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Kinetic Studies on the Micellar Catalyzed Reaction of Phenacyl Bromide with Phenol-Triethylamine in Aqueous-Organic Mixed Solvents

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Kinetics of the reaction between phenacyl bromide and phenol-triethylamine in the presence of sodium lauryl sulphate (NaLS) as surfactant in aqueous-organic mixed solvents at 30°C have been studied conductometrically using Guggenheim's method under pseudo-first-order conditions. Etherification takes place in the presence of micelles, whereas quaternization in its absence. It is supported by product analysis.

Aromatic ethers have wide applications in the field of agrochemicals as herbicides, fungicides, etc. Hence, we have attempted to get aryl ethers from the reaction between phenacyl bromide and phenol(s)-tertiary amine under equimolar concentration in various organic solvents at different polarity ranges[1–3]. Phenol(s) with $pK_a \geq 7.15$ did not give phenacyl phenyl ether in all the polarity ranges of these solvents; instead, quaternization took place. We have tried with the same reaction in micellar medium, where we found the formation of ethers[4]. However, there is no kinetic investigation on this reaction for providing the mechanism. Hence, it is decided to carry out kinetic studies on the reaction and here we report our findings.

EXPERIMENTAL

Phenol, triethylamine, acetone and methanol were purified as mentioned in the literature before use. NaLS (AnalaR) sample was used as received. Phenacyl bromide was prepared as reported elsewhere[2]. Micellar solution was prepared by dissolving NaLS above its Critical Micelle Concentration (CMC) (0.6 g, 300 mL) in methanol-water 70% (V/V) and stirring continuously for about 1 h. This micellar solution was used as medium for the preparation of the solution of phenacyl bromide (0.025 mol dm^{-3}) and phenol-triethylamine (0.25 mol dm^{-3}). The conductances of these solutions were measured separately after attaining the temperature of the thermostat (± 0.1°C) using flat-bottomed test tube with B–24 ground joined containing a small magnetic stirring bar. The solution of phenol-triethylamine (0.25 mol dm^{-3}, 10 mL) was pipetted out into the test tube containing the solution of phenacyl bromide (0.025 mol dm^{-3}, 10 mL) and simultaneously a stop watch was started at about half addition from the pipette. The well-cleaned conductivity cell was immediately placed in the test tube containing the reaction mixture and noted the conductance readings. The reaction mixture had been stirred continuously during the measurement of conductance by water-powered magnetic stirrer[5]. The conductance was measured at convenient interval of time till geting constant value. The rate constant k_1 was determined by using appropriate equation[6] by the method of Least Squares Analysis. The same procedure was followed for the reaction in the

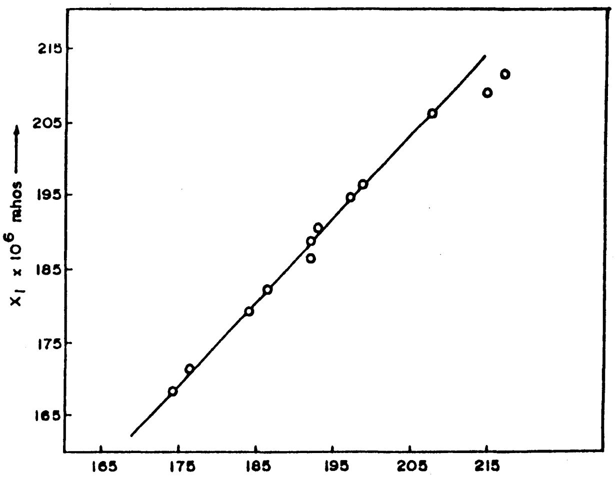

Fig. 1. Plot of x_1 Vs x_2 for the reaction of $PhCOCH_2Br$ with PhOH—NEt_3 in the Presence of Micelles of NaLS in 70% Methanol at 30°C
[$k_1 = 0.023\ min^{-1}$, $k_2 = 0.092\ dm^3\ mol^{-1}\ min^{-1}$; r = 0.999, n = 8]

absence of micelles and phenol. A typical kinetic run is presented here (Table-1) (Fig. 1). Second order rate constant (k_2) has been derived from k_1 by usual method.

TABLE-1
CONDUCTANCE DATA OF THE REACTION BETWEEN PHENACYL BROMIDE AND EQUIMOLAR MIXTURE OF PHENOL AND TRIETHYLAMINE IN 70% METHANOL (V/V) AT 30°C IN THE PRESENCE OF MICELLES OF NaLS
[$PhCOCH_2Br$] = 0.025 M; [PhOH] = [NEt_3] = 0.25 M

Time (min)	Cond. (mhos × 10^6)	Time (min)	Cond. (mhos × 10^6)
0	1.683	21	1.866
3	1.713	27	1.901
6	1.741	30	1.918
9	1.768	33	1.933
12	1.795	36	1.949
15	1.819	39	1.960
18	1.844	42	1.972

Product Analysis: Equal volumes of equimolar (25 mL, 0.1 mol dm^{-3}) solutions of phenacyl bromide and PhOH—NEt_3 in micellar medium were mixed under kinetic conditions and kept overnight with constant stirring at 30°C. The colourless, powdered mass was filtered off and dried under *vacuo*; m.p. 70–71 °C; yield 90%. It was identified as phenacyl phenyl ether by comparing melting point with authentic sample.

RESULTS AND DISCUSSION

The rate constants for the reaction of phenacyl bromide with phenol-triethylamine in the presence and absence of micelles were determined in 70%

methanol or acetone (V/V) at 30°C. Control experiments were done in the absence of phenol. The values of rate constants are presented in Table-2.

TABLE-2
RATE CONSTANTS OF THE REACTION OF PHENACYL BROMIDE WITH $PhOH—NEt_3$ IN THE PRESENCE AND ABSENCE OF MICELLES IN 70% METHANOL OR ACETONE (V/V) AT 30°C

$PhCOCH_2Br$ mol dm^{-3}	PhOH mol dm^{-3}	NEt_3 mol dm^{-3}	k_1 min^{-1}	$k_2 = k_1/[Nu]$ dm^3 mol^{-1} min^{-1}
70% methanol (V/V) in the absence of micelles				
0.025	0.25	0.25	0.033	0.132
(0.025)	–	(0.25)	(0.037)	(0.148)
70% methanol (V/V) in the presence of micelles				
0.025	0.25	0.25	0.023	0.092
(0.025)	–	(0.25)	(0.091)	(0.364)
70% acetone (V/V) in the absence of micelles				
0.025	0.25	0.25	0.052	0.208
(0.025)	–	(0.25)	(0.058)	(0.232)
70% methanol (V/V) in the absence of micelles				
0.025	0.25	0.25	0.064	0.148
(0.025)	–	(0.25)	(0.112)	(0.448)

Values in parenthesis are for the reaction in the absence of phenol.

The rate of quaterinization of triethylamine by phenacyl bromide ($k_2 = 0.48$ dm^3 $mol^{-1}min^{-1}$) was retarded to about 10% when phenol was added ($k_2 = 0.132$ dm^3 mol^{-1} min^{-1}). The TLC analysis of this reaction mixture did not show ether formation. The presence of phenol in the reaction mixture may disturb the mobility of the ions, which in turn affects the conductance.

Similar observation is seen in 70% acetone-water (V/V) mixed solvents. However, the rate of quaternization in acetone-water is about 1.60 times greater than the rate in methanol-water (Table-2.) Hydrogen bonding formation between the reactive species and aq. organic mixed solvents which in turn cause the solvation may be one of the factors for this difference in rate. The magnitude of the strength of H-bonding by latter solvents is higher than the strength in the former solvents.

Entirely different situation was observed when reaction was switched over to micellar environment. The rate of quaternization in micellar medium ($k_2 = 0.364$ dm^3 mol^{-1} min^{-1}) was found to be 2.75 times enhanced to that of the rate of quaternization ($k_2 = 0.132$ dm^3 mol^{-1} min^{-1}) in the absence of micellar medium. The presence of phenol decreased the rate ($k_2 = 0.092$ dm^3 $mol^{-1}min^{-1}$ to about fourfold less than the rate of quaternization. The product analysis of this reaction mixture has proved the formation of ether.

Rate acceleration of quaternization and etherification reactions in micellar solutions can be attributed to electrostatic and hydrophobic interactions between the substrate and the surfactant aggregate, since sodium lauryl sulphate is an anionic surfactant (Fig. 2). It forms anionic micellar solution in aq. organic mixed medium. The environment of the micellar solution is shown in Fig. 3.

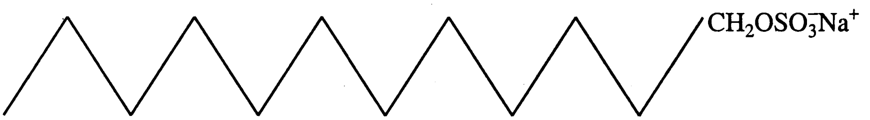

Fig. 2.

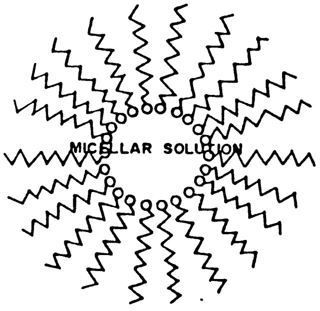

Fig. 3.

The alkyl chain of NaLS aggregates to have a hydrophobic region. The head group sulphate ion of NaLS possessing negative charge is in the bulk solution which behaves as hydrophilic region. The aromatic part of the reagents such as phenacyl bromide and phenol may be highly populated in the micelles; on the other hand, the polar part of the reagents such as —CO—CH_2Br of phenacyl bromide, —OH of phenol and NEt_3, may be concentrated in the hydrophilic region. This may facilitate the generation of the phenolate ion to act as nucleophile with phenacyl bromide to give ether, whereas triethylamine behaves as a co-surfactant[7]. In the absence of phenol, NEt_3 acts as nucleophile and quaternization takes place readily. The SN^2 mechanism may be proposed for etherification as well as quaternization.

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