The Kinetics of Solvolysis of 1-(3-Chloro-4-methylphenyl)- and 1-(3-Chloro-4-t-butylphenyl)-1-methylethyl Chlorides in Aqueous Acetone [1]

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1-(3-Chloro-4-methylphenyl)- and 1-(3-chloro-4-t-butylphenyl)-1-methylethyl chloride have been prepared from the corresponding alcohols by action of hydrogen chloride. The alcohols were prepared by the reaction of methylmagnesium iodide with the ester of the corresponding disubstituted benzoic acid. The solvolysis rates of the two alkyl chlorides have been measured in 90% aqueous acetone at various temperatures. The energies of activation for the solvolysis reactions have been calculated. The results are compared with those obtained for cumyl chloride and its mono-substituted derivatives. The observed and calculated rate constants of solvolysis have been compared and it has been found that the observed rate constant for 1-(3-chloro-4-methylphenyl)-1-methylethyl chloride is 79% of the predicted value, while for 1-(3-chloro-4-t-butylphenyl)-1-methylethyl chloride it is 44%. This decrease in the observed rate constant as compared with the calculated value might be due to the steric interaction between the 3-Cl and 4-alkyl group. It also shows that the calculations of the rates of solvolysis of 3-chloro-*p*-alkylcumyl chlorides based upon additivity, underestimate the retarding effect of the chlorine substituent.

FOR the majority of reactions of polysubstituted benzenes, it has been found that the effect of 3- and 4-substituents can be satisfactorily correlated by the modified Hammett equation,[2] $\log k/k_0 = \rho^+\Sigma\sigma^+$.

The extension of the Hammett equation to polysubstituted benzene derivatives has been made for side-chain reactions.[2] The essential features of these treatments are the assumptions that the contribution of each substituent is constant and that the influence of the substituents are simply additive.

In the present investigation the rate of solvolysis of 1-(3-chloro-4-methylphenyl)- and 1-(3-chloro-4-t-butylphenyl)-1-methylethyl chlorides have been measured in 90% aqueous acetone at various temperatures. The observed rate constants are compared with the calculated values. The observed and calculated differences in the free energy of activation ($\Delta G - \Delta G_0$) for the two compounds are also compared.

EXPERIMENTAL

1-(3-*Chloro*-p-*tolyl*)-1-*methylethyl Chloride*.—(a) *Methyl* 3-*chloro*-p-*toluate*.[3] Chlorine gas (24·9 g., 0·35 mole) was bubbled during 8 hr. through a molten mixture of methyl *p*-toluate (0·3 mole) and anhydrous aluminium chloride (0·8 mole) maintained at 28—29° in the dark. The reaction mixture was poured into water and the ester was extracted with ether. Distillation under reduced pressure gave the product, b.p. 144—146°/28 mm., n_D^{25} 1·5283 (lit.,[4] b.p. 119—121°/10 mm., m.p. 28—29°).

(b) 1-(3-*Chloro*-p-*tolyl*)-1-*methylethanol*. Methyl 3-chloro-

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[1] M. Hassan, B. Mudawi, and A. Salama, *J. Chem. Soc.* (*B*), 1970, 928.

[2] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 243; *Science*, 1953, **118**, 246.

[3] D. E. Pearson, H. W. Pope, W. W. Hargrove, and W. E. Stamper, *J. Org. Chem.*, 1958, **23**, 1416.

[4] G. Renckhoff, Ger.P. 1,168,412/1964 (*Chem. Abs.*, 1964, **61**, 1802).

p-toluate was treated with methylmagnesium iodide to give 1-(3-chloro-*p*-tolyl)-1-methylethanol, b.p. 86°/0·4 mm., m.p. 42—43°, in 87% yield (Found: C, 65·2; H, 7·15; Cl, 19·2. Calc. for $C_{10}H_{13}ClO$: C, 65·0; H, 7·1; Cl, 19·2%).

The chloride was prepared from the alcohol by saturating the latter with hydrogen chloride.[5]

1-(3-*Chloro-4-t-butylphenyl*)-1-*methylethyl Chloride*.—(a) *Ethyl 3-chloro-4-t-butylbenzoate*. 3-Chloro-4-t-butylbenzoic acid [6] was esterified with dry ethanol and conc. sulphuric acid. The ester, b.p. 120—122°/0·4 mm., n_D^{25} 1·5185 was obtained in 55% yield (Found: C, 64·1; H, 6·9. Calc. for $C_{13}H_{17}ClO_2$: C, 64·8; H, 7·1%).

TABLE 1

Compound	Temp.	$10^5 k_1$ (sec.$^{-1}$)
1-Phenyl-1-methylethyl chloride	25°	12·25 ± 0·30
1-(3-Chloro-*p*-tolyl)-1-methylethyl chloride	15	1·15 ± 0·04
	25	3·83 ± 0·11
	35	11·09 ± 0·13
1-(3-Chloro-4-t-butylphenyl)-1-methylethyl chloride	25	1·22 ± 0·02
	35	4·27 ± 0·08
	45	11·69 ± 0·21

TABLE 2

Compound	Temp.	$10^5 k_1$ (sec.$^{-1}$) (average)	E_a (kcal./mole)
1-(3-Chloro-*p*-tolyl)-1-methylethyl chloride	15°	1·15	
	25	3·83	19·8
	35	11·09	
1-(3-Chloro-4-t-butylphenyl)-1-methylethyl chloride	25	1·22	
	35	4·27	21·4
	45	11·69	

TABLE 3

Rate constants, relative rates, and activation parameters for the solvolysis of substituted phenyl(methyl)ethyl chlorides in 90% aqueous acetone

Substituent	$10^5 k_1$ (sec.$^{-1}$) at 25°	Rel. rate	E_a (kcal.)	$\Delta H^\ddagger$ (kcal.)	$\Delta S^\ddagger$ (cal. deg^{-1})	$\Delta G - \Delta G_0$ (kcal./mole)
H	12·4	1·00	19·5	18·8	−12·4	0·0 [a]
3-Me	24·8	2·00	19·4	18·6	−11·8	−0·41 [a]
4-Me	322	26·0	17·8	17·3	−12·0	−1·92 [a]
4-t-Bu	178	14·4	17·9	17·3	−13·3	−1·56 [a]
3-Cl	0·194	0·0156	21·3	20·7	−15·1	+2·46 [b]
3-Me, 5-Me	47·3	3·82				−0·793 [c]
H	12·25	1·00				0·0 [d]
3-Cl, 4-Me	3·83	0·313	19·8	19·5	−13·3	+0·688 [d]
3-Cl, 4-t-Bu	1·22	0·0996	21·4	20·8	−11·2	+1·37 [d]

[a] Ref. 5. [b] Ref. 7. [c] Ref. 10. [d] Present work.

(b) 1-(3-*Chloro-4-t-butylphenyl*)-1-*methylethanol*.—Ethyl 3-chloro-4-t-butylbenzoate was treated with methylmagnesium iodide to give 1-(3-chloro-4-t-butylphenyl)-1-methylethanol, m.p. 78—80° (from methanol) (55% yield) (Found: C, 68·4; H, 8·5; Cl, 15·9. Calc. for $C_{13}H_{19}ClO$: C, 68·8; H, 8·4; Cl, 15·6%).

The chloride was obtained from the alcohol as before.

Acetone was purified by refluxing it with potassium permanganate; it was then distilled, dried ($CaSO_4$), and fractionated.

Kinetic Measurements.—The stock solvent was prepared by mixing pure dry acetone (1811 ml.) and boiled, distilled water (189 ml.); this was adjusted by adding small amounts of acetone or water to give a value of $k_1 = 12·25 \pm 0·30 \times 10^{-5}$ sec.$^{-1}$ at 25° for 1-phenyl-1-methylethyl chloride. After adjustment, the exact solvent composition was calculated to be 90·51 : 9·49% v/v acetone to water.

The procedure for the kinetic measurements was the same as that of Brown *et al.*[7] The rate measurements were made at three different temperatures for each chloride and the activation energies were calculated. Table 1 gives a summary of the rate measurements. Table 2 gives the data for calculation of the activation energies for the solvolytic reaction of the two carbinyl chlorides.

DISCUSSION

The kinetics are similar to those found for similar systems [5,7] and proceed through the intermediate carbonium ion which is obtained through the ionisation of the alkyl chloride:

$$RR'\text{-}C_6H_3\cdot CMe_2Cl \rightleftharpoons RR'\text{-}C_6H_3\cdot\overset{+}{C}Me_2 + Cl^-$$

According to the ionisation scheme, S_N1 solvolytic displacement reactions involve first-order kinetics as shown by the constancy of the rate coefficient through the course of a single run.

Data for the solvolysis of compounds of the type $R\text{-}C_6H_4\cdot CMe_2Cl$ in 90% aqueous acetone at 25° as recorded by Brown and his co-workers [5,7] together with the data obtained for the compounds under investigation under the same experimental conditions, are shown in Table 3.

The values of the enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of activation were obtained according to the procedure described by Cagle and Eyring.[8] The difference in the free energy of activation ($\Delta G - \Delta G_0$) was calculated from the following relation: $\Delta G - \Delta G_0 = -2·303RT \log_{10} k/k_0$, where k is the rate constant of the substituted compound and k_0 is the rate constant of the unsubstituted compound.

Chlorine substituent in the *meta*-position of phenyl(methyl)ethyl chloride reduces the rate of solvolysis over that of the parent compound by a factor of 60. In 1-(3-chloro-4-alkylphenyl)-1-methylethyl chlorides the rates are reduced by factors of 80 and 140 over that of the 4-methyl and 4-t-butyl derivatives respectively.

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[5] H. C. Brown, J. D. Brady, M. Grayson, and W. H. Bonner, *J. Amer. Chem. Soc.*, 1957, **79**, 1897.

[6] P. Kovacic and J. Miller, *J. Org. Chem.*, 1965, **30**, 1587.

[7] H. C. Brown, Y. Okamoto, and G. Ham, *J. Chem. Amer. Soc.*, 1957, **79**, 1906.

[8] F. W. Cagle and H. Eyring, *J. Amer. Chem. Soc.*, 1951, **73**, 5628.

Additive Effect of Substituents and the Hammett Equation.—The extension of the Hammett equation to polysubstituted benzene derivatives has been suggested by Jaffé[2] for side-chain reactions. The essential features of these treatments are the assumptions that the contribution of each substituent is constant and that the influences of the substituents are simply additive provided that serious steric interaction is absent.

The values of the electrophilic substituent constant σ^+ for the following substituents are known.[9]

Substituent	3-Me	4-Me	4-t-Bu	3-Cl
σ^+	−0·066	−0·311	−0·256	+0·399

The calculated rate constant k_1 for the disubstituted phenyl(methyl)ethyl chloride can be obtained from the modified Hammett equation, $\log k/k_0 = \rho^+\Sigma\sigma^+$, and taking the value of the reaction constant[9] $\rho^+ = -4{\cdot}54$ for the solvolysis in 90% aqueous acetone at 25°. The observed and calculated values of the rate constants are given in Table 4.

TABLE 4

Disubstituted phenyl(methyl)ethyl chlorides

Substituent	10^5k_1 (sec.$^{-1}$) at 25° (observed)	10^5k_1 (sec.$^{-1}$) (calculated)	$k_{\text{obs}}/k_{\text{calc}}$
3-Cl, 4-Me	3·83	4·88	0·79
3-Cl, 4-t-Bu	1·22	2·75	0·44
3-Me, 5-Me	47·3 *	49·3	0·96

* Ref. 10.

The observed rate constant for 1-(3-chloro-*p*-tolyl)-1-methylethyl chloride is 79% of the calculated value, while for 1-(3-chloro-4-t-butylphenyl)-1-methylethyl chloride it is 44%. This decrease in the observed rate constant as compared with the calculated value might be due to steric interaction between the 3-Cl and 4-alkyl group, and it shows that the additivity calculations probably underestimate the retarding effect of the chlorine substituent in the 3-position on the solvolysis of 4-alkyl-t-cumyl chloride. In the case of 1-(3,5-dimethylphenyl)-1-methylethyl chloride which was reported by Brown[10] to show excellent additivity, the calculated value of k_1 is nearly equal to the observed value.

The divergences from additivity are also set out in terms of free energies of activation in Table 5.

TABLE 5

Divergences between observed and calculated differences in free energy of activation for the disubstituted t-cumyl chlorides

Substituent	$(\Delta G - \Delta G_0)$ (observed) (kcal)	$(\Delta G - \Delta G_0)$ (predicted) * (kcal)	$(\Delta G - \Delta G_0)$ − $(\Delta G - \Delta G_0)$ (observed) (predicted) (kcal)
3-Cl, 4-Me	+0·688	+0·54	+0·148
3-Cl, 4-t-Bu	+1·37	+0·90	+0·470
3-Me, 5-Me	−0·793 †	−0·82	+0·027

* Predicted values in this column were calculated using the equation,[11] $(\Delta G - \Delta G_0)_{xy} = (\Delta G - \Delta G_0)_x + (\Delta G - \Delta G_0)_y$. † Calculated from the rate constant by Brown[10] (see Table 4).

The limitations of the additivity treatment is also illustrated by the nitration and chlorination of the chlorotoluenes. The calculated values for the orientation in the nitration[12] of the chlorotoluenes from the partial rate factors for toluene and chlorobenzene, are low when the position of substitution is *meta* to a chlorine atom. In the chlorination[13] of *o*- and *p*-chlorotoluene, the experimental rates are only 70% of the predicted value.

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[9] H. C. Brown and L. M. Stock, *Adv. Phys. Org. Chem.*, 1963, **1**, 89.

[10] H. C. Brown and J. D. Cleveland, *J. Amer. Chem. Soc.*, 1966, **88**, 2051.

[11] B. Jones and J. Robinson, *J. Chem. Soc.*, 1955, 3848.

[12] P. B. de la Mare and J. H. Ridd, ' Aromatic Substitution,' Butterworths, London, 1959, p. 88.

[13] L. M. Stock and F. W. Baker, *J. Amer. Chem. Soc.*, 1962, **84**, 1661.