Tetrahedron, 1965, Vol. 21, pp. 535 to 537. Pergamon Press Ltd. Printed in Northern Ireland

ELECTROPHILIC CATALYSIS IN SOLVOLYTIC REACTIONS—VI*

CATALYSED HYDROLYSIS OF 1-PHENYLALKYL CHLORIDES

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(*Received* 15 April 1964; *in revised form* 4 *November* 1964)

Abstract—The hydrolysis of four 1-phenylalkyl chlorides (CHPhAlkCl where Alk = Me, Et, i-Pr, t-Bu) in aqueous acetone and catalysed by $HgCl_2$ has been kinetically examined. The decrease in rate, as the series is ascended, is less in the presence than absence of the catalyst, particularly for the last two compounds. This is attributed to the operation of an additional inductomeric polarizability called into play by the catalyst. The mass-law effect, due to added chloride ions is significant only for 1-phenylethyl chloride, showing the importance of steric inhibition of resonance for the other three compounds.

THE marked drop in the rate of S_N1 solvolysis of the series CHPhAlkCl (where Alk = Me, Et, i-Pr and t-Bu) has been attributed to the steric inhibition of resonance in the carbonium ion.[1]

Winstein has suggested that in addition, steric resistance to solvation may be a contributory factor, particularly for the neopentyl compound.[2] Data for the hydrolyses in aqueous acetone in the presence or absence of mercuric chloride are set out in Tables 1 and 2.

Three peculiarities are apparent: Firstly, the relative rates (at 25°) for the normal and catalysed reactions are, respectively, Me:Et:i-Pr:t-Bu as 296:59:15·6:1 and 180:39·2:12:1. This means that the diminution in the rate of hydrolysis as the series is ascended is less in the catalysed than in the normal reactions, this effect being particularly large with the isobutyl and neopentyl compounds. Secondly, the catalytic efficiency increases along the series, as shown by the values of $(k_{cat} - k_{normal})/k_{normal}$ which are 84·6, 86·7, 100·7 and 142·9 for the Me, Et, i-Pr and t-Bu compounds respectively. This is contrary to theoretical expectation since, other conditions being the same, the increase in rate should be in the order of increasing ease of heterolysis of the C—Cl bond. Thus Anantaraman[3] found the catalytic efficiency for the hydrolysis to increase in the order t-BuCl < CHPhMeCl < Ph_2CHCl. Thirdly, the decrease in the heats of activation observed on passing from the normal to the catalysed reaction, is in the order Me < Et < i-Pr < t-Bu. Here again the reverse trend is the more likely. These three observations indicate the presence of a factor in the catalysed reaction which differentially favours the hydrolysis in the order Me < Et < i-Pr < t-Bu.

It is suggested that inductomeric polarizability of the alkyl groups attached to the seat of substitution is called into play by the catalyst. The inductomeric effect should increase in the order Me < Et < i-Pr < t-Bu in agreement with observation. The

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* Parts I–V: *Proc. Ind. Acad. Sci.* **49A**, 111 (1959); *J. Amer. Chem. Soc.* **82**, 1574 (1960); *Z. Phys. Chem.* **216**, 21 (1961); *J. Sci. ind. Res.* **21B**, 598 (1962); *Naturwissenschaften*, **50**, 497 (1963).

[1] G. Baddeley, J. Chadwick and H. T. Taylor, *J. Chem. Soc.* 368 (1951); see also E. L. Eliel, in M. S. Newman, *Steric Effects in Organic Chemistry* p. 88, J. Wiley, New York (1956).

[2] S. Winstein & B. K. Morse. *J. Amer. Chem. Soc.* **74**, 1133 (1952).

[3] R. Anantaraman, *Ph.D. Thesis* London (1950).

alkyl groups are positioned very close to the point of attack and the catalyst has a large dipole moment and considerable electronegative properties and, therefore, induces a substantial inductomeric effect from the alkyl groups. Berliner has similarly explained the iodination of *p*-alkyl phenols[4] and *p*-alkylanilines.[5]

An alternative possibility in the catalysed hydrolyses is the occurrence of Wagner-Meerwein rearrangement. The neopentyl compound for which this possibility is greatest, gives the unrearranged alcohol during solvolysis in aqueous ethanol.[1] Skell and Hauser[6] reported a 30% rearrangement in the silver–ion catalysed solvolysis, but Winstein and Morse showed conclusively that the proportion of rearranged products does not exceed 2%. As we could not isolate any rearranged material in the catalysed hydrolysis, this possibility has been eliminated.

The entropies of activation are lower for the catalysed solvolysis, and the values decrease as the series is ascended. As the entropy factor is less favourable for the higher homologues, it is suggested that steric hindrance interferes with the approach of the catalyst molecule. For benzyl chloride, where such an effect is unlikely, the entropy factor is more favourable for the catalysed hydrolysis.[7]

Chloride ions may affect the rate of the catalysed reaction in three ways; (i) increased rate by ionic-strength effect (ii) decreased rate due to "common-ion" effect, (iii) decreased rate due to catalyst inactivation through complex-formation, e.g., $HgCl_3^-$, $HgCl_4^=$.

(i) The magnitude of the ionic-strength effect is smaller in the catalysed than the normal reaction.[3,8] For t-butyl chloride, the normal reaction itself hardly shows any such effect[9] and for 1-phenylethyl chloride, although there is a substantial ionic-strength effect in the normal hydrolysis, it can only just be detected in the catalysed reaction.[10] Since the ionic-strength should increase with resonance stability of the carbonium ion, this effect is of no importance for any of the four alkyl chlorides.

(ii) The peculiar ability of mercuric chloride to induce a mass-law effect in S_N1 reactions,[3] is, as Ingold has explained,[11] due to its capacity for catalysing both the forward and back reactions of the rate-determining stage. More specifically, Bunton has pointed out that the reason for the catalysis of the back-reaction is that the species formed in the forward reaction, particularly $HgCl_4^=$ should be more nucleophilic (towards carbon) than chloride ions.[12] Consequently, the tendency for the display of the mass-law effect is enhanced substantially. Thus, 1-phenylethyl chloride shows no detectable mass-law effect in its normal solvolysis,[10] but a moderate effect is present in the catalysed hydrolysis.[3] On the other hand, in the catalysed hydrolysis of t-butyl chloride, no such effect is noted presumably because the t-butyl cation is unstable.[13]

(iii) As mercuric chloride forms a number of complexes, its contribution in

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[4] E. Berliner and F. Berliner, *J. Amer. Chem. Soc.* **76**, 6179 (1954).

[5] E. Berliner, F. Berliner and I. Nedilow, *J. Amer. Chem. Soc.* **76**, 507 (1954).

[6] P. S. Skell and C. R. Hauser, *J. Amer. Chem. Soc.* **64**, 2633 (1942).

[7] S. Koshy and R. Anantaraman, *J. Amer. Chem. Soc.* **82**, 1574 (1960).

[8] P. J. Chakko, *M.Sc. Thesis* Kerala (1961).

[9] E. D. Hughes, *J. Chem. Soc.* 255 (1935).

[10] E. D. Hughes, C. K. Ingold and A. D. Scott, *J. Chem. Soc.* 1201 (1937).

[11] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 359 Bell, London (1953).

[12] C. A. Bunton, *Nucleophilic substitution at a saturated carbon atom* p. 154. Elsevier (1963).

[13] C. G. Swain and R. B. Moseley, *J. Amer. Chem. Soc.* **77**, 3727 (1955); C. A. Bunton and B. Nayak, *J. Chem. Soc.* 3854 (1959).

depressing the rate of the catalysed hydrolysis can be achieved by choosing an alkyl chloride, in which the rate depression can only be due to inactivation of the catalyst owing to complex-formation and not due to ionic-strength or mass-law effects. t-Butyl and t-amyl chlorides are two such reference compounds. Table 2 shows that rate-depressions for the alkyl chlorides other than 1-phenylethyl are similar and therefore the ionic-strength and mass-law effects are negligible. The higher reduction observed with 1-phenylethyl chloride reflects the additional contribution due to the mass-law effect. In the other cases this effect is not important due to the instability of the respective carbonium ions. In the case of t-BuCl and t-AmCl, resonance is limited and in the other three, resonance is sterically inhibited.

TABLE 1.* KINETICS OF THE HYDROLYSIS OF 1-PHENYLALKYL CHLORIDES
Solvent 80% aqueous acetone; $HgCl_2$ = 0·075 M

	10^4k		$10^4k_{25°}$		$\Delta H^{\pm}_{25°}$(k.cal/mole)		$\Delta S^{\pm}_{25°}$(e.u.)	
	Normal	Catalysed	Normal	Catalysed	Normal	Catalysed	Normal	Catalysed
CHPhMeCl	0·117 (50°)	0·429 (20°)	0·00846	0·724	21·1	17·6	—15·5	—18·5
CHPhEtCl	0·0198 (45°)	1·12 (45°)	0·0018	0·1579	22·6	17·8	—13·6	—20·7
CHPhi-PrCl	0·00540 (45°)	0·344 (45°)	0·000475	0·0483	22·2	17·9	—17·5	—22·1
CHPht-BuCl	0·0235 (80°)	0·705 (80°)	0·0000279	0·00403	24·9	19·0	—14·1	—24·4

* All rate-coefficients are first order expressed in reciprocal seconds.

TABLE 2. EFFECT OF ADDED CHLORIDE IONS ON THE CATALYSED HYDROLYSIS
Solvent 80% aqueous acetone; $HgCl_2$ = 0·075 M

	T°C	10^4k			% Reduction in rate	
		Cl = nil	Cl = 0·05	Cl = 0·10	Cl = 0·05	Cl = 0·10
t-BuCl	20	0·582	—	0·115	—	80·2
t-AmCl	20	1·05	0·530	0·196	49·5	81·1
CHPhMeCl	20	0·429	0·176	0·0491	59·0	88·4
CHPhEtCl	45	1·12	0·548	0·188	51·1	83·2
CHPhi-PrCl	54·8	0·824	0·402	0·143	51·2	82·6
CHPht-BuCl	80	0·705	0·355	0·146	49·7	79·3

EXPERIMENTAL

Materials. The alkyl chlorides were prepared by standard methods. Their rates of solvolysis in 80% EtOHaq were in close agreement with literature values.[1] Acetone was purified by the method of Conant and Kirner.[14] Large stock of solvent was made up by volume at room temp to facilitate comparative measurements.

Kinetic measurements. For experiments at ordinary temp, the reaction mixture was contained in a volumetric flask while at higher temp, the sealed-bulb technique was used. Aliquots were removed at suitable intervals, added to 150 ml cold dry acetone containing a slight excess of neutral KI (to destroy the $HgCl_2$) and the liberated acid titrated against standard NaOHaq using lacmoid as the indicator. First order rate co-efficients were calculated using the standard formula. Duplicate runs gave value in good agreement.

The product of the catalysed hydrolysis of 1-phenyl-neopentyl chloride was converted into the half ester with phthalic anhydride. A high yield of the ester was obtained the m.p. was undepressed on admixture with an authentic sample.

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[14] J. B. Conant and W. R. Kirner, *J. Amer. Chem. Soc.* **46**, 246 (1924).