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Effect of α-Alkyl Substituents in the Solvolysis of Cumyl Chloride in 90% Aqueous Organic Solvents

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The substitution of methyl group of cumyl chloride by bulky alkyl groups reduces the rate of solvolysis in 90% aqueous organic solvents. The difficulty in attaining coplanarity at the transition state reduces the delocalization of the charge by resonance and thus retards the rate of solvolysis. The linear plot obtained when log k_1 is plotted against Charton's steric parameter 'υ' (upsilon) indicates the rate is controlled by steric factors rather than the electronic factors. The similar values of reaction constant 'ρ^+' in the para substituted compounds of cumyl chloride and ethylmethylbenzyl chloride indicate the steric contribution of ethyl group is negligible.

Key Words: α-Alkyl substituents, Solvolysis, Cumyl chloride.

INTRODUCTION

The stability of carbonium ion centre in cumyl system by the formation of delocalized carbocation *via* resonance stabilization through π-bonds of benzene ring was established in our previous paper[1]. Any factor that can increase the electron density at the carbocation centre stabilizes the transition state and thereby accelerates the rate of solvolysis involving these kinds of substrates. We studied this aspect by replacing the methyl group of cumyl chloride by ethyl, isopropyl and *t*-butyl groups.

EXPERIMENTAL

Alcohols were prepared by the Grignard reaction of alkyl/aryl magnesium halides with corresponding ketones in dry ether[2]. They were purified by fractional distillation at reduced pressure. Purity was ensured by TLC and authenticities were established by IR and NMR spectra. Cumyl alcohol and its *p*-substituted derivatives were converted to corresponding chlorides by passing dry HCl gas[3]. Other alcohols were converted to chlorides by reaction with thionyl chloride in order to prevent rearrangement[4]. All these chlorides were found to eliminate HCl during fractional distillation under reduced pressure and on storage. The fractionally distilled cumyl chloride and undistilled cumyl chloride gave same value of rate constant for solvolysis. The other tertiary chlorides were therefore used without distillation[3]. The chlorides were stored in dry condition at subzero temperature and stored for a maximum period of two weeks.

The titrimetric estimation of HCl using lacmoid indicator in dry acetone was employed for the rate determination in 90% aqueous acetone. Conventional thermostat with Jackson thermometer was used for temperature control. For maintaining low temperature a cryostat assembly was used. Rate measurements at higher temperatures were done by ampoule techniques.

Solvolysis rate constants in 90% aqueous acetonitrile were determined by Hitachi 220A spectrophotometer with thermostatic cell holder by monitoring the product peak.

RESULTS AND DISCUSSION

The solvolysis rate of cumyl chloride* in 90% aqueous acetone is 1200 times more than that of *t*-butyl chloride[7] at 25°C (Table-1) due to the resonance stabilization involved in the transition state of cumyl chloride. When the methyl group of cumyl chloride is successively replaced by ethyl, isopropyl and *t*-butyl groups, a large reduction in the rate of solvolysis is observed (Table-1). Similar substitutions in *t*-butyl chloride cause a rate acceleration[8]. The electron donating inductive effect increases moderately in the order Me < Et < *i*-Pr < *t*-Bu. The hyperconjugative contributions decrease in the series Me > Et > *i*-Pr > *t*-Bu. The steric requirements of these groups increase sharply in the same order[9]. The rate enhancement in substituted *t*-butyl chlorides is mainly due to the relief of steric strain during the formation of carbocation that is a change from *sp*^{3} initial state to *sp*^{2} transition state (B-strain[9]).

TABLE-1
KINETIC DATA FOR THE SOLVOLYSIS OF α-METHYL-α-ALKYLBENZYL CHLORIDES AND t-BUTYL CHLORIDE* IN 90% AQUEOUS ACETONE

α-substituent	Temp. (°C)	$10^4 k_1 s^{-1}$	$10^4 k_1 s^{-1}$ at 298 K	$\Delta H^{\#}$ 298 K (kJ mol^{-1})	$-\Delta S^{\#}$ 298 K (J mol^{-1}K^{-1})	$\Delta G^{\#}$ 298 K (kJ mol^{-1})
Methyl	18.0	0.738	1.57	74	70	95
	24.0	1.45				
	33.0	3.51				
	45.0	10.9				
Ethyl	18.0	0.204	0.450	79	63	98
	24.0	0.399				
	33.0	1.08				
	45.0	3.53				
i-propyl	33.0	0.359	0.148	80	68	101
	39.5	0.693				
	45.0	1.19				
	55.0	3.20				
t-butyl	65.0	0.203	0.00251	89	72	111
	75.0	0.500				
	85.0	1.24				
	95.0	2.88				
t-butyl chloride*	25.0		0.00131	91	68	112

*Data from Ref 7.

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*The value obtained is slightly higher than that reported by earlier workes[3–5]. The rates of solvolysis were highly sensitive to minor changes in water content; the same batch of solvents were used for all rate measurements by preparing a 50 L solvent.

Replacement of one of the methyl groups in *t*-butyl chloride by phenyl group does not alter the electronic contributions or steric strains from α-alkyl groups. If we consider only the above-discussed factors in cumyl chloride, a rate enhancement by a sterically bulkier phenyl is expected. Instead of rate acceleration, a deceleration of rate due to steric effect is observed. Since the resonance stabilization of the formed carbocation plays an important role in facilitating $S_N{}^1$ reaction in benzylic system, steric inhibition of resonance should lead to a drop in rate. The large reduction in rate is due to the loss of coplanarity in the transition state. For the maximum resonance stabilization of the carbocation, the benzene ring and the alkyl groups attached to the α-carbon atom should be coplanar. The coplanarity is interfered when the alkyl group is larger.

The data in Table-1 showed that a change from α-methyl to α-butyl reduces the rate from 1000 to 1.6. The loss of coplanarity reduces the resonance contribution from the benzene ring towards the carbocationic centre thereby destabilizes the carbonium ion. Thus the initial state destabilization by the bulkier group is not the deciding factor, but the destabilization of transition state by the reduction in resonance contribution causes the rate retardation in the solvolysis of α-alkyl substituted cumyl chlorides. The successive increase in the enthalpy of activation from 74 to 89 kJ mol^{-1} and the free energy from 95 to 111 kJ mol^{-1} supports the difficulty in the attainment of transition state. The entropy value remains almost constant indicating similar transition state in all these substrates. Tanida and Matsumura[10] demonstrated the large reduction in the rate of solvolysis when *t*-butyl groups replaced both the methyl groups of *p*-nitrobenzoate of cumyl alcohol. Moreover, they have shown that hyperconjugative contribution from the *para*-substituents in this bulky substrate is substantially lower than that of the cumyl system.

The steric as well as electronic factors can alter the rate of solvolysis in α-alkyl substituted cumyl chlorides. The β-isotopic effect of *p*-nitrobenzoate of α-substituted cumyl alcohol showed that the hyperconjugative electron donation by the hydrogens of α-methyl groups can contribute to the stabilization of carbocation centre[11, 12]. The steric requirements of alkyl groups (methyl to *t*-butyl) increase sharply comparing with polar effect. The Taft equation[13] developed using basic and acidic hydrolysis of benzyl esters helps to separate these two effects. A number of refinements were suggested for the steric factor 'Es' in the Taft equation[14]. When the steric parameters suggested by different authors were plotted against log k_1 values, the best fit was observed for Charton's steric factor 'υ' (upsilon)[15]. Charton's steric factor is based on the van der Waals' radii of different groups[16]. The good correlation (correlation coefficient 0.991) suggests that the solvolysis of α-alkyl substituted cumyl chlorides is controlled by the steric factors rather than the electronic factors.

The delocalized nature of the positive charge in cumyl chloride implies that specific, localized interactions of solvent molecules with the carbocation are unlikely[17]. Furthermore, in the transition state of cumyl chloride solvolysis, the cumyl cation and chloride anion will both have a strong preference for solvation by a sheath of water molecules. A change of organic component of the solvent, keeping the concentration of water constant, causes only a general variation in rate without specifically affecting the reaction centre. A more polar aprotic solvent can increase the rate of solvolysis by stabilizing the charged transition state of the carbonium ion. The rate of solvolysis of cumyl chloride and its α-alkyl substituted derivatives in 90% aqueous acetonitrile showed a 10-fold enhancement in rate (Table-2). This factor is almost constant in all α-alkyl substituted cumyl chlorides. The enthalpy and free energy of activation are less. The solvation of ions in aqueous acetonitrile is more than that of aqueous acetone (dielectric constants of acetonitrile and acetone at 25°C are 35.9 and 20.6 respectively). The plot of log k_1 *vs.* Charton's steric constant 'ν' showed a linear correlation with a correlation coefficient of 0.995. These observations further confirm that a change in solvent does not affect the variation in rate in the α-alkyl substitution showing that the steric parameters are the deciding factors for the rate of solvolysis in cumyl chloride.

TABLE-2
KINETIC DATA FOR THE SOLVOLYSIS OF α-METHYL-α-ALKYLBENZYLCHLORIDES IN 90% AQUEOUS ACETONITRILE

α-substituent	Temp (°C)	$10^4\ k_1\ s^{-1}$	$10^4\ k_1^{-1}\ s^{-1}$ at 298 K	$\Delta H^{\#}$ 298 K (kJ mol^{-1})	$-\Delta S^{\#}$ 298 K (J $mol^{-1}K^{-1}$)	$\Delta G^{\#}$ 298 K (kJ mol^{-1})
Methyl	6.0	2.55	16.3	65	81	89
	12.0	4.74				
	18.0	8.72				
	24.0	14.7				
Ethyl	6.0	0.80	5.96	70	71	91
	12.0	1.56				
	18.0	3.03				
	24.0	5.40				
	33.0	12.7				
i-propyl	24.0	1.86	2.07	76	62	94
	33.0	4.77				
	39.5	8.86				
	45.0	15.1				
t-butyl	45.0	0.207	0.0240	82	77	105
	55.0	0.531				
	65.0	1.360				
	75.0	3.230				

TABLE-3
KINETIC DATA FOR THE SOLVOLYSIS OF α-METHYL-α-ALKYLBENZYL CHLORIDES IN 90% AQUEOUS ACETONE

α-substituent	Temp. (°C)	$10^4 k_1 s^{-1}$	$10^4 k_1 s^{-1}$ at 298 K	$\Delta H^{\#}$ 298 K (kJ mol^{-1})	$-\Delta S^{\#}$ 298 K (J $mol^{-1} K^{-1}$)	$\Delta G^{\#}$ 298 K (kJ mol^{-1})
p-Substituted cumyl chloride:						
methyl	3.3	4.75	37.0	62	82	86
	12.0	11.0				
	18.0	20.2				
	40.0	1.68				
bromo	33.0	0.706	0.293	80	63	99
	39.5	1.39				
	45.0	2.28				
	55.0	6.27				
p-Substituted ethylmethylbenzyl chloride:						
methyl	3.3	1.16	13.9	76	46	89
	12.0	3.32				
	18.0	6.69				
	24.0	12.3				
bromo	33.0	0.200	0.0764	88	49	102
	39.5	0.408				
	45.0	0.752				
	55.0	2.140				

Rate and activation parameters are determined for the *p*-methyl and *p*-bromo substituted derivatives of cumyl chloride and α-ethyl substituted cumyl chloride in 90% aqueous acetone (Table-3). As expected for an $S_N{}^1$ reaction the *p*-methyl enhances the rate and *p*-bromo retards the rate of solvolysis. The ρ^+ value calculated by the application of Brown equation[18] $\log k/k_0 = \rho^+\sigma^+$, gave a value –4.55 for cumyl chloride (correlation coefficient 0.9997) and –4.89 for α-ethyl substituted cumyl chloride (correlation coefficient 0.9999). The literature value for unimolecular solvolysis of cumyl chloride is –4.54[18, 19]. The α-ethyl substitution does not alter the value of ρ^+ to substantial amount indicating that minor steric factor of the α-ethyl group is not preventing the electronic participation from the *para* substituent to the carbocationic centre. The ρ^+ value reported[10] for *p*-nitrobenzoate of α,α-dibutyl cumyl alcohol, having high steric hindrance in 70% aqueous acetone is –2.91 (for *p*-nitrobenzoate of cumyl alcohol in 70% acetone is –3.74). This observation supports the findings of Brown and Periaswamy[20] by ^{13}C NMR studies, that fully developed benzylic carbocationic centre is able to overcome their steric difficulties in achieving coplanarity with the aromatic ring by minor costs in energy.

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