

## Kinetic Studies on the Reaction between Benzyl/ Phenacyl Chloride and N,N-Dimethylaniline in Acetone-Water Mixed Solvents

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Rate constants ( $k_1$ ) for the reaction between benzyl chloride (BC)/phenacyl chloride (PC) and N,N-dimethylaniline (DMA) have been determined conductometrically under pseudo-first-order conditions. Second order rate constants ( $k_2$ ) were evaluated in the usual way. The effect of electron withdrawing —CO— group  $\alpha$ -to chlorine is not felt on the values of  $k_2(\text{PC} + \text{DMA})$ . The marked effect of acetone-water solvent composition on the rate is known from correlation technique with  $\log k_2(\text{BC}/\text{PC} + \text{DMA})$  with Grunwald-Winstein's (Y) and Kosowar (Z) of solvent polarity parameters.

**Key Words:** Kinetics, Reaction, Benzyl chloride, Phenacyl chloride, N,N-Dimethyl-aniline, Solvents.

### INTRODUCTION

Kinetics of the reactions of active halide(s) containing electron-withdrawing group  $\alpha$ -to halogen such as EWG—CH<sub>2</sub>Br (EWG = —COPh, —COOEt) with triethylamine were studied in various solvents.<sup>1,2</sup> Solvent effects were reported in these reactions, where correlation technique was employed to evaluate the effect of solvents. The  $\log k_2$  of these reactions were correlated with solvent parameters at macroscopic and microscopic levels. It may be concluded that more than one interaction of solvent parameters has to be considered to understand the effect of solvents on the rate. In the case of mixed solvents, it is reported that many chemical phenomena have been affected by the particular composition of component of aqueous-organic mixed solvents, which is called as critical region of mixed media.<sup>3</sup> The critical region for PhCOCH<sub>2</sub>Br + NEt<sub>3</sub> reaction was found as 10% water content in acetone-water (v/v).<sup>4</sup> We inquest to study the effect of aqueous acetone mixed solvents on the reaction of benzyl chloride/phenacyl chloride with N,N-dimethyl aniline for which no such work is reported. We present here our findings.

### EXPERIMENTAL

Benzyl chloride (BC) and phenacyl chloride (PC) (Koch-Light Laboratories Ltd) were used as such. N,N-dimethylaniline (DMA) (E. Merck) and acetone (E. Merck) were used after distillation.

### Conductance measurements: A typical run

Conductivity experiments were carried out using Equiptronics digital conductivity meter, model No. EQ660.

The solutions of BC/PC ( $0.1 \text{ mol dm}^{-3}$ , 25 mL) and DMA ( $1.0 \text{ mol dm}^{-3}$ , 25 mL) in acetone were prepared. The conductivity experiments were carried out as reported elsewhere.<sup>4</sup> The reaction mixture was kept overnight at room temperature to measure  $C_\infty$ . The pseudo-first-order rate constant ( $k_1$ ) was derived from the conductivity data using the equation (1) by plotting  $\log C_\infty - C_t$  against 't' by applying the method of least squares analysis.

$$k_1 = \frac{2.303}{t} \log \frac{C_\infty - C_0}{C_\infty - C_t} \quad (1)$$

where  $C_0$ ,  $C_t$  and  $C_\infty$  are the conductances at times  $t_0$ ,  $t$  and  $t_\infty$  respectively. Second order rate constants ( $k_2$ ) were evaluated using the equation (2).

$$k_2 = \frac{k_1}{[\text{DMA}]} \quad (2)$$

**Product Analysis:** The solutions of BC (1.58 g,  $0.5 \text{ mol dm}^{-3}$ ) and DMA (1.51 g,  $0.5 \text{ mol dm}^{-3}$ ) in acetone (25 mL) were mixed and kept overnight at room temperature. The solid product which formed was filtered off, washed well with acetone and recrystallized from ethanol, yield 2.56 g (80%), m.p. 104–06°C. IR (KBr) and  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) of the compound were recorded and identified as N,N-dimethyl-N-phenyl benzemethaminium chloride.

IR: 2980–2950 ( $\nu(\text{C—H})$ ), 1380–1420 ( $\nu(\text{C—N}^+)$ )  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$  7.92–7.10 (m, Ar), 5.56 (s,  $-\text{CH}_2-\text{Ar}$ ), 3.80 (s,  $\text{N}^+\text{Me}_2$ ) ppm.

The same procedure was followed for PC (1.92 g,  $0.5 \text{ mol dm}^{-3}$ ) and DMA (1.51 g,  $0.5 \text{ mol dm}^{-3}$ ) in acetone (25 mL) reaction to give the solid product, yield 2.84 g (80%), m.p. 96–97°C. The spectra IR (KBr),  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ) of the compound were recorded and identified as N,N-dimethyl-N-phenyl phenacyl methaminium chloride. IR : 2985–2950 ( $\nu(\text{C—H})$ ), 1710 ( $\nu(\text{C=O})$ ), 1390–1410 ( $\nu(\text{C—N}^+)$ )  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  :  $\delta$  8.12–7.89 (m, Ar), 3.92 (s,  $\text{N}^+\text{Me}_2$ ) ppm.

## RESULTS AND DISCUSSION

The rates of the reaction of BC/PC with DMA in acetone-water mixed solvents with the water content up to 25% (v/v) at 30°C were determined by conductometric method under pseudo-first-order conditions (eq. (1)). The values of first-order rate constants ( $k_1$ ) were obtained from conductivity data by the method of least squares analysis. The values of second order rate constants ( $k_2$ ) were evaluated from the usual method (eq. 2). The results are presented in Table-1.

Conductance of the reactions under equimolar concentration was found too slow to measure. Then the reactions have been switched over to pseudo-first-order conditions.

The compound PC is more polar and highly reactive due to the presence of carbonyl group  $\alpha$ -to chlorine than to that of BC. However, the rate data (Table-1) show that both compounds have behaved in similar way. This indicates that the polar effect of PC may be suppressed by serious steric hindrance from DMA.

TABLE-1  
RATE CONSTANTS OF THE REACTION BETWEEN BENZYL/PHENACYL  
CHLORIDE AND N,N-DIMETHYLANILINE

[BC/PC] = 0.1 dm<sup>-3</sup> mol; [DMA] = 1.0 dm<sup>-3</sup> mol; Temp. 30°C

Solvent: Acetone-water mixed solvents

% of water in acetone (v/v)	10 <sup>3</sup> × k <sub>1</sub> , min <sup>-1</sup>		10 <sup>3</sup> × k <sub>2</sub> , mol <sup>-1</sup> dm <sup>3</sup> min <sup>-1</sup>	
	BC	PC	BC	PC
0	1.5737	1.5131	1.5737	1.5131
5	1.6121	1.6120	1.6121	1.6120
10	1.7760	1.7650	1.7760	1.7650
15	1.8420	1.8230	1.840	1.8230
20	1.9190	1.9300	1.9190	1.9300
25	2.0260	2.0340	2.2060	2.0340

The values of rate constants ( $k_2$ ) against solvent composition give a linear plot (Fig. 1). This shows that these reactions may be more sensitive towards solvent polarity as seen in most of the Menshutkin type reactions. Every addition of water into acetone will increase the polarity of the mixed solvents which is in turn the cause for increasing the rate. The quaternization of DMA by BC/PC is dipole-dipole reaction which gives ionic product through the formation of highly charged transition state and undergoes S<sub>N</sub>2 type process (Scheme-1). The hydroxylic component in acetone-water may interact strongly with the negatively charged part of the activated state through H-bonding. This may stabilize the activated state and thereby facilitate the reaction to be faster.<sup>5</sup>

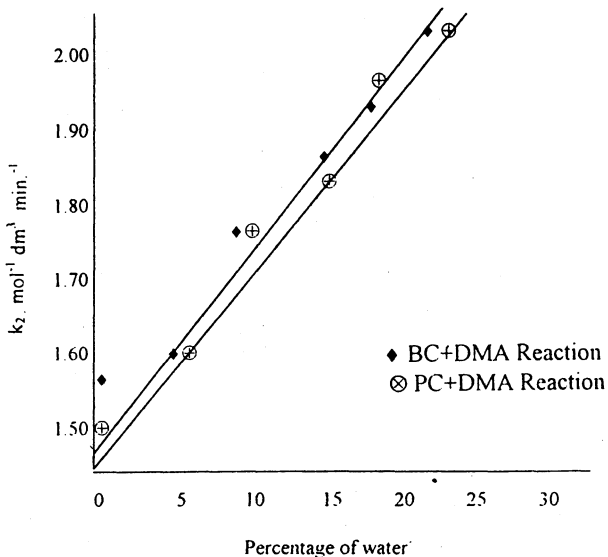
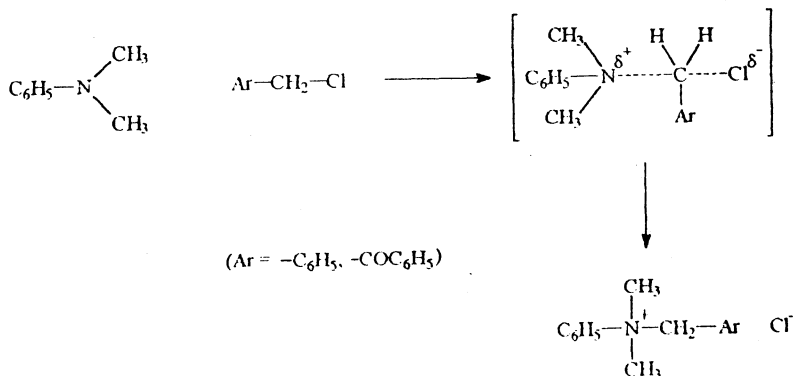


Fig. 1 Plot of  $k_2$  vs. solvent composition

The interaction of solvent polarity on the rates of reaction of BC/PC with DMA may be further supported by simple linear regression analysis of log  $k_2$  against



Scheme-I

solvent polarity scale 'Y' of Grunwald-Winstein<sup>6</sup> and 'Z' of Kosowar.<sup>7</sup> To apply Grunwald-Winstein equation (3),

$$\log k_2 = \log k_0 + mY \quad (3)$$

The values in Table-2 have been fitted into equation (3) by least squares analysis. The regression equations (4) and (5) for BC/PC + DMA, are:

$$\log k_{2(\text{BC} + \text{DMA})} = 2.685 + 0.039Y \quad (4)$$

$r = 0.996, \text{SD} = 0.003, n = 5$

$$\log k_{2(\text{PC} + \text{DMA})} = 2.685 + 0.04Y \quad (5)$$

$(r = 0.993, \text{SD} = 0.004, n = 5)$

The good relationship between  $\log k_2$  of BC/PC with DMA and the Y values of the solvent mixtures are known from  $r = 0.996/0.993$  and the standard deviation of the estimate  $\text{SD} = 0.003/0.004$ . The low value of the slope  $m = 0.039$  (BC)/ $0.04$  (PC) indicates that these two reactions are not susceptible to solvolysis but sensitive to the polarity and follow  $\text{S}_{\text{N}}2$  type pathway. Kosowar proposed a term Z to characterize the solvent polarity derived from the phenomenon of solvatochromism in terms of energy.<sup>7</sup> The linearity resulting from the plot of  $\log k_2$  against Z (Table-2) (regression equations (6) and (7) shows the dependence of rate of these reactions on solvent polarity.

$$\log k_{2(\text{BC} + \text{DMA})} = 0.458 + 0.01Z \quad (6)$$

$(r = 0.994, \text{SD} = 0.004, n = 5)$

$$\log k_{2(\text{PC} + \text{DMA})} = 0.443 + 0.01Z \quad (7)$$

$(r = 0.991, \text{SD} = 0.005, n = 5)$

TABLE-2  
BC/PC + DMA REACTION:  $\log k_2$  vs. Y AND Z VALUES

% of water in acetone (v/v)	$4 + \log k_2$		Y-values	Z-values
	BC	PC		
5	1.207	1.207	-2.706	72.9
10	1.249	1.246	-1.656	76.6
15	1.265	1.260	-1.308	78.7
20	1.283	1.283	-0.673	80.7
25	1.306	1.308	-0.308	82.1

## Conclusion

The values of rate constants of the reaction of N,N-dimethylaniline with benzyl chloride are found same as that of the reaction with phenacyl chloride in all ranges of water content in binary solvent mixtures. The effect of —CO— group  $\alpha$ -to chlorine is not felt on the rate data. The electronic effect in PC may be suppressed by a serious steric effect exhibited by DMA. The reaction between BC/PC + DMA is the Menshutkin type dipolar-dipolar reaction which gives the ionic product through the formation of highly charged transition state ( $S_N2$ ). The reactions are sensitive to the solvent polarity which is revealed from the rate data in acetone-water binary solvents. The correlation technique involving  $\log k_2$  of the reactions with solvent polarity scales Y of Grunwald-Winstein and Z of Kosowar is found successful.

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