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Salt Effects on the Rate of Solvolysis of Cumyl Chloride and its *p*-Methyl Derivative

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Effect of added electrolytes, $LiClO_4$, LiCl and LiBr on the rate of solvolysis of cumyl chloride in 90% aqueous acetone showed that special salt effect is operative and there is an indication of slight mass law effect, while the studies in 80% aqueous DMSO confirmed the presence of mass law. These effects are more pronounced in *p*-methyl derivative. It can be rationalized in terms of hyperconjugative electron release of methyl group through the π-bonds of phenyl ring to the carbocationic centre at the rate determining step.

Key Words: Salt effects, Solvolysis, Cumyl chloride.

INTRODUCTION

Brown and coworkers[1] used cumyl chloride as a standard substrate for the determination of substituent constant. This substrate is characterized by its transition state stability by the formation of delocalized carbocation *via* resonance stabilization through π-bonds of benzene ring[2]. A number of carbocation intermediates were suggested for the unimolecular solvolysis reaction[3] **(Scheme-1)**. The determination of the exact pathway is very difficult. The salt effects on the solvolysis reaction can throw some light in this regard.

EXPERIMENTAL

Cumyl alcohol was prepared[4] by the Grignard reaction of chlorobenzene and acetone in dry ether. For *p*-methyl derivative, *p*-methyl acetophenone and methyl iodide were used. Alcohols were purified by fractional distillation at reduced pressure. Purity was ensured by TLC and authenticities were established by IR and NMR spectra. Alcohols were converted to corresponding chlorides by passing dry HCl gas[5].

The titrimetric estimation of HCl using lacmoid indicator in dry acetone was employed for the rate determination. Conventional thermostat with Jackson thermometer was used for temperature control. For maintaining low temperature (3.3°C) a cryostat assembly was used. Mass law effect of *p*-methyl derivative was not studied because of low solubility of salts at low temperature.

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RESULTS AND DISCUSSION

The effect of added salts, $LiClO_4$, LiCl and LiBr in the rate of solvolysis of 2-chloro-2-phenyl propane (cumyl chloride) in 90% aqueous acetone was investigated. The dependence of rate on the concentration of added salts was given in Fig. 1 (Table-1). LiCl and LiBr showed a linear relation ship in all concentrations. $LiClO_4$ showed initial steep rate acceleration which then decreased to the normal linear acceleration. This is the characteristic plot for a substrate which shows special salt effect[6]. In S_N1 reaction in which if there is a solvent separated ion pair **(Scheme-1)** the ClO_4^- ions trap the solvent separated ion pair to give $R^+\|ClO_4^-$, which being unstable under these conditions goes to product. Hence, the amount of solvent separated ion pair that would have returned to the starting materials is reduced and the rate of the overall reaction is increased.

$$\begin{array}{ccccccc} RCl & \rightleftharpoons & R^+Cl^- & \rightleftharpoons & R^+\|Cl^- & \rightleftharpoons & R^+|+Cl^- \\ & & \text{Intimate ion pair} & & \text{Solvent separated} & & \text{Dissociate} \\ & & & & \text{ion pair} & & \text{ion pair} \end{array}$$

Scheme-1. Intermediates in the S_N1 solvolysis reaction

Nair and Shaji[7] reported a special salt effect in solvolysis of aralkyl system that is in the hydrolysis of 1-*p*-anisyl-2,2-dimethyl butyl chloride in 80% aqueous acetone. Even though this system is secondary, the resonance stabilization of the methoxy group and the neighbouring group participation by the β-methyl group stabilizes the carbonium ion. It is noteworthy that the *p*-tolyl and phenyl group instead of anisyl in the same substrate do not show the special salt effect. The stabilization of carbonium ion is thus a primary condition for the occurrence of special salt effect. The tertiary systems are more stable and there is all possibility for them to show special salt effect. But special salt effect is not reported in *t*-butyl chloride solvolysis. The substitution of one of the methyl groups of *t*-butyl chloride by phenyl group stabilizes the transition state by the resonance effect of phenyl group and hence shows the special salt effect.

The extrapolation of the linear portion of the curves to zero salt concentration gives a value of rate constant (k^0_{ext}) which is more than the measured value (k^0_t), under identical condition, without the added salt. The k^0_{ext}/k^0_{tt} value obtained for the cumyl chloride is 1.08. Shleyer and coworkers[8] showed that k^0_{ext}/k^0_t value 1.06 obtained for the solvolysis of *p*-chlorobenzhydryl chloride in 80% aqueous acetone is due to special salt effect. Nair and Shaji[7] reported a value 1.07 for the hydrolysis of 1-*p*-anisyl-2,2-dimethyl butyl chloride in 80% aqueous acetone. A *p*-methyl substituent stabilizes the carbocation intermediate by the hyperconjugative electron donation through the π-electron system of benzene ring. *p*-Methyl cumyl chloride showed k^0_{ext}/k^0_t value of 1.18 supporting the above suggestion (Fig. 1).

LiCl and LiBr showed linear increase with the increase in concentration of the salt. The rate enhancement in the case of LiCl is much smaller than that of LiBr (Table-1). The possible reasons for this effects are: (a) The salt induced medium effect of chloride ion rendering the aqueous acetone an effectively drier solvent[9].

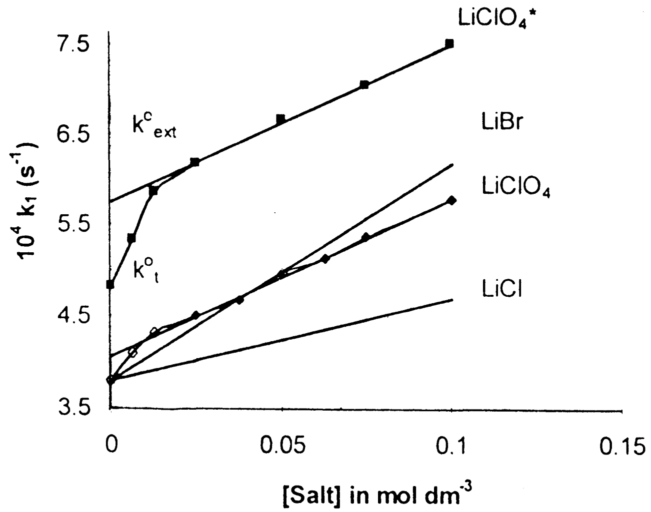

Fig. 1. Effect of added salts on the rate of solvolysis of cumyl chloride (34.0°C) and its *p*-methyl derivative (3.3°C) in 90% aq. acetone

(b) The mass law effect. A system with appreciable mass law effect will show a negative salt effect, *i.e.*, a linear reduction in rate with the increase in concentration of added salt. Moreover, the extrapolated curve of rate *vs.* concentration meets the y-axis at a value appreciably smaller than the rate with zero concen-

TABLE-1
EFFECT OF ADDED SALTS ON THE RATE OF SOLVOLYSIS OF CUMYL CHLORIDE AND ITS *p*-METHYL DERIVATIVE IN 90% AQUEOUS ACETONE

[Salt]	Rate in $10^4 k_1$ (s^{-1})			
	Cumyl chloride at 34°C			*p*-Methyl derivative at 3.3°C
	$LiClO_4$	LiCl	LiBr	$LiClO_4$
Nil	3.79	3.79	3.79	4.82
0.00625	4.09	—	—	5.34
0.0125	4.31	3.91	—	5.86
0.0250	4.51	4.02	4.40	6.18
0.0375	4.68	4.14	—	—
0.0500	4.96	4.24	5.00	6.66
0.0625	5.13	4.35	—	—
0.0750	5.37	4.47	5.58	7.05
0.1000	5.79	4.68	6.16	7.51

[RCl] = 0.010 mol dm^{-3}

tration of the salt[7]. Another observable property is the decrease in the first order rate constants during the course of reaction[10]. If slight mass law is operative, the ionic strength effect can overweigh the mass law effect thereby masking the above observable properties. Therefore a slight mass law operative in a system having salt induced medium effect[11] and ionic strength effect is very difficult to observe. The present data do not provide a conclusive picture of mass law effect. But the smaller linear increase observed for common ion in comparison with non common ion is a strong indication of mass law.

80% aqueous DMSO is a highly ordered solvent system through extensive hydrogen bond with sufficient polarity (Trouten constant values for DMSO and water are 124 and 109 J K^{-1} mol^{-1}), where salt induced medium effect is absent[12]. Effect of added salts, LiCl, LiBr, $LiClO_4$, NaCl and NaBr on the rate of solvolysis of cumyl chloride in 80% aqueous DMSO, were studied along with a compound not showing mass law, *t*-butyl chloride and a compound showing mass law, benzhydryl chloride (Table-2). For a compound showing mass law, the common ion reduces the rate of the reaction. The addition of other salts causes almost the same rate enhancement. For a compound not showing mass law all salts including salt of common ion cause same rate acceleration. Thus solvolysis of cumyl chloride showed mass law effect in 80% aqueous DMSO solvent. The substantial variation in rate with the addition of salts for solvolysis of *p*-methyl cumyl chloride confirms the suggestion that mass law effect is more pronounced in reactions involving more stabilized carbocation intermediate.

TABLE-2

EFFECT OF ADDED SALTS (0.1000 mol dm^{-3}) ON THE RATE OF SOLVOLYSIS REACTIONS IN 80% AQUEOUS DMSO

Salt	*t*-Butyl chloride (50.0°C)		Benzhydryl chloride (33.0°C)		Cumyl chloride (18.0°C)		*p*-Methyl cumyl chloride (3.3°C)	
	a	b	a	b	a	b	a	b
—	0.878	—	2.61	—	5.02	—	15.7	—
LiCl	0.959	+9.2	2.36	–9.5	4.94	–2	13.5	–14
LiBr	0.960	+9.3	3.10	+18.8	5.61	+12	23.9	+52
$LiClO_4$	0.960	+9.3	3.06	+17.2	5.68	+13	24.5	+56
NaCl	0.958	+9.1	2.37	–9.2	4.96	–13	14.1	–10
NaBr	0.961	+9.5	3.13	+19.9	5.60	+12	24.2	+54

[RCl] = 0.010 mol dm^{-3}; a = Rate in $10^4 k_1$ (s^{-1}); b = % variation of rate.

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