	2.93	3.43	5.30	6.75	45.5	42.9	131
2-Cl	-0.24	6.90	11.2	19.3	33.0	80.6	78.5	6.02
2-CH_3	-0.15	8.90	12.3	24.9	40.5	80.9	78.4	3.02
H	0.00	5.76	8.51	13.5	30.4	81.2	79.8	1.69
2-CF_3	0.10	3.98	6.30	10.1	15.7	70.5	68.0	44.0

Reaction mechanism and substituent effects: Since the total order of the reaction is two, a bimolecular type of reaction is proposed as shown in the following mechanism via an S_N2-type transition state (Scheme 1).

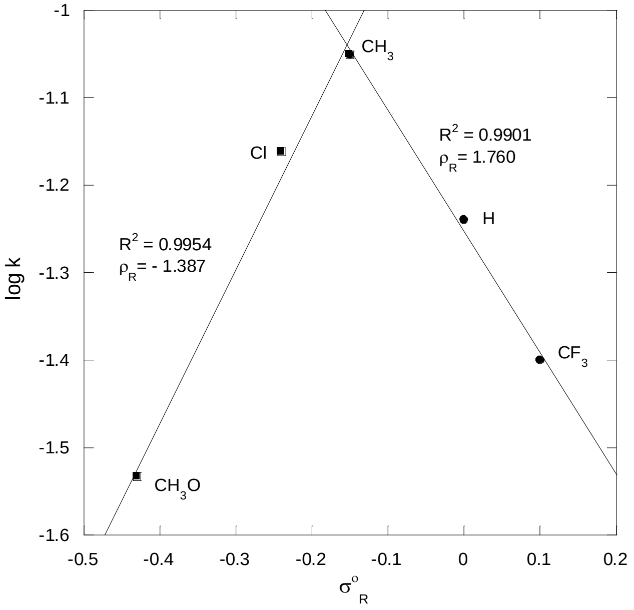
Structure reactivity: The rates decreased with increase in resonance contribution or with increase in the σ^0_R value of electron donating substituents (X) like methoxy (σ^o_R = -0.43), Cl (σ^o_R= -0.24), at ortho position of the amine till σ^0_R value becomes -0.15 for methyl (σ^o_R= -0.15) and then the rates decreased with decrease in resonance contribution or with increase in σ_R value of electron withdrawing substituents (X) like H and CF_3 ($\sigma^o_R$of H = 0.00 and $\sigma^o_R$of CF_3= 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 (Figure 1). σ^o_R values are from reference 10. 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.



Scheme 1

X = *ortho*-OCH_3, *ortho*-CH_3, H, *ortho*-Cl, *ortho*-CF_3

Figure 1: Plot of log *k* versus σ^o_R



Mechanistic implications of $\Delta S^{\neq}$: The formation of the transition state involves the combination of two reactants to give one species. This would result in a loss of several translational degrees of freedom of the reactants, leading to high negative entropy of activation.

Effect of temperature: The rate constants (k) for the reaction of benzylamines were found to increase with increase in temperature. The activation energy (E_a) is evaluated from Arrhenius plots of ln k versus 1/T and activation parameters were evaluated from Eyring plots of ln k/T versus 1/T and these values are presented in the table-1. The negative $\Delta S^{\neq}$ values indicate that the loss of entropy during the formation of unstable ionic transition state, which promotes a high degree of solvation and hence loss in entropy.

Isokinetic relationship: An isokinetic plot is obtained in the present work when $\Delta H^{\neq}$ is plotted against $\Delta S^{\neq}$ according to the equation $\Delta H^{\neq} = \beta\ \Delta S^{\neq}{}_{+}$ constant, the slope of which corresponds to an isokinetic temperature β of 281 K, which is well below the experimental temperature range (298–313 K) used in the present reactions to study the effect of temperature on reaction rates. According to isokinetic theory [11], this means that the effect exerted by the *ortho*- substituted of benzyl amines, both the processes i.e. formation and the heterolysis of the transition state are controlled predominantly by entropy.

It has been asserted that apparently linear correlations of $\Delta H^{\neq}$ with $\Delta S^{\neq}$ are sometime misleading and the evaluation of β by means of the equation $\Delta H^{\neq} = \beta\ \Delta S^{\neq}{}_{+}$ constant, lacks statistical validity [12]. Exner [13] describes an alternative method for the treatment of experimental data. If the rates of several reactions in a series have been measured at different temperatures and log k_2 (at T_2) is linearly related to log k_1 (at T_1), i.e., according to the equation, log k_2 = a + b log k_1, so that β can be evaluated using the equation, $\beta = T_1T_2 (1–b)/(T_1 - T_2b)$. We have calculated the isokinetic temperature β as 275K by plotting log k_2 at 313 K versus log k_1 at 303 K as the value of β (275) is lower than the experimental temperature 298 K. This indicates that the rate is governed by entropy of activation [14].

CONCLUSION

The reactions of *ortho*- substituted benzylamines with benzyl bromide follow a S_N2 type reaction. The reactions are entropy controlled.

ACKNOWLEDGMENTS

One of the authors RR is grateful to UGC for a fellowship.

REFERENCES

[1] L. P. Hammett, Some Relations between Reaction Rates and Equilibrium Constants, *Chem. Rev.*, **1935**, 17, 125.
[2] C. K. Ingold, Mechanisms of acid and base catalyzed hydrolysis of esters, *J. Chem. Soc.*, **1930**, 1032.
[3] R. W. Taft, *J. Am. Chem. Soc.*, **1952**, 74, 2729.
[4] J. O. Schreck, *J. Chem. Edn*., **1971**, 48, 103 and references cited therein.
[5] G. M. Santerre, C. J. Jr. Hanrote, T. I. Crowell, *J. Am. Chem. Soc.*, **1958**, 80, 1254.
[6] H. H. Szmant, C. Harmuth, *J. Am. Chem. Soc.*, **1964**, 86, 2909.
[7] R. Fucks, D. M. Carltoo, *J. Am. Chem. Soc.*, **1963**, 85, 104.
[8] I. H. Um, J. Y. Lee, H. T. Kim, S. K. Bae, *J. Org. Chem.*, **2004**, 69, 2436.
[9] R. Ravi, R. Sanjeev and V. Jagannadham, *Int. J. Chem. Kinet.*, **2013**, (DOI 10.1002/kin.20818), 45,803-810
[10] J. March, "Advanced Organic Chemistry", 4th Edition, John Wiley & Sons, **1992**, p. 283.

[11] J. E. Leffler, E. Grunwald, Rates and Equilibria of Organic Reactions, Wiley: New York, **1963**.
[12] E. S. Lewis, Investigations of Rates and Mechanisms of Reactions, 3rd Ed. Wiley: New York, **1974**.
[13] O. Exner, *Collect Czech. Chem. Commun.*, **1972**, 3, 1425.
[14] J. E. Leffler, *J. Org. Chem.*, **1955**, 20, 1202.

AUTHORS' ADDRESSES

1. **V. Jagannadham**
Department of Chemistry,
Osmania University,
Hyderabad-500007, INDIA
2. **R. Ravi**
Department of Chemistry,
Osmania University,
Hyderabad-500007, INDIA
3. **R. Sanjeev**
Department of Chemistry,
Ashoka Institute of Engineering and Technology,
Hyderabad-508252, INDIA