Steric Relations between Ionisation of Aralkyl Chlorides and Dissociation of Anilinium Ions. Part I.

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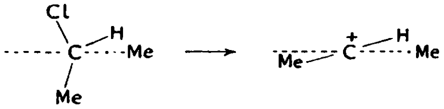
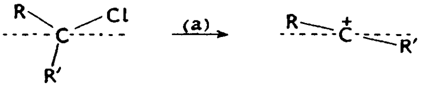
[Reprint Order No. 5024.]

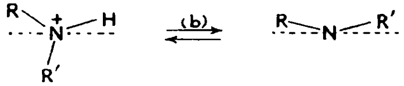
Rates of solvolysis of the chlorides R·CHPhCl in 80% aqueous ethanol, where R is methyl, ethyl, propyl, *iso*propyl, 1-ethylpropyl, *tert.*-butyl, and 1 : 1-dimethylpropyl severally, have been determined. Reactivity decreases in the order R = primary > secondary > tertiary alkyl group and, since this is the order of increasing basic strength of the aniline derivatives R·NHPh, it is argued that this is the order of increasing steric hindrance of ionisation of the chlorides and of dissociation of the corresponding anilinium ions.

A complete theory of the effect of substituents on (*a*) reaction rate and (*b*) equilibrium incorporates the change of steric interaction effected by the difference in intramolecular spatial configuration between (*a*) reactant and transition state and (*b*) reactant and product. This change, which, whether unimolecular or bimolecular reactions are concerned, is not related to the probability of approach of reactants, was first introduced to account for facilitation of reaction by bulky substituents adjacent to the reacting group and for several of the *ortho*-effects of aromatic chemistry (Baddeley, *Nature*, 1939, **144**, 444). Later (Baddeley and Chadwick *J.*, 1951, 368), it was shown to account for the slow unimolecular ethanolysis of 1-*o*-tolylethyl chloride relative to that of 1-chloroindane. The carbon skeleton of the latter chloride has essentially the planar configuration required for maximum resonance stabilisation of the corresponding cation and, apart from steric interaction incurred by the chlorine atom, ionisation of this chloride is neither sterically facilitated nor sterically hindered. On the other hand, if we assign to 1-*o*-tolylethyl chloride the preferred configuration (I) in which steric interaction is a minimum, the methyl group of the side-chain being well separated from the plane of the ring (represented by a broken line), its unimolecular solvolysis is hindered (i) by the energy needed to bring this methyl group into or closer to the plane of the ring and (ii) by loss of resonance energy in the corresponding cation should this, from steric causes, be non-planar. Anomalies in reactivity caused by combination of these two energy terms are difficult to estimate since they are not readily disentangled from inductomeric and electromeric effects.

Hammett and Pfuger (*J. Amer. Chem. Soc.*, 1933, **55**, 4079) showed that a linear relation exists between the logarithm of the rate constants (log *k*) of one series of reactions and the logarithm of the equilibrium constants (log *K*) of another distinct series. It is equivalent to a linear relation between the influence of substituents on the free energy of activation in the reactions considered in respect of velocity and their influence on the standard free-energy change between initial and final states in corresponding dissociations (Burkhardt, *Nature*, 1935, **136**, 684; Burkhardt, Ford, and Singleton, *J.*, 1936, 17). Relations of this type have been afforded by reactions of benzene derivatives and, in general, are limited to the field of *meta-* and *para*-derivatives, *i.e.*, to change of substituent in a part of the molecule considerably removed from the reacting group; they demonstrate the similarity between the ways in which composition and structure of a reactant affect rates and equilibria, and "can be reduced to a matter of electron displacements alone" (Hammett, *loc. cit.*). On the other hand, *ortho*-substituents frequently introduce steric factors, operating to different degrees in different reactions and more complex than simple steric hindrance of the type envisaged by Victor Meyer (Hughes, *Quart. Reviews*, 1948, **2**, 107), which provide deviations from the above relation. These deviations are now applied in an attempt to recognise steric hindrance of ionisation of aralkyl chlorides Ar·CRR'Cl; our purpose was served by relating log *k* for unimolecular solvolysis (reaction *a*) to pK_a for dissociation of the corresponding anilinium ions Ar·$\overset{+}{N}$RR'H (reaction *b*).

(I) 



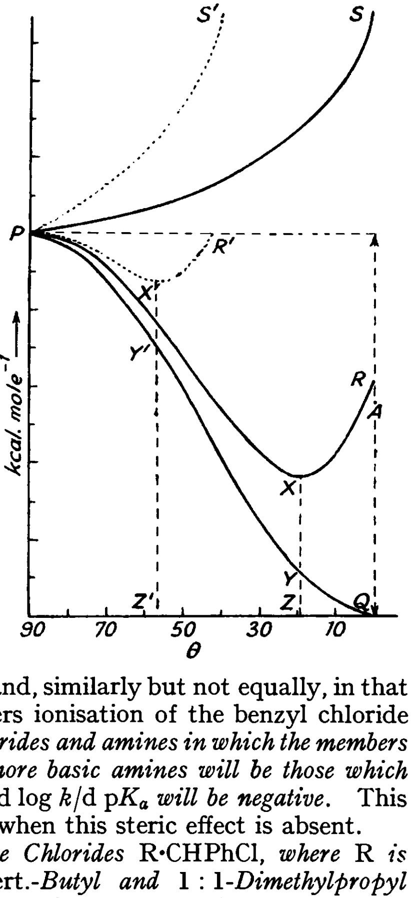


The electron displacements incurred by these two processes are oppositely directed and in general, therefore, *steric effects apart, change in constitution which increases the rate of ionisation, decreases the dissociation; the more basic amines are those which correspond to the*

TABLE 1. *Solvolysis of benzyl chlorides and dissociation of anilinium ions in 50% aqueous ethanol.*

X	$X{\cdot}C_6H_4{\cdot}CH_2Cl$ log $10^6k_{83{\cdot}0}$	$X{\cdot}C_6H_4{\cdot}NH_2$ p$K_{a\ 25{\cdot}0}$	X	$X{\cdot}C_6H_4{\cdot}CH_2Cl$ log $10^6k_{83{\cdot}0}$	$X{\cdot}C_6H_4{\cdot}NH_2$ p$K_{a\ 25{\cdot}0}$
p-Me	5·21	5·07	*p*-I	3·87	3·66
p-F	4·45	4·56	*m*-F	3·60	3·50
m-Me	4·33	4·69	*m*-Cl	3·57	3·41
H	4·19	4·58	*m*-Br	3·52	3·38
p-Cl	3·98	3·94	*m*-I	3·49	3·36
p-Br	3·89	3·82	*p*-NO_2	0·69	*ca.* 0·9

more reactive chlorides and vice versa; d log *k*/d pK_a *is positive.* This relation is illustrated in Table 1 by the rates of hydrolysis of several *m-* and *p*-substituted benzyl chlorides in 50% aqueous ethanol at 83·0° (Olivier, *Chem. Revews*, 1935, **16**, 183) and the basic strengths of the corresponding aniline derivatives in 30% aqueous ethanol at 25·0° (Bennett, Brooks, and Glasstone, *J.*, 1935, 1821). It can also apply when the substituent is directly attached to the reacting groups; for example, reactivity increases in the series $Ph{\cdot}CH_2Cl < Ph{\cdot}CHMeCl < Ph{\cdot}CMe_2Cl$ and basic strength increases in the corresponding series of amines $Ph{\cdot}NH_2 < Ph{\cdot}NHMe < Ph{\cdot}NMe_2$ (Bell and Bayles, *J.*, 1952, 1518). (It does not apply when the substituent, *e.g.*, the phenyl group, can provide electronic displacements directed either towards or away from the reacting group : reactivity *increases* in the series of chlorides $Ph\cdot CH_2Cl < Ph_2CHCl < Ph_3CCl$, whereas basic strength *decreases* in the corresponding series of amines $Ph\cdot NH_2 > Ph_2NH > Ph_3N$.) On the other hand, since ionisation process (*a*) and dissociation (*b*) incur similar changes in intramolecular configuration, they are probably affected by similar changes in steric interaction : aralkyl chloride and anilinium ion, being comparatively free from mesomeric phenomena, will prefer those configurations in which R and R′, should these be bulky groups, avoid the plane of the benzene ring whereas these groups must lie in or near this plane in the benzyl cation and in the amine if these are to have maximum resonance energy. Thus both reactions are hindered by the increase in steric interaction as R and R′ approach the plane of the ring and by loss of resonance energy in the benzyl cation and in the amine if these, for steric reasons, are not approximately planar. These two energy terms, say for a benzyl cation, are represented graphically in the Figure. Let *P* be the energy content of the ion when mesomeric energy is zero and intra-ionic steric interaction a minimum, *i.e.*, when the angle (θ) between the plane of the side-chain carbonium ion and that of the ring is 90° ; and let *PQ*, given by $-A \cos^2 \theta$ where *A* is the mesomeric energy when $\theta = 0°$, and *PS* represent the change of mesomeric and of steric interaction respectively with change of θ. Algebraic addition of *PQ* and *PS* provides *PR*, and the minimum at *X* represents the benzyl cation ; its energy content is greater by the amount *XZ* than that it would have been if steric interaction were independent of θ ; *XZ* is compounded of the energy of steric interaction *XY* and the loss of resonance energy *YZ*. (Change in the curve *PS* or *PQ* will alter the ratio *XY*/*YZ* ; *e.g.*, $X'Y'/Y'Z' \neq XY/YZ$.) In this way, incursion of intramolecular steric interaction effects an increase in the energy content of the benzyl cation and, similarly but not equally, in that of the corresponding aromatic amine, and thus hinders ionisation of the benzyl chloride and dissociation of the anilinium ion. *In a series of chlorides and amines in which the members differ mainly in the magnitude of this steric effect, the more basic amines will be those which correspond to the less reactive chlorides and* vice versa ; $d \log k/d\, pK_a$ *will be negative.* This relation is the opposite of that which usually obtains when this steric effect is absent.



Steric Hindrance of Unimolecular Solvolysis of the Chlorides R·CHPhCl, *where* R *is Methyl, Ethyl, Propyl,* iso*Propyl, 1-Ethylpropyl,* tert.*-Butyl and* 1 : 1*-Dimethylpropyl severally.*—These chlorides ionised inconveniently slowly in absolute ethanol, and 80% (by volume) aqueous ethanol was used; increased rate of reaction in solvent of higher dielectric constant or of greater solvating power is typical of the unimolecular solvolysis of such compounds, as also is the progressive diminution in value of the rate coefficient when the extent of reaction exceeds 65—70% (Hughes, Ingold, *et al.*, many papers from 1935). The reactions do not involve rearrangement of side-chain; each chloride was hydrolysed in 50% aqueous acetone and in each instance the corresponding alcohol was isolated and identified; Skell and Hauser (*J. Amer. Chem. Soc.*, 1942, **64**, 2633) had previously demonstrated that unimolecular solvolysis of 1-phenyl*neo*pentyl halides ($R = Bu^t$) proceeds without rearrangement. Since *neo*pentyl isomerises to the 1 : 1-dimethylpropyl cation (Hughes, Ingold, *et al.*, *J.*, 1946, 192; *Nature*, 1951, **167**, 986; 1951, **168**, 65), the comparative stability of the 1-phenyl*neo*pentyl cation and of the 2 : 2-dimethyl-1-phenylbutyl cation ($R = CMe_2Et$) is presumably effected by spread of positive charge into the benzene ring.

The kinetic data are assembled in Table 2 while, in Table 3, the reactivities of these chlorides are compared with those of a corresponding series of alkyl chlorides $R{\cdot}CMe_2Cl$ and with the dissociation constants of corresponding series of aromatic and aliphatic amines R·NHPh and $R{\cdot}NH_2$ respectively. Differences between members of a series are greater for the aromatic than for the aliphatic compounds and these greater differences seem to originate largely in differences in magnitude of steric interaction of the side-chain and the benzene ring since the order of *decreasing* reactivity of the chlorides R·CHPhCl: R = Me, Et, Pr^i, Bu^t is that of increasing basic strength of the amines R·NHPh, *i.e.*, since $d \log k / d\, pK_a$ is negative.

TABLE 2. *Constants of the Arrhenius equation,* $k = Ae^{-E/\mathbf{R}T}$, *for the formation of hydrogen chloride by the solvolysis of the chlorides* R·CHPhCl *in* 80% *aqueous ethanol.*

R	$10^7k_{45\cdot0}$ (sec.$^{-1}$)	$10^5k_{65\cdot0}$ (sec.$^{-1}$)	E (kcal./mole)	ΔE	$10^{-10}A$ (sec.$^{-1}$)
Methyl	1180	793	20·4	1	1·0
Ethyl	273	190	20·7	1	0·38
Propyl	327	218	20·3	1	0·24
*iso*Propyl	58·7	50·0	22·9	3·5	2·5
1-Ethylpropyl	145	116	22·3	3	2·3
tert.-Butyl	2·18	2·35	25·4	6	4·8
1 : 1-Dimethylpropyl	4·58	4·64	24·8	5·5	3·9

TABLE 3. *Relative reactivites of the chlorides* R·CHPhCl *and* $R{\cdot}CMe_2Cl$ *in* 80% *aqueous ethanol, and the dissociation constants of the amines* R·NHPh *and* $R{\cdot}NH_2$ *in water at* 25·0°.

	R·CHPhCl (i)		$R{\cdot}CMe_2Cl$ (ii)		R·NHPh (iii)	$R{\cdot}NH_2$ (iv)
R	$\log 10^9k_{45\cdot0}$	E	$\log ak_{25\cdot0}$	E	pK_a	pK_a
Me	5·07	20·4	5·00	22·2	4·85	10·64
Et	4·44	20·7	5·20	21·0	5·10	10·67
n-Pr	4·51	20·3	5·18	21·2	5·02	10·58
i-Pr	3·77	22·9	4·95	21·4	5·50 (i)	10·63
t-Bu	2·34	25·4	5·08	21·4	7·10	10·45

(i) Determined by potentiometry (see Part II). (ii) Hughes, *loc. cit.*; Hughes *et al.*, *Nature*, 1951, **167**, 987. (iii) Verearschi and Rumpf, *Compt. rend.*, 1949, **228**, 1655; 1949, **229**, 1152. (iv) Hall and Sprinkle, *J. Amer. Chem. Soc.*, 1932, **54**, 3469.

If it is assumed that variation in the value of E (Table 2) is caused wholly by variation in steric effect, and that the magnitude of this effect when R is methyl is the same as that between the methyl groups in *cis*-2-butene (Baddeley and Chadwick, *loc. cit.*), *i.e.*, *ca.* 1 kcal./mole, then steric hindrance of ionisation of these chlorides can be assigned the energy values ΔE in Table 2. Of these values, that for the *tert.*-butyl group (*ca.* 6 kcal./mole) is similar in magnitude to the energy of mesomeric interaction of a phenyl group with an amino-, carbonyl, or vinyl group; this similarity is in accord with evidence of steric hindrance of mesomerism in *N-tert.*-butylaniline (Hickinbottom, *J.*, 1933, 946), pivalophenone (Cherrier, *Compt. rend.*, 1947, **225**, 1306; Ramart-Lucas *et al.*, *Bull. Soc. chim.*, 1937, 481; 1942, 850; 1949, 454; 1952, 422), and α-*tert.*-butylstyrene (Ramart-Lucas, Proc. XIth Intern. Congr. Pure & Appl. Chem., London, 1947, Vol. II, p. 267).

EXPERIMENTAL

Materials.—*Chlorides.* 1-Phenyl*neo*pentyl alcohol (22 g.) was gradually added with stirring to ice-cold thionyl chloride (44 g.). The mixture was kept overnight and excess of thionyl chloride was removed under reduced pressure. The residue, in ethereal solution, was washed with water and dilute sodium hydrogen carbonate solution, and dried (K_2CO_3). Distillation under nitrogen gave 1-phenyl*neo*pentyl chloride (18 g.), b. p. 71—72°/0·5 mm. This procedure gave the following tabulated chlorides in yields of 70—85%.

Compound R·CHPhCl		Cl (%)	
R	B. p./mm.	Found	Calc.
Methyl	39—40°/0·5	25·2	25·3
Ethyl	61—62°/0·5	23·2	23·2
Propyl	97—98°/10	21·2	21·3
*iso*Propyl	63—64°/0·5	21·1	21·3
1-Ethylpropyl	122—123°/15	18·2	18·3
tert.-Butyl	71—72°/0·5	19·4	19·7
2 : 2-Dimethylpropyl	123—124°/15	18·1	18·3

Alkylphenylcarbinols R·CHPh·OH.—Those with R = methyl, ethyl, and propyl were obtained by reduction of the corresponding ketones with aluminium *iso*propoxide or lithium aluminium hydride; those with R = *iso*propyl, *tert.*-butyl, and 1 : 1-dimethylpropyl were obtained by interaction of benzaldehyde and the appropriate alkylmagnesium halide (Conant and Blatt, *J. Amer. Chem. Soc.*, 1928, **50**, 554; Favorski *et al.*, *Bull. Soc. chim.*, 1936, 239). 2-*Ethyl*-1-*phenylbutan*-1-*ol*, b. p. 126—127°/13 mm. (Found: C, 81·2; H, 10·1. $C_{12}H_{18}O$ requires C, 80·9; H, 10·1%), was similarly obtained; 3-bromopentane, b. p. 116—119°/760 mm., was prepared from pentan-3-ol, b. p. 116—117°/760 mm., which, in turn, was obtained by interaction of ethyl formate and ethylmagnesium bromide.

Solvent.—Aqueous ethanol (80% EtOH by volume) was obtained by addition of distilled water to ethanol which had been purified by the process described by Lund and Bjerrum (*Ber.*, 1931, **64**, 210). One batch of solvent was used throughout.

Determination of Rates of Solvolysis of the Chlorides R·CHPhCl.—(a) *Where* R *was a primary or secondary alkyl group.* A flask was charged with solvent (80 c.c.), fitted with a ground-in stopper, and placed in the thermostat; after *ca.* 0·5 hr., enough freshly distilled chloride was added to provide an approx. 0·05M-solution, and the mixture was shaken vigorously. At selected times, samples (5 c.c.) were pipetted into ice-cold absolute ethanol (50 c.c.) and titrated (bromocresol-green as indicator) with sodium hydroxide solution (0·025N).

(b) *When* R *was a tertiary alkyl group.* The reaction mixture was prepared as above, except that the flask was placed in an ice-water bath; samples (5 c.c.) were pipetted into glass tubes and these were sealed and placed in the thermostat. At selected times, reaction tubes were cooled in ice and water, and their contents were transferred by ethanol (50 c.c.) to a conical flask and titrated as described above.

The rate coefficients were derived from the equation $k = (1/t) \ln (T_\infty - T_0)/(T_\infty - T_t)$, in which the symbols have their usual significance, and are listed in Table 2. Each reaction was duplicated. The experimental errors were less than 3%.

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