



## KINETICS OF QUATERNIZATION BETWEEN N, N-DIMETHYLANILINE AND BENZYL CHLORIDE IN POLAR SOLVENTS-A REVISIT TO MENSCHUTKIN REACTION

P. Bashpa<sup>1</sup>, P. Rajendran<sup>2</sup>, K. Bijudas\*<sup>1</sup>

<sup>1</sup>Department of Chemistry, N. S. S. College, Manjeri, Malappuram, Kerala, India

<sup>2</sup>Department of Chemistry, Government Victoria College, Palakkad, Kerala, India

\*Corresponding author: [bijudask@gmail.com](mailto:bijudask@gmail.com)

### ABSTRACT

This work reports an extension of Menshutkin reaction and involves the studies on kinetics of quaternization reaction between N,N-Dimethylaniline and benzyl chloride in acetone and in other various solvents at 300 K. The progress of the reaction was followed by measuring the conductance of the product formed at regular intervals of time. The effect of [benzyl chloride] and [N,N-Dimethylaniline] on reaction rate was studied under pseudo-first order condition and the rate showed first order dependence on both [benzyl chloride] and [N,N-Dimethylaniline]. The effect of dielectric constant of the medium on reaction rate was studied by employing various solvents such as methyl ethyl ketone, isopropyl alcohol, ethyl alcohol, methyl alcohol and acetonitrile and the rate is found to increase with increase in dielectric constant of the medium. The linear plot with a negative slope on plotting  $\log k_2$  against  $1/D$  where  $D$  is the dielectric constant of the medium indicates the existence of a highly charged or a polar transition state during the progress of the reaction. The quaternization reaction was also carried out at different temperatures so as to compute the various thermodynamic parameters like activation energy, enthalpy of activation, entropy of activation and Gibb's free energy change. The higher value of activation energy is attributed for a slower reaction which is sterically controlled rather than thermodynamically controlled. The negative value of entropy of activation ( $\Delta S^*$ ) indicates some sort of surrendering of disorder in the transition state on its formation which proves that it is highly ordered with sufficient charge separation and polar in character. The product after purification was analysed by melting point and infra-red spectral analysis and is proved to be N-Benzyl-N,N-dimethylphenylmethanaminium chloride. A plausible mechanism in accordance with the obtained experimental results is reported.

**Keywords:** Menshutkin reaction, Kinetics, Quaternization, N,N-Dimethylaniline, Benzyl chloride, Phase transfer catalysis.

### 1. INTRODUCTION

Nikolai Aleksandrovich Menshutkin, a pioneer in the field of chemical kinetics has discovered a new reaction in which a tertiary amine can be transformed into a quaternary ammonium salt by reacting it with an alkyl halide [1-2]. Later, this reaction was named after him as Menshutkin reaction. Quaternary ammonium salts are positively charged polyatomic ions of the structure  $NR_4^+X^-$ , where R is an alkyl group or an aryl group and X is usually a halide ion. Quaternary ammonium salts are used as disinfectants, surfactants, fabric softeners, antistatic agents and also in the food service industry as sanitizing agents. Menshutkin reaction refers to the reaction between a tertiary amine with an alkyl halide to produce quaternary ammonium salts. Even though this reaction was reported in 1890, it becomes very

significant after the introduction of phase transfer catalysis (PTC) where quaternary ammonium salts are used as catalysts in chemical industry today.

PTC is relatively a newer technique that can be used to carry out most of the chemical transformations under mild conditions with improved results [3-6]. PTC technique is now utilized in many applications, from research in chemistry to full-scale synthetic production of chemicals like pharmaceuticals, fine chemicals, polymers, dyes etc. Cost reduction and pollution prevention are the two most powerful driving forces in the chemical industry today, and these can be achieved to a great extent by the phase transfer catalysis technique, if properly adopted [7-8]. The phase transfer catalyst (PTC) is a vehicle and it transfers anionic reactants into non-polar media and the transferred anions make the

reaction to take place with ease. This is quite significant when we see that reactions between substrate located in an organic phase and reactant located in the aqueous phase are slow and ineffective [9-10]. The commonly used PT catalysts are quaternary ammonium and phosphonium salts in which the former one is comparatively cheaper and easily available [11-13]. The wide use of quaternary ammonium salts as PT catalysts in various chemical industries today has increased the significance of Menshutkin reaction.

Menshutkin reaction is also considered as an important example for studying effect of solvents upon the rates of reactions and subsequent experimental and theoretical investigations were proved its significance [14-16]. Menshutkin had conducted the reaction between triethylamine and ethyl iodide in 39 solvents. He found that the reaction rate increased dramatically with the polarity of the solvent employed and he concluded that a reaction cannot be separated from the medium in which it is carried out. Unfortunately, the deep implications of this pioneering study of Menshutkin have not been considered for many years. The Menshutkin reaction is different from a true  $SN_2$  reaction where the reactants are uncharged, in contrast to most of the usual  $SN_2$  reactions where one of the reactants is charged. In the last few years there have been an outgrowing number of theoretical papers dealing with the solvent effect on various reactions upholding the significant contributions of Menshutkin in the field of chemical kinetics [17-22].

The study of the influence of dielectric constants of solvents forms an important aspect in chemical kinetics in deducing the mechanism of the reaction. The excessive use of quaternary ammonium salts as PT catalyst in our earlier studies prompted us to carry out the preparation of it by applying Menshutkin reaction [23-25]. More over very little works have been reported on kinetic and mechanistic studies of quaternization between N,N-Dimethylaniline (DMA) and benzyl chloride (BC) or such systems in polar solvents [26-28]. The present paper reports the kinetics of quaternization reaction between benzyl chloride and N,N-Dimethylaniline in acetone. Kinetic parameters such as order of the reaction with respect to both the reactants and the effect temperature on the reaction rates were also studied to compute various thermodynamic parameters. The effect of dielectric constant of the medium was carried out by employing methyl ethyl ketone, isopropyl alcohol, ethyl alcohol, methyl alcohol and acetonitrile as solvents apart from acetone. The product of the reaction was purified and analyzed by melting point and infra-red spectral

technique. A plausible mechanism in accordance with the observed results was also suggested.

## 2. EXPERIMENTAL

### 2.1. Material

All the chemicals used were of analar quality. Benzyl chloride (E-Merck, India) was used as such and N,N-Dimethylaniline, acetone, ethyl alcohol, methyl alcohol, methyl ethyl ketone, isopropyl alcohol and acetonitrile (E-Merck, India and Sisco Research Laboratories Pvt. Ltd., India) were used after distillation.

### 2.2. Methods

Kinetic investigations were carried out by measuring conductance at various temperatures using a digital conductivity meter (Equiptronics EQ 664 A). Benzyl chloride ( $0.05 \text{ mol dm}^{-3}$ ) in acetone (25 mL) was mixed with N,N-Dimethylaniline ( $0.5 \text{ mol dm}^{-3}$ ) in acetone (25mL) which were previously equilibrated in a constant temperature bath at 300 K. Aliquots of reaction mixture were taken out at regular intervals of time and the conductance was measured for about two hours. The reaction mixture was kept overnight at room temperature to measure conductance at the completion of reaction. The pseudo-first order rate constant ( $k_{obs}$ ) was derived from the conductivity data using the equation 1 by plotting  $\log C_{\infty} - Ct$  against time 't' where  $C_{\infty}$  is the conductance at infinite time,  $Ct$  is the conductance at a time 't' and  $C_0$  is the initial conductance by applying the method of least squares analysis. The values of second order rate constants ( $k_2$ ) were evaluated by the usual method as in equation 2.

$$k_{obs} = \frac{2 \cdot 303}{t} x \log \left( \frac{c_{\infty} - c_0}{c_{\infty} - c_t} \right) \dots 1$$

$$k_2 = \frac{k_{obs}}{[DMA]} \dots 2$$

The reaction was carried out at 300 K by varying [BC], keeping same [DMA] to determine the order of the quaternization reaction with respect to [BC] and by varying [DMA] with same [BA] for determining order with respect to [DMA]. The reaction was also followed at 305 K, 310 K and 315 K to determine the activation parameters. Activation energy ( $E_a$ ) was determined by plotting  $\log k_2$  against  $1/T$  and enthalpy of activation ( $\Delta H^*$ ) was determined by plotting  $\log k_2/T$  against  $1/T$ . The impact of changes in dielectric constant of the medium on reaction rate was studied by employing other solvents such as methyl ethyl ketone, isopropyl alcohol, ethyl alcohol, methyl alcohol and acetonitrile. Values of  $\log k_2$  against  $1/D$  (dielectric constant of the medium)

are plotted to study the nature of transition state. The product formed was analysed by melting point and infrared spectral technique.

### 3. RESULTS AND DISCUSSION

Stoichiometry of the reaction was established by equilibrating known [BC] with known [DMA] and found that one mole of BC is equivalent to one mole of DMA which is given in scheme 1.



#### Scheme 1: Stoichiometry of quaternization

The product of quaternization was subjected to infra-red spectral analysis and the following peaks obtained. A broad peak obtained in the region 2980-2960  $\text{cm}^{-1}$  (aromatic C-H stretching), a strong peak at 3170-3080  $\text{cm}^{-1}$  (N-H stretching), peak at 2865-2979  $\text{cm}^{-1}$  (saturated C-H stretching), peak at 1640  $\text{cm}^{-1}$  (C=C stretching vibration) and a strong peak at 1380-1400  $\text{cm}^{-1}$  (C-N+ stretching) proves that the product formed on quaternisation is N-Benzyl-N,N-dimethylphenylmethanaminium chloride whose melting point was found to be 104°C which is in accordance with the reported value available in literature.

The rate data of the quaternization reaction with different concentrations of BC keeping the [DMA] constant at 300 K is presented in table 1.

Under the condition, when [DMA]  $\gg$  [BC], the plots of

log [BC] versus time were found to be linear which indicates the first order dependence of the reaction on [BC]. This was further confirmed from the constant values of the specific rates ( $k_{\text{obs}}$ ) for the different concentrations of the benzyl chloride for a given [DMA]. This result is given in the first set of  $k_{\text{obs}}$  values in in table 1. The observed rate constants with different [DMA] and the same [BC] (set of  $k_{\text{obs}}$  values given in second set of table 1) increase linearly with increase in [DMA]. Plot of log  $k_{\text{obs}}$  against log [DMA] was found to be linear ( $r = 0.9999$ ) with a slope of unity showing that the reaction is first order with [DMA] and is given in fig. 1. The quaternization reaction is found to be of second order overall.

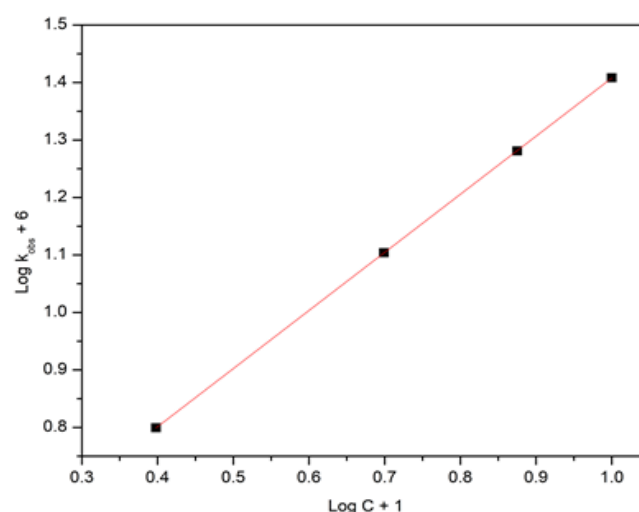


Fig. 1: Plot of log  $k_{\text{obs}}$  against log C

Table 1: Effect of [BC] and [DMA] on the rate of quaternization reaction

[DMA] $\times 10^1$ ( $\text{mol dm}^{-3}$ )	[BC] $\times 10^2$ ( $\text{mol dm}^{-3}$ )	$k_{\text{obs}} \times 10^5$ ( $\text{s}^{-1}$ )	$k_2 = \frac{k_{\text{obs}}}{[\text{DMA}]} \times 10^5$ ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )
5.0	2.5	1.24	2.48
5.0	5.0	1.22	2.44
5.0	7.5	1.20	2.40
5.0	12.5	1.22	2.44
2.5	5.0	0.63	2.53
5.0	5.0	1.22	2.44
7.5	5.0	1.91	2.55
10	5.0	2.56	2.56

Temperature - 300 K, Medium - Acetone

Kinetics of quaternization reaction was studied in the temperature range 300 K to 315 K and is presented in table 2. The values of different activation parameters are also computed and presented in table 2.

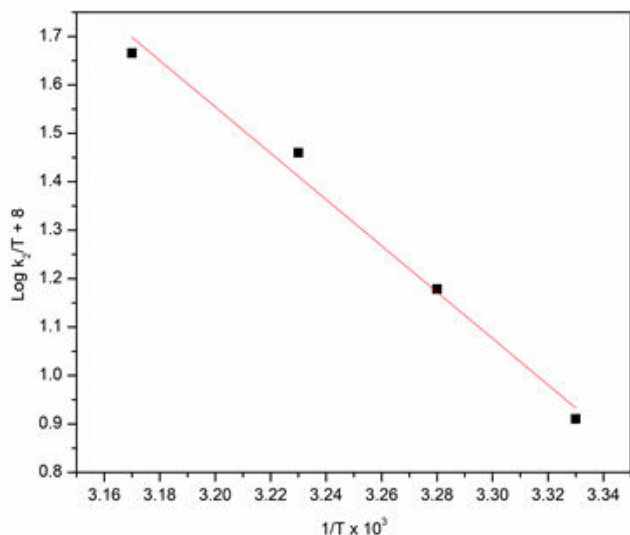
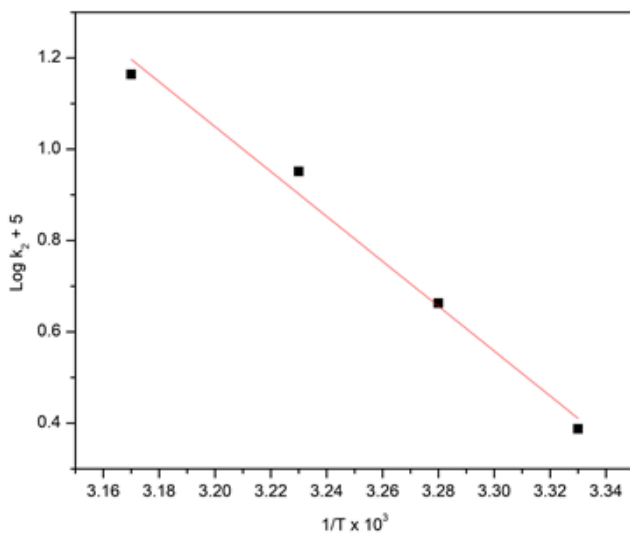
The reaction rate is found to be increased considerably

with increase in temperature. The activation energy ( $E_a$ ) is determined by plotting log  $k_2$  against  $1/T$  ( $r = 0.9940$ ) and the activation enthalpy is determined by plotting log  $k_2/T$  against  $1/T$  ( $r = 0.9938$ ) which is given in figure 2 and 3.

**Table 2: Effect of temperature and activation parameters for the quaternization reaction**

Temperature (K)	$k_{\text{obs}} \times 10^5$ ( $\text{s}^{-1}$ )	$k_2 \times 10^5$ ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )	$E_a$ ( $\text{kJ mol}^{-1}$ )	$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$-\Delta S^\ddagger$ ( $\text{JK}^{-1} \text{mol}^{-1}$ )	$\Delta G^\ddagger$ ( $\text{kJ mol}^{-1}$ )
300	1.22	2.44	94.01	91.52	28.30	100.0
305	2.30	4.60				
310	4.47	8.94				
315	7.29	14.58				

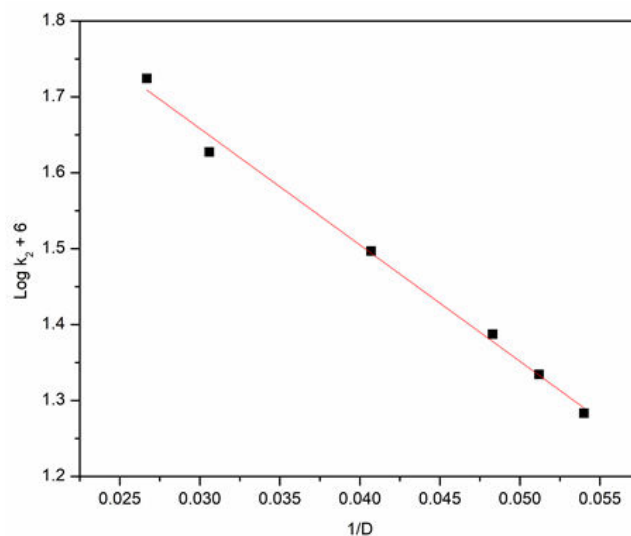
$[DMA] \times 101 = 5.0 \text{ mol dm}^{-3}$ ,  $[BC] \times 102 = 5.0 \text{ mol dm}^{-3}$  Medium = Acetone

**Fig. 2: Plot of  $\log k_2$  against  $1/T$** **Fig. 3: Plot of  $\log k_2/T$  against  $1/T$** 

The comparatively large  $E_a$  &  $\Delta H^\ddagger$  values indicate that the reaction is highly temperature sensitive showing that reaction rate is moderate at room temperature, but increases considerably with increase of temperature. The negative value of the entropy of activation indicate

surrendering of disorder when reactants are converted to transition state. Qualitatively, a negative value of  $\Delta S^\ddagger$  corresponds to an increase in molecular order and a loss of excited degree of freedom in the activated complex relative to the reactant molecules which corresponds to a highly ordered activated complex and this implies a large involvement of steric factors in the transition state. The  $\Delta G^\ddagger$  which is the free energy of activation is considerably larger indicating a comparatively rigid transition state formed between the reactants. The effect of dielectric constant of the medium on quaternization reaction was studied in solvents such as ethyl methyl ketone, isopropyl alcohol, acetone, ethyl alcohol, methyl alcohol and acetonitrile and is given in table 3.

The rate has increased with increase in dielectric constant of the medium which indicates that the transition state through which the reaction take place is highly polar or charged, which is reported elsewhere in the case of quaternary salts [29-30]. Values of  $\log k_2$  against  $1/D$  at 300 K are plotted and found to be linear ( $r = 0.9971$ ) with a negative slope as given in figure 4 which once again confirms that the transition state is highly charge separated and polar.

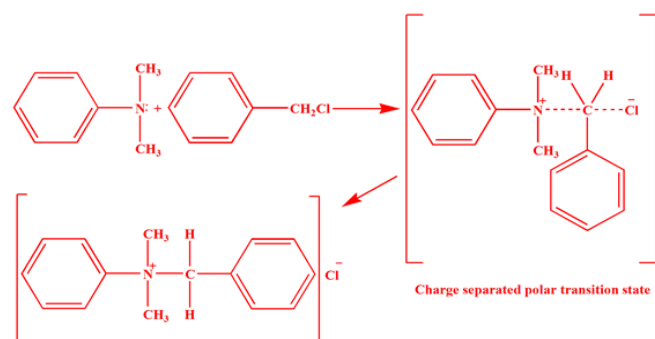
**Fig. 4: Plot of  $\log k_2$  against  $1/D$**

**Table 3: Effect of dielectric constant of the medium on the quaternization reaction**

Sl. No.	Solvents	Dielectric constant (D)	$k_{\text{obs}} \times 10^5 \text{ (s}^{-1}\text{)}$	$k_2 \times 10^5 \text{ (dm}^3 \text{ mol}^{-1} \text{ s}^{-1}\text{)}$
1	Methyl ethyl ketone	18.51	0.96	1.95
2	Isopropyl alcohol	19.92	1.08	2.16
3	Acetone	20.7	1.22	2.44
4	Ethyl alcohol	24.55	1.57	3.14
5	Methyl alcohol	32.70	2.12	4.24
6	Acetonitrile	37.50	2.65	5.30

$[DMA] \times 101 = 5.0 \text{ mol dm}^{-3}$   $[BC] \times 102 = 5.0 \text{ mol dm}^{-3}$ , Temperature - 300 K

Thus benzyl chloride on quaternization with N,N-dimethylaniline in acetone giving a quaternary ammonium salt (N-Benzyl-N,N-dimethylphenylmethanaminium chloride) through a charge separated transition state. The quaternary ammonium salt formed is highly sterically hindered and thus the rate of formation of is very slow at normal temperature. A plausible mechanism in accordance with the experimental evidences obtained is given in fig. 5.



**Fig. 5: Mechanistic path of quaternization reaction**

#### 4. CONCLUSIONS

The kinetics of quaternization reaction between benzyl chloride and N,N-Dimethylaniline was carried out forming N-Benzyl-N,N-dimethylphenylmethanaminium chloride as the product in acetone at 300 K and the reaction was followed conductometric method. The effect of concentration of both substrates on reaction rate was studied. The effect of temperature on reaction rate was also studied to determine various activation parameters. The impact of changes in dielectric constant of the medium was studied by employing various solvents which suggests the formation of a highly polar and charge separated transition state. A plausible mechanism is suggested in accordance with the experimental evidences. The product formed is a very sterically hindered quaternary ammonium salt and hence the rate of formation is very low. Kinetic studies on the

formation of such quaternary ammonium salts are scanty which points out the significance of the present work.

#### Conflict of interest

Authors hereby declare that there is no conflict of interest on publication of this manuscript.

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