Conductance Study of Benzyl Bromide Reaction with Cyclicamines in Aqueous-Ethanol Medium

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Abstract

Nucleophilic substitution reaction of benzyl bromide and cyclicamines in ethanol aqueous intermediate reactivity can suggest that the nucleophile increases through their pKa values. A linear correlation exists between computed values of the dipole moment, rate and electronegativity of the nucelophiles. The two reactants suggest that frontier molecular orbital interactions ion-solvation and correlation of time with the HOMO-LUMO breach of that the reaction. But it is not orbital controlled as well as forbidden by the electrostatic interactions along with mixed solvent composition between the reactants. The influence on the solvation of ions before reaction has been discuss with facilitate by R-factor. Thermodynamic properties are evaluate and report. The consequences of the learning to be interpreted in terms of ion-solvent exchanges and solvent properties comparing with electrostatic interaction between the reactants.

Keywords: Benzylaton, Correlation Solvolysis, Frontier molecular orbital interactions, Ion-solvation, HOMO-LUMO break.

1. Introduction

Any solvent influence the rates of a reaction through solvating the reactants in addition to the transition condition outstanding to dipolar effect[1-4]. In benzylic carbon is of broad synthetic utility and has received exceptionally detailed attention by chemists. Fundamental concepts like steric effects, polar effects, nucleophilicity, solvent property and structure action correlations have been urbanized through this study[5]. The effect of nucelophile and the effect of substituent on the rate of the reaction. The near studies agreement by means of the effect of nucleophile, lying on the rate of reaction of benzyl bromide through cyclic amine in aqueous ethanol solvent mixtures.

Many powerful tools are provides quantum chemistry which facilitate us in evaluate electron densities at different atoms of a molecule[6-10], in predicting the reaction site, in explaining the order of reactivity of closely related reagents towards a given substrate, in predicting the transition state structure, etc. In the present communication the authors report their observations on the conductance behaviour of cyclicamines in aqueous mixtures of ethanol. With this end in view, we comprise attempted Austin Model 1 calculations here to explore the frontier orbital relations. Correlation regression analysis of frontier molecular orbital interactions through the order of reactivity of these three nucleophiles with benzyl bromides have as well been accepted out. By studying the reaction in different solvents parameters one can get an insight in to solvation of reactants/transition state and relative contribution of solvent property in solvating them. With this end in view the authors have studied the effect of sixteen different solvents on the reaction rate between benzyl bromide and cyclicamines are correlated the rate constant with different solvent parameters. From the results of this correlation analysis, a solvation model[11-12] is proposed with the help of the Linear analysis correlation model obtained by linear salvation energy relation model.

2. Experimental

Benzyl bromide (Macron Fine Chemicals™ grade) be used without further distillation. Solvent ethanol be of Sd-fine make and it was distilled before utilize. Preliminary study of the reaction between benzyl bromide and cyclicamines indicate that Hydrogen Bromide as is one of the products of the reaction. Progress of the reaction was followed by studying the conductance of the reaction combination at different time intervals at different percentage of aqueous organic mixtures. Direct reading digital conductivity bridge (CM 180 Eleco model) equipped with a glass conductivity cell was used to measure the conductance of the system. INSREF stable temperature (King KV model) bath was used to continue the temperature. Accuracy of the bath temperature was maintained at $\pm\ 0.05^{o}$C.

The solutions of nucleophiles of appropriate concentration were equipped by dissolving fitting in aqueous ethanol mixtures . The solution of benzyl bromide be arranged 20 min prior to starting the experiment (to prevent ion-solvation) by dissolving the required volume of the compound in ethanol. The reactions were initiate by combination the thermally equilibrated solutions of the nucleophile and the substrate at the appropriate temperatures. These rate constants determined in duplicate runs be originate to be reproducible within $\pm$ 0.2% error. The reactions be studied in the temperature range 283-313 K.

However the mass spectrum of the product references shows a molecular ion peak at 267 m/z on behalf of that the product is $C_4H_8N_2$ $(CH_2C_6H_5)_2$. That is both the –NH hydrogens are replaced by benzyl groups. The melting point of this compound denoted as 305K. This is varied with the composition in solvent mixture.

It is observed that the conductivity of the solution in each solvent system is increased with increase in the temperature. It is invented

that these variations have to follow Arrhenius relation like rate process. So the energy of activation of the conducting procedure is obtained from the Arrhenius relationship

i.e., $\qquad \Lambda^0 = A\,e^{-Ea/RT}$ $\qquad$ ….. $\qquad$ (1)

Where $\qquad$ A is a constant

$\qquad$ E_a is activation energy of the conducting process

$\qquad$ R is gas constant

$\qquad$ T is the temperature

E_a values are obtained by correlating $\log\Lambda^0$ values with 1/T through resources of linear least square analysis shown in Table 2. These standards are obtainable diverse with correlated values. These values indicate that they are highly dependent on the proportion of organic solvent in the mixture and more in 80% organic solvent.

3. Results And Discussion

The Table 1 results shows that the relativities of the cyclicamines studied in the present system are in the order: 80 %(v\v) ethanol more which is also the order of their pK_a values[10]. Since there is a conceptual relationship between nucleophilicity and solvation to enhance the strength of the relation further, three parameters are added to the above equation, this inclination is expected. Electron donating ability of the nucleophile depends on other factors like electro negativity, polarizability and hardness parameters. These parameters are interrelated and can be calculated from the energies of frontier molecular orbitals (HOMO and LUMO).

To evaluate the influence of these factors on rate, semiempirical molecular orbital calculations performed on the reactants used in the present system. These calculations are performed using Austin Model 1, is method for the quantum calculation of molecular electronic structure in computational chemistry method[11] included in the software packages MOPAC7 (ver. 7.1) geometry calculations in the ground state were completely optimized until the lowest energy conformation was found. Some of the results of these calculations, heats on formation ΔH_f, dipole moment μ, energies of frontier molecular orbitals are presented given the nature of electro negativities of the nuleophiles. The reduce in the dipole moment of the cyclic amine increases its reactivity with the substrate benzyl bromide according to:

$\log k_{II}$ = -1.65(0.04) - 0.23μ (0.06); r = 0.97(0.03) …(2)

It indicates that the reactions in benzyl bromide with cyclic amine are not greatly influenced via the nature of the amines. Entropies of activation are negative as expected for bimolecular reactions. The small difference of activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ for the reaction of benzyle bromide with cycliamine in Ethanol may be due to a slight solvent participation in the transition state. The thermodynamic parameters computed and presented in Table 1 indicate that these be moreover strongly influenced by the nature of the nucleophile. This may be due to solvation of the nucleophiles to different degrees. Solvation of a reagent decreases its energy and stabilizes it. However, the free energy of activation $\Delta G^{\#}$ is virtually constant (72.30 $\pm$ 0.45 kJ mol^{-1}) indicating that similar type of reaction scheme operates through the three nucleophiles studied. The reaction have moreover be calculated at different temperatures and the thermodynamic parameters $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ are evaluate.

When the solute in solvent mixture it can give solute-solute and ion-solvent interaction. From the temperature effect on rate, different thermodynamic activation Parameters parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ are evaluated and presented in Table 1. The entropy of activation $\Delta S^{\neq}$ values are all negative ranging from -2 to -67 JK^{-1} mol^{-1} suggesting that the overall solvation of the transition state is more than the reactants. The differential free energy of activation $\delta\Delta G^{\#}$, $\delta\Delta G^{\#}_s$ shows in table-1 and 3.

is controlled by the electrostatic contact connecting the reactants, the rate increase with decrease in electronegativity, decrease in dipole moment and increase in ion-solvation. The free energy of activation $\Delta G^{\neq}$ is nearly constant in all the solvents (87.65 ± 3.44) KJ/mol^{-1} suggesting the operation of a unified mechanism in every one the solvents used indicated that more stabilized in the solvation known as it is second order kinetic reaction and may potentially be useful for describing electrostatic solvent effects.

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4. Conclusion

The frontier molecular orbital interactions and correlation of rate by means of HOMO-LUMO break of the two reactants suggest so because in the direction of the reaction is not orbital controlled but

Table. 1 Second order rate constants and thermodynamic active parameters [benzyl bromide] at 283-313K in aqueous-ethanol mixtures.

Solvent Aqueous-Ethanol(v/v)	$k \times 10^3$ dm^3 mol^{-1} s^{-1} at TK				$\Delta H^{\neq}$ (kJmol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
	283	293	303	313			
20% Ethanol	3.42	6.45	10.73	18.27	83.54	-14	87.50
40% Ethanol	2.96	5.82	9.44	15.79	83.87	-16	88.87
60% Ethanol	2.14	3.94	6.64	10.46	80.25	-30	89.68
80% Ethanol	2.62	4.44	7.12	10.65	70.90	-60	89.25
100% Ethanol	2.44	4.26	6.23	9.86	72.37	-56	86.55

Table 2. Computed Values of E_a (kJ mol^{-1}) for benzyl bromide compound in reaction at different compositions(v/v) of aqueous-ethanol mixtures.

E_a Values	0%	20%	40%	60%	80%	100%
From conductance	Ethanol	Ethanol	Ethanol	Ethanol	Ethanol	Ethanol
	9.12	11.06	17.68	19.74	10.75	4.77
From computational	Ethanol	Ethanol	Ethanol	Ethanol	Ethanol	Ethanol
	24.12	41.07	54.46	69.36	70.04	62.24

Table 3. Computed change in free energy (ΔG_a) and transfer (ΔG_t) Benzyl bromide in aqueous mixtures of ethanol at different temperatures in kJ mol^{-1}

T(K)	0% Ethanol		20% Ethanol		40% Ethanol		60% Ethanol		80% Ethanol		100%Ethanol	
	ΔG_a	ΔG_t	ΔG_a	ΔG_t	ΔG_a	ΔG_t	ΔG_a	ΔG_t	ΔG_a	ΔG_t	ΔG_a	ΔG_t
283	-4.76	-	-3.89	0.87	-5.73	-0.18	-4.92	-0.03	-4.51	0.05	-5.34	0.58
293	-4.03	-	-5.15	1.47	-10.08	0.09	-5.21	0.25	-4.73	0.34	-5.69	0.17
303	-9.15	-	-5.39	3.76	-6.54	2.61	-5.48	0.60	-5.21	0.68	-5.44	0.64
313	-9.51	-	-5.92	3.59	-6.89	2.62	-5.89	0.61	-5.86	0.61	-6.38	0.52