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Salt Effects in the Solvolysis of Some Alkyl Chlorides in Different Solvent Systems

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The effect of different salts on the rates of solvolysis of *t*-butyl, *t*-pentyl, dimethylethylcarbinyl, and tri-ethylcarbinyl chlorides has been studied in aq. DMSO, aq. acetone and aq. ethanol. Generally, the pattern of results show increased salt effect in the order NaCl < NaNO₃ < LiClO₄. For the first two salts, the effect decreases as the series is ascended, and for the last, the reverse trend is obtained. Discussion is largely based on the interplay of two factors, viz. effect on the stability of the initial state and solvent structure-induced ion pairing.

SALT effects on the rates of S_N1 reactions have been discussed by several workers[1-6], and it is clear that the Hughes-Ingold method of applying the Debye-Hückel theory is an over-simplification[7]. The factors which have to be taken into consideration are: (i) effect on the initial and transition states, and (ii) salt-solvent interactions. Because of the simultaneous operation of several of these factors, it has not been possible to assess their relative importance under various situations. One approach to the problem, which we have adopted here, is to study the effect of various electrolytes in different solvent systems, on substrates which have close structural similarities.

The alkyl chlorides were prepared by the standard methods[8]. The procedure adopted has been described earlier[9]. The variation in the values of the rate constants between replicate runs did not exceed 2%.

The kinetic data on the solvolysis of *t*-butyl, *t*-pentyl, diethylmethylcarbinyl, and triethylcarbinyl chlorides in the presence and absence of electrolytes are given in Tables 1 and 2. Data in 80% aq. DMSO have already been reported[10], which have been discussed on the basis that there is no selective ion solvation[11]. In 90% aq. DMSO, the percentage increase in the rate were as follows (65°): *t*-butyl: 0·1M NaCl, +16·1; 0·1M LiClO₄, +8·8; Et₃CCl: 0·1M NaCl, +23·4; 0·1M LiClO₄, +11·3. The ionic atmosphere effect should be larger for *t*-butyl chloride[8]. It is known, however, that dipolar aprotic solvents can solvate polarizable transition states of both S_N2[12], and S_N1[13] reactions, and further that anion solvation increases with polarizability[12]. It follows that solvation by DMSO will be greater for the transition state of triethylcarbinyl chloride in the presence of perchlorate ion. A combination of these two factors can account for the results.

In 50% aq. acetone, the concentration dependence of the rate in the presence of NaCl and NaNO₃ is not linear while for LiClO₄ there is a linear relationship. The linear relationship can be explained by assuming solvent structure-induced ion pairing effect[4]. The results with NaCl and NaNO₃ can be attributed to a salt-induced medium effect. The data in 60% aq. acetone can be accounted for as follows. Because of the preferential solvation of chloride ions by water, it is likely that the alkyl chloride will be salted into acetone. This effect should increase with the size of the alkyl chloride. Such salting-in has been observed earlier[14]. The salting-in effect of nitrate is less than that of chloride[3], and so this salt shows larger rate increases. The effect of LiClO₄ is ascribed to solvent structure-induced ion pairing effect. The data in 80% aq. acetone can be accounted for similarly.

In 90% aq. acetone, the percentage increase in rate in the presence of 0·1M NaBr and 0·1M LiClO₄

TABLE 1 — EFFECT OF ADDED ELECTROLYTES ON THE RATE OF SOLVOLYSIS OF ALKYL CHLORIDE ON AQ. ACETONE

Alkyl chlorides (0·05M)	$10^4 k_1$ (sec⁻¹)	% of k_1 in the presence of					
		NaCl		NaNO₃		LiClO₄	
	(normal)	0·05M	0·1M	0·05M	0·1M	0·05M	0·1M
50% AQ. ACETONE (20°C)							
Me₃CCl	1·29	+3·1	+4·7	+5·4	+7·0	+5·4	+10·9
60% AQ. ACETONE (35°C)							
Me₃CCl	1·80	+5·0	+6·7	+10·0	+12·2	+10·6	+16·7
Me₂EtCCl	2·71	+4·4	4·4	+6·3	+9·2	+10·0	+16·6
Et₂MeCCl	3·79	+2·4	+1·6	+6·9	+8·7	+10·8	+18·7
Et₃CCl	3·94	−0·3	−2·5	+5·6	+7·9	+11·4	+18·6
80% AQ. ACETONE (58°C)							
Me₃CCl	0·850	+15·3	+22·4	+12·6	+23·5	+15·7	+27·1
Me₂EtCCl	1·17	+11·1	+19·7	+11·1	+19·7	+14·5	+28·2
EtMe₂CCl	1·65	+10·3	+10·3	+9·1	+15·2	+13·9	+27·9
Et₃CCl	1·72	+5·2	+3·5	+7·6	+16·3	+14·5	+28·5

NOTES

TABLE 2 — EFFECT OF ADDED ELECTROLYTES ON THE RATES OF SOLVOLYSIS IN AQUEOUS ALCOHOLS

RCl(0·5M)	$10^4 k_1$(sec^{-1}) (normal)	% of k_1 in the presence of		
		NaCl (0·1M)	NaNO$_3$ (0·1M)	LiClO$_4$ (0·1M)
70% AQ. ETHANOL (35°C)				
Me$_3$CCl	1·23	+4·9	+9·8	+17·1
Et$_3$CCl	2·83	+2·1	+11·0	+23·3
80% AQ. ETHANOL (45°C)				
Me$_3$CCl	1·07	+6·5	+14·0	+22·4
Et$_3$CCl	2·70	+7·0	+15·9	+31·1
80% AQ. METHANOL (40°C)				
Me$_3$CCl	1·38	+6·5	+11·6	+18·8
Et$_3$CCl	6·34	+7·1	+14·0	+23·2
90% AQ. METHANOL (40°C)				
Me$_3$CCl	0·349	+14·6	+21·2	+28·9
Et$_3$CCl	1·96	+9·7	+17·4	+27·6

are as follows: *t*-butyl: 0·1M NaBr, +82·5, 0·1M LiClO$_4$, +74·3; Et$_3$CCl: 0·1M NaBr, +54·2, 0·1M LiClO$_4$, +65·1%. The salts will exist mainly as ion pairs and this will lead to (a) reduced effect on the initial state, (b) reduced ionic atmosphere effect, and (c) stabilization of the transition state due to dipole-dipole interaction[15].

The rate data in aqueous alcoholic solvents (Table 2) can be interpreted in terms of the ionic atmosphere effect, salt-induced medium effect, and solvent structure-induced ion-pairing effect. The effect of first factor should be larger while that of the other two should be smaller with decrease in water content of the medium.

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Estimation of pK_{BH^+} of Some Mesoionic Thiones

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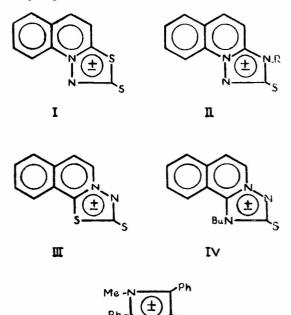East India Pharmaceutical Works Ltd, Calcutta 700061

Apparent second order rate constants (k'_2) for the reactions between mesoionic thiones and chloroacetate are determined in 50% (*v/v*) buffer-methanol mixture at $pH = 3·40$, temp. $= 30°$ and $\mu=0·1$. These were in turn used for estimating pK_{BH^+} values with the help of a regression equation $\log k'_2 = 2·3322 + 0·7745 (pK_{BH^+})$. Calculated data are in accord with the experimental values.

EARLIER we described[1] a kinetic approach to determine pK_{BH^+} of some mesoionic thiones using the following regression equation,

$$\log k'_2 = 2·3322 + 0·7745(pK_{BH^+}) \qquad ...(1)$$

where $r = 0·989$, std dev.$= 0·108$ and k'_2 is the apparent second order rate constant for reactions with chloroacetic acid. It was also suggested that this equation might be profitably utilized to predict the pK_{BH^+} of other mesoionic thiones which are not amenable to direct experimental conditions for pK_{BH^+} determinations. As pK_{BH^+} reflects an important intrinsic property of a system and only a limited number of compounds have been examined so far[2], it was decided to examine the scope and validity of Eq. (1) in the light of additional experimental data with other mesoionic compounds recently reported by us[3,4].