157. *The Ionic Dissociation and Reactivity of Some Arylmethyl Chlorides.*

By S. F. Mason.

The anomalous variation of the free energy of ionisation of the triarylmethyl chlorides in liquid sulphur dioxide with the delocalisation energy of the carbonium ions produced has been shown to be due to concomitant variations in the electron interaction and solvation energies. The relative free energies of activation for the solvolysis of a series of arylmethyl chlorides are found to be governed by the electron interaction and solvation energies of the corresponding carbonium ions, as well as their delocalisation energies.

It has been shown[1] that a regular relation exists between the ionisation constants of a series of triarylmethyl chlorides, measured in sulphur dioxide at 0°, and the delocalisation energy, calculated by the Hückel approximation, of the triarylmethyl ions produced by the ionisation. The plot of the free energy of ionisation, ΔG_1, against $E_D\beta^{-1}$, the delocalisation energy of the carbonium ion expressed in terms of the carbon–carbon resonance integral, β, is given in Fig. 1*A* for the compounds in which the steric hindrance is constant, *i.e.*, there are *o*–*o*′-contacts only. The plot of ΔG_1 against $E_D\beta^{-1}$ is curved, and the averaged slope suggests that β has a value of about —40 kcal./mole. The free energy of dissociation, ΔG_2, of the hexa-arylethanes to triarylmethyl radicals in benzene solution at 25° is also a smooth function of $E_D\beta^{-1}$ (Fig. 1*B* and *C*), the delocalisation energy of a radical and of the corresponding carbonium ion being identical according to the Hückel approximation. For compounds in which again the steric effect is constant (*o*–*o*′-contacts between the aryl groups in the ethanes and the radicals), two distinct curves

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[1] Streitwieser, *J. Amer. Chem. Soc.*, 1952, **74**, 5288.

are obtained, one for the series of compounds in which the aryl groups are phenyl or *p*-diphenylyl residues (Fig. 1*B*), and the other for the series in which the groups are phenyl or 2-naphthyl residues (Fig. 1*C*), the averaged slopes of these curves giving β about −25 kcal./mole.

The equilibria of triarylmethyl systems are not adequately explained on the basis of the Hückel approximation, which, if valid, would require the relations of Fig. 1 to be linear with slopes giving β the value appropriate to the approximation, namely,[2] −20 kcal./mole. In calculating π-electron energies by the Hückel method, no account is taken of electron interaction, overlap, changes in compressional energy, and, in the present case, the non-planarity of the conjugated system. The effects of the last three factors on a given triarylmethyl radical and the corresponding ion are the same, so that they cannot account for the different apparent β values obtained from Fig. 1*A* and Figs. 1*B* and *C*.

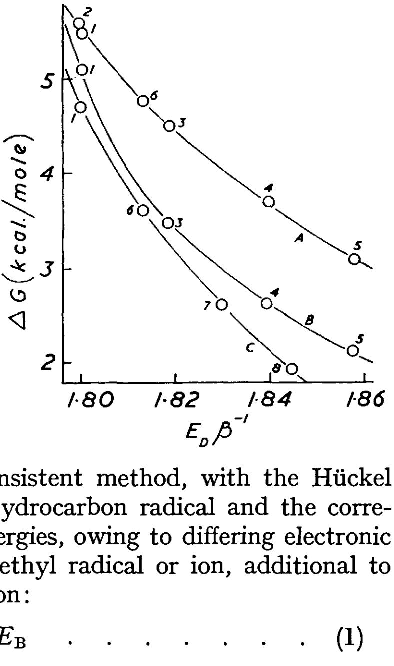

FIG. 1. *A, Variation of the free energy of ionisation of triarylmethyl chlorides with the delocalisation energy of the carbonium ion produced. B and C, Variation of the free energy of dissociation of hexa-arylethanes with the delocalisation energy of the radicals produced. The ordinate of B has been raised, and that of C lowered, by 0·2 kcal./mole. The numbers refer to the substances in Table* 1.

However, it has been shown[3] by a simplified self-consistent method, with the Hückel molecular orbitals as a base, that an odd alternant hydrocarbon radical and the corresponding carbonium ion possess different resonance energies, owing to differing electronic interactions. The resonance energy, E_R, of an arylmethyl radical or ion, additional to that of the aromatic nucleus, is given[3] by the expression:

$$E_R = E_D \pm E_C + E_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the second term on the right-hand side of equation (1) being positive for the radical and negative for the carbonium ion. The first term, E_D, is due to the delocalisation of the π-electrons over a σ-core field which is more extensive in the arylmethyl system than in the aromatic nucleus, and it is equivalent to the Hückel delocalisation energy:

$$E_D = 2[\sum{}'_{r>s} P_{rs(ArMe)} - \sum{}'_{r>s} P_{rs(Nuc)}]\beta \quad . \quad . \quad . \quad . \quad (2)$$

where P_{rs} is the mobile bond order between the atoms r and s, the sums $\sum'$ being taken over adjacent atoms, and ArMe refers to the arylmethyl radical or ion and Nuc to the corresponding aromatic nucleus. The second term, E_C, arises from the lower probability that a pair of electrons shall be situated on a given atom in the delocalised than in the fixed-bond state of the arylmethyl system:

$$E_C = \tfrac{1}{2}\sum\nolimits^{st}_{s>t} C_{or}{}^2\, C_{ot}{}^2(\gamma_{11} - \gamma_{rt}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where C_{or} is the coefficient of the non-bonding molecular orbital at atom r, the sum $\sum^{st}$ is taken over starred atoms, and γ_{rt} is the electron repulsion integral between atoms r and t.

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[2] Coulson, " Valence," Oxford Univ. Press, 1952, p. 240.

[3] Brickstock and Pople, *Trans. Faraday Soc.*, 1954, **50**, 901.

The third term, E_B, is due to the smaller probability that pairs of electrons shall be found on neighbouring atoms in the arylmethyl system than in the aromatic nucleus:

$$E_B = \tfrac{1}{2}\left[\sum_r^{st}\sum_s^{un} P_{rs}^2(\gamma_{12} - \gamma_{rs})_{ArMe} - \sum_{r>s} P_{rs}^2(\gamma_{12} - \gamma_{rs})_{Nuc}\right] \quad . \quad . \quad (4)$$

where $\sum^{un}$ refers to summation over unstarred atoms, and the other symbols have their former significance.

Evaluation of E_D and, particularly, E_B for the triarylmethyl radicals and ions is laborious, though an approximate value for E_D is readily found[4] from the coefficient of the non-bonding molecular orbital at the exocyclic atom. However, E_O, which represents one-half of the energy difference between a radical and the corresponding carbonium ion, can be calculated from the coefficients of the non-bonding molecular orbital and repulsion integrals evaluated by the point-charge approximation.[3] Values of E_O (Table 1) indicate that triarylmethyl ions are more stable than the corresponding radical by some 60—70 kcal./mole. ΔG_1 is an empirical measure of the free-energy change of the overall ionisation equilibrium:

$$Ar_3CCl \rightleftharpoons Ar_3C^+ + Cl^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and ΔG_2 of the dissociation equilibrium:

$$Ar_3C{-}CAr_3 \rightleftharpoons 2Ar_3C\cdot \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Thus it may be expected that

$$\Delta G_1 - \tfrac{1}{2}\Delta G_2 = -2E_O + \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Values of $(\Delta G_1 - \tfrac{1}{2}\Delta G_2)$ listed in Table 1 show that the differential in this quantity in the series from triphenylmethyl to tris-*p*-diphenylylmethyl (0·88 kcal./mole) and the differential in $-2E_O$ (8·89 kcal./mole) agree in sign but not in magnitude.

TABLE 1. *The free energy of ionisation of the triarylmethyl chlorides* RR′R″CCl (ΔG_1) *in liquid sulphur dioxide at* 0—0·12° ; *the free energy of dissociation of the hexa-arylethanes* $(RR'R''C\cdot)_2$ (ΔG_2) *in benzene at* 25°; *the delocalisation energy* ($E_D\beta^{-1}$) *of the corresponding carbonium ion and radical*; *the charge dispersal energy difference* ($2E_O$) *between the latter*; *and the summed squares of the Hückel charges* ($\sum_r q_r^2$) *of the carbonium ion. Energies are given in kcal./mole.*

	Substituents [a]								
No.	R	R′	R″	ΔG_1	ΔG_2	$(\Delta G_1 - \tfrac{1}{2}\Delta G_2)$	$E_D\beta^{-1}$	$2E_O$ [h]	$\Sigma_r q_r^2$ [i]
1	Ph	Ph	Ph	5·48 [b]	4·90 [d]	3·03	1·8004 [c]	61·89	0·1482
2	*m*-C_6H_4Ph	,,	,,	5·64 [b]	—	—	1·7990 [c]	—	—
3	*p*-C_6H_4Ph	,,	,,	4·53 [b]	3·27 [e]	2·89	1·8184 [c]	65·16	0·1333
4	,,	*p*-C_6H_4Ph	,,	3·72 [b]	2·45 [f]	2·50	1·8396 [c]	68·13	0·1209
5	,,	,,	*p*-C_6H_4Ph	3·13 [b]	1·96 [f]	2·15	1·8578 [c]	70·78	0·1096
6	2-$C_{10}H_7$	Ph	Ph	4·80 [c]	3·84 [f]	2·88	1·8134 [c]	63·54	0·1411
7	,,	2-$C_{10}H_7$	,,	—	2·85 [f]	—	1·830 [g]	—	—
8	,,	,,	2-$C_{10}H_7$	—	2·15 [f]	—	1·845 [g]	—	—

[a] Data for compounds containing a 1-naphthyl group or two or more *m*-diphenylyl groups are omitted from the Table as the steric factors in these compounds differ from those of the compounds listed. [b] Lichtin and Leftin, *J. Phys. Chem.*, 1956, **60**, 164. [c] Ref. 1. [d] Calc. from the data of Muller and Muller-Rodloff, *Annalen*, 1935, **521**, 89. [e] Calc. from the data of Marvel, Mueller, and Ginsberg, *J. Amer. Chem. Soc.*, 1939, **61**, 2008. [f] Calc. from the data of Marvel, Shackleton, Himel, and Whitson, *ibid.*, 1942, **64**, 1824. [g] Calc. from the empirical relation, $-E_D\beta^{-1} = 2{\cdot}60 - 1{\cdot}45C_{ox}$, based on Dewar's theory.[4] [h] Calc. by Brickstock and Pople's method.[3] [i] Calc. from the coefficients of the N.B.M.O., obtained by the method of Longuet-Higgins (*J. Chem. Phys.*, 1950, **18**, 275).

The failure of equation (7) to hold quantitatively suggests that the resonance energy of a triarylmethyl ion, whilst rising steeply relatively to that of the corresponding radical in the series studied, is partly offset by another differential energy factor, such as that due to the solvation of the ions. The solvation energy of an ion can be divided into three

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[4] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.

main terms:[5] that due to cavity formation; that due to dielectric saturation in the primary solvation shell of the ion; and that due to the Born charging. The cavities formed in a solvent by a triarylmethyl ion and a chloride ion should not differ greatly from those formed by the corresponding undissociated triarylmethyl chloride, and the energy of cavity formation should not vary widely in the series. The positive charge on any one carbon atom of a triarylmethyl ion is small (the maximum charge is 0·308 in the present series), so that there may be no dielectric saturation in the primary solvation sheath of the ion. Should such saturation occur, the interaction energy between a triarylmethyl ion and solvent dipoles in the first co-ordination shell is given by the expression:

$$E_{\mathrm{I}} = \textstyle\sum_{\mathrm{r}}\sum_{z} q_{\mathrm{r}} eze/d \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where q_{r} is the fraction of a positive charge on atom r, and d is the distance between that atom and the fractional charge, z, of the dipole of a solvent molecule in the first solvation shell, e being the electronic charge. It may be expected that $\sum_z ze^2/d$ does not vary greatly from one charged centre to another in a triarylmethyl ion, or, more particularly, from one ion to another, and since $\sum_{\mathrm{r}} q_{\mathrm{r}}$ is unity for each carbonium ion, E_{I} should not be a differential energy term in the present series. However, the free energy of the Born charging of a triarylmethyl carbonium ion, ΔG_{S}, given by equation (9), should vary considerably from one ion to another:

$$\Delta G_{\mathrm{S}} = -\textstyle\sum_{\mathrm{s}} q_{\mathrm{r}}{}^2 e^2(1 - 1/D)/2R \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where D is the dieletric constant of the solvent, and R is the effective radius of the charged centre, atom r, in the carbonium ion. If a Hückel distribution of charge is assumed for the carbonium ions, $\sum_{\mathrm{r}} q_{\mathrm{r}}{}^2$ varies from 0·148 for the triphenylmethyl to 0·110 for the tris-*p*-diphenylylmethyl ion (Table 1). Thus the solvation energy due to the Born charging falls as the resonance energy of the carbonium ion, relatively to that of the corresponding radical, rises in the series. Moreover, the changes in solvation and resonance energy are proportional one to the other in the series, $\sum_{\mathrm{r}} q_{\mathrm{r}}{}^2$, the variable parameter in the equation (9) for the Born charging energy, being a smooth, nearly linear, function of E_{C}, the charge dispersal energy (Fig. 2*A*). After allowance for changes in the solvation energy, equation (7) becomes:

$$\Delta G_1 - \tfrac{1}{2}\Delta G_2 = \Delta G_{\mathrm{S}} - 2E_{\mathrm{C}} + \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and it is found that the experimental data for $(\Delta G_1 - \tfrac{1}{2}\Delta G_2)$ are accounted for quantitatively by equation (10) if R is given the value of $0{\cdot}8(1 - 1/D)$ Å. When D is identified with the bulk dielectric constant (15·35) of liquid sulphur dioxide at 0°, the value for R becomes 0·75 Å, which is close to the ionic radius of carbon[6] (0·58 Å) but larger. In calculating solvation energies due to the Born charging it is necessary to employ effective radii larger than the ionic radii of the ions solvated in order to allow for the polarised solvent molecules in the primary co-ordination shell.[5] Dielectric saturation may not occur in the ions of the present series (see above), but, for carbonium ions, it is necessary to allow also for substituents attached to the positively charged carbon atom.[6]

The variation of the ionisation constants of the triarylmethyl chlorides with the energy parameters discussed above has a bearing on their reactivities. It has been argued[7] that conjugated carbonium ions, such as allyl and benzyl, cannot have a resonance energy since allyl and benzyl chloride are solvolysed in formic acid only 10^2—10^4 times as fast as primary alkyl chlorides,[8,9] whilst if the allyl and benzyl carbonium ions are stabilised by the Hückel delocalisation energy (*ca.* 15 kcal./mole) they should be solvolysed some 10^{10}—10^{13} times as fast. The self-consistent field treatment[3] suggests that allyl and benzyl ions

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[5] Eley and Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093; Latimer, Pitzer, and Slansky, *J. Chem. Phys.*, 1939, **7**, 108; Pearson, *ibid.*, 1952, **20**, 1478.

[6] Franklin, *Trans. Faraday Soc.*, 1952, **48**, 443.

[7] Franklin and Lumpkin, *J. Chem. Phys.*, 1951, **19**, 1073.

[8] Bateman and Hughes, *J.*, 1940, 945.

[9] Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 25.

have much larger resonance energies (*ca.* 60 kcal./mole, Table 2), so that they might be expected to be solvolysed some 10^{44} times as fast as primary alkyl chlorides. However, the charge of a conjugated carbonium ion is delocalised, so that, by equation (9), such ions have a smaller solvation energy due to the Born charging than alkyl ions in the same solvent. For the benzyl ion $\sum_r q_r^2$ (equation 9) has the value of 0·387 (Table 3), whilst for an alkyl ion the value of this parameter is unity. Thus the resonance energy of a conjugated carbonium ion compensates for its loss of Born charging solvation energy, which, in general, is proportional to $(1 - \sum_r q_r^2)$. On this basis it is found that if, as the data [8, 9] suggest, the free energy of activation for the solvolysis of benzyl chloride in formic acid is some 5 kcal./mole lower than that of a primary alkyl chloride, the effective radius of a charged centre in the benzyl ion (R, equation 9) is 1·77 Å, when D is given the value of the bulk dielectric constant of formic acid (58·5 at 16°). A study of the ionisation constants of the triarylmethyl chlorides gave R the value of 0·75 Å (see above). The larger value obtained for the benzyl ion may be due in part to the dielectric saturation of the solvent round the exocyclic atom, owing to the considerable charge (0·57), so that the effective radius for the Born charging is increased. However, the large value for R, in part at least, is apparent only, arising from the assumption (equation 9) that the separation of charge between the carbonium and the chloride ions is as complete in the solvolytic transition state of benzyl chloride as in the ionic equilibria of the triarylmethyl chlorides.

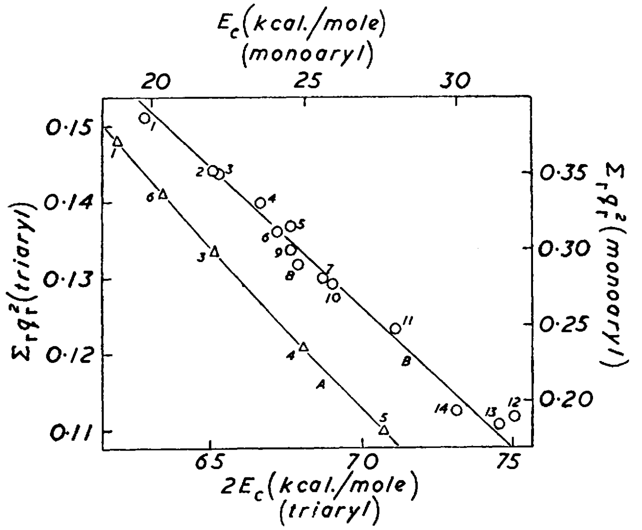

FIG. 2. *A, Variation of the difference in resonance energy between a triarylmethyl ion and the corresponding radical,* $2E_C$, *with the parameter,* $\sum_r q_r^2$, *governing the solvation energy of the carbonium ion due to the Born charging (numbers refer to the substances in Table* 1). *B, Variation of the charge dispersal energy,* E_C, *of monoarylmethyl ions with the solvation energy parameter,* $\sum_r q_r^2$. *(Numbers refer to the substances in Table* 3.)

TABLE 2. *The delocalisation* (E_D), *charge dispersal* (E_C), *and bond–bond interaction energy* (E_B) *of some conjugated carbonium ions* (in kcal./mole).

Ion	E_D [a]	E_C [c]	E_B [d]
Allyl	−45·6 [b]	14·6 [b]	0
Benzyl	−39·7	19·8 [b]	−2·0
2-Naphthylmethyl	−41·0	22·3	−3·3
1-Naphthylmethyl	−44·8	24·8	−3·3
9-Anthrylmethyl	−52·4	30·0	−8·9

[a] Calc. from equation (2) with $\beta = -55{\cdot}1$ kcal./mole (ref. 3). [b] Ref. 3. [c] Calc. from equation (3) with $\gamma_{11} = 242{\cdot}7$, $\gamma_{13} = 125{\cdot}9$ kcal./mole, and the point charge approximation values for larger distances. [d] Calc. from equation (4) with $\gamma_{12} = 168{\cdot}3$, γ_{14} (*cis*) $= 113{\cdot}0$ kcal./mole, and the point charge approximation values for larger distances.

An analysis of the effect of added salt on the rates of solvolysis of alkyl and arylmethyl halides in 90% aqueous acetone has shown[10] that the separation of charge in the transition state is not complete in these reactions, though the fractional positive charge is delocalised in the partly formed arylmethyl ion. For a degree of ionisation, α, with the assumption that the delocalised charge follows the Hückel distribution in the partly formed arylmethyl, equation (9) becomes:

TABLE 3. *The logarithms of the rate constants for the reaction of the monoarylmethyl chlorides:* I, *S_N2 reaction with potassium iodide in acetone.* II, *Solvolysis in water* (6·1%)*-formic acid* (54·1%)*-dioxan* (39·8%). III, *Solvolysis in water* (5·8%)*-formic acid* (34%)*-dioxan* (60·2%). IV, *Solvolysis in moist formic acid* (0·38M *in water*). *The delocalisation energies* ($E_D\beta^{-1}$), *coefficient of the N.B.M.O. at the exocyclic atom* (C_{ox}), *charge dispersal energies* (E_C), *and the summed squares of the Hückel charges* ($\sum_r q_r^2$) *of the corresponding carbonium ions.*

No.	Aryl	log *k* (25°) I[a]	II[a]	III[a]	IV[b]	C_{ox}	$E_D\beta^{-1}$	E_C[f] (kcal./mole)	$\Sigma_r q_r^2$
1	Phenyl	−3·19	−7·61	—	−6·94	0·756	0·722[c]	19·8	0·387
2	2-Phenanthryl	−2·91	−7·13	—	−5·55	0·737	0·74[d]	22·1	0·351
3	2-Naphthyl	−2·86	−7·09	—	−5·59	0·728	0·744[e]	22·3	0·350
4	2-Triphenylenyl	—	—	—	−5·43	0·728	0·74[d]	23·7	0·331
5	3-Phenanthryl	−2·85	−6·45	—	−4·80	0·714	0·76[d]	24·6	0·315
6	4-Phenanthryl	−2·51	−5·77	—	—	0·700	0·78[d]	24·2	0·311
7	1-Phenanthryl	−2·58	−6·55	−7·50	−4·77	0·680	0·80[d]	25·7	0·282
8	1-Naphthyl	−2·64	−6·26	−7·31	−4·36	0·671	0·812[e]	24·8	0·290
9	9-Phenanthryl	−2·58	−6·38	−7·36	−4·31	0·668	0·813[c]	24·6	0·297
10	3 : 4-Benzo-2-phenanthryl	−2·55	−5·33	−6·80	—	0·667	0·81[d]	26·0	0·278
11	2-Chrysenyl	—	—	—	−2·89	0·641	0·84[d]	28·0	0·247
12	3-Pyrenyl	−2·08	−3·02	−4·46	—	0·603	0·88[d]	31·9	0·190
13	1 : 2-Benz-10-anthryl	−1·56	—	−4·35	—	0·560	0·92[d]	31·4	0·185
14	9-Anthryl	−1·42	—	−4·16	—	0·535	0·951[c]	30·0	0·194

[a] Ref. 12 and Brandli, Dujardin, Fierens, Martin, and Planchon, *Helv. Chim. Acta*, 1956, **39**, 1501. [b] Ref. 11. [c] Calc. by the L.C.A.O. method without overlap. [d] Calc. from the empirical relation, $E_D\beta^{-1} = 1{\cdot}50 - 1{\cdot}03C_{ox}$, based on Dewar's theory.[4] [e] Wheland, *J. Amer. Chem. Soc.* 1941, **63**, 2025. [f] Calc. by the method of ref. 3.

$$\Delta G_S = -\textstyle\sum_r q_r^2 \alpha^2 e^2 (1 - 1/D) 2R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and since $1 > \alpha > 0$, effective radii calculated by equation (9) are too large. The incomplete ionisation of an arylmethyl chloride in a transition state has the effect of reducing both the solvation and the resonance energy of the carbonium ion, but not all of the terms contributing to the latter energy are reduced proportionately. Equations (2), (3), (4), and (11) suggest that a partly formed arylmethyl ion has a delocalisation energy proportional to α, but solvation, ΔG_S, and electron interaction energies, E_C and E_B, proportional to α^2. Thus the variation in the free energy of activation, $\Delta G^‡$, in a series of arylmethyl chlorides for a given reaction should be given by the equation:

$$\Delta G^‡ = \alpha E_D + \alpha^2(\Delta G_S + E_B - E_C) + \text{Constant} \quad . \quad . \quad . \quad . \quad (12)$$

The logarithms of the rate constants of a series of arylmethyl chlorides have been correlated with the coefficient of the non-bonding molecular orbital at the exocyclic atom in the corresponding carbonium ion, a parameter proportional to the Hückel delocalisation energy,[4] for a number of reactions, examples of which are given in Fig. 3 and Table 3. The rate constants for the S_N2 reaction of the arylmethyl chlorides with potassium iodide in acetone give good correlation with the Hückel delocalisation energy expressed in terms of the carbon–carbon resonance integral, $E_D\beta^{-1}$ (Fig. 3*A*), but plots of the solvolyses in water–formic acid–dioxan (Fig. 3*B*) and in formic acid (Fig. 3*C*) involve scatter and give apparent β values (*ca.* −40 and −60 kcal./mole respectively) much larger than the Hückel value[2] (−20 kcal./mole).

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[10] Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979.

From equation (12) it is apparent that when α is small, as in the S_N2 reaction, the solvation and electron interaction terms, and their variations within the series of arylmethyl derivatives, are very small. Thus the delocalisation energy, E_D, remains the major variable in the series, and the relative rate constants of S_N2 reactions should give good correlation with E_D, as is found (Fig. 3*A*). However, when α approaches unity, as in S_N1 reactions, all of the energy terms on the right-hand side of equation (12) become important variables determining the relative free energies of activation in the series of arylmethyl chlorides. The electron interaction energies, E_B and E_C, whilst showing a general trend towards larger values as the delocalisation energy, E_D, increases, are not smooth functions of E_D (Tables 2 and 3), and $\sum_r q_r^2$, the parameter determining the solvation energy of a conjugated carbonium ion due to the Born charging, shows similarly only a general trend towards smaller values as E_D increases (Table 3). However, changes in the charge dispersal energy, E_C, and the solvation energy, ΔG_S, mutually compensate to some degree in the monoarylmethyl as in the triarylmethyl ions (see above), as E_C and $\sum_r q_r^2$ are related in the monoarylmethyl series (Fig. 2*B*), though not so smoothly as in the triarylmethyl series (Fig. 2*A*). In particular, the 3-pyrenylmethyl ion has rather a large charge dispersal energy, E_C, in relation to its value of the solvation energy parameter, $\sum_r q_r^2$ (Fig. 2*B*, Table 3), a divergence perhaps connected with the absence of charge on a starred atom in this ion. The divergence suggests that 3-pyrenylmethyl chloride should be a particularly reactive compound, as is found (Fig. 3*B*, Table 3).

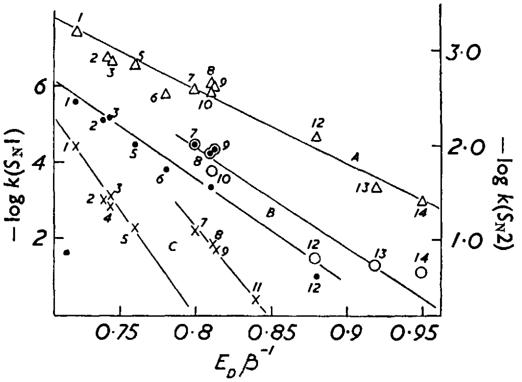

FIG. 3. *Relation between the delocalisation energies of the arylmethyl ions and the logarithms of the relative rate constants for the reaction of the arylmethyl chlorides.*
A (△) *Potassium iodide in acetone.*
B (●) *Solvolysis in water* (6·1%)*-formic acid* (54·1%)*-dioxan* (39·8%); (○) *solvolysis in water* (5·8%)*-formic acid* (34%)*-dioxan* (60·2%).
C (×) *Solvolysis in moist formic acid* (0·38M *in water*). (*Numbers refer to the compounds in Table* 3.)

The partial compensation between the charge dispersal, E_C, and solvation energy, ΔG_S, has the effect of leaving the bond-bond interaction term, E_B, as an important source of deviation from correlations between the delocalisation energy, E_D, and the relative rate constants for the S_N1 reactions of a series of arylmethyl chlorides. The calculated values of the bond-bond interaction term, E_B, show (Table 2) that, whilst it is small, E_B increases rapidly with the number of condensed rings in the arylmethyl system, owing to the increasing number of electrons delocalised over the exocyclic bond on carbonium-ion formation, and that the value of E_B depends on the particular aromatic nucleus substituted, and not on the position at which the exocyclic methyl group is attached, in the case of naphthalene and perhaps more generally. Such properties of the bond-bond interaction term, E_B, suggest, from equation (12), that, in correlations between E_D and the relative rate constants for the S_N1 reactions of a series of arylmethyl chlorides, the larger polycyclic derivatives should be more reactive than smaller congeners with the same delocalisation energy, and that, of the derivatives of a given aromatic nucleus, notably naphthalene and perhaps other nuclei, those with the smaller delocalisation energies should react faster, and those with the larger delocalisation energies more slowly, than their E_D values would indicate. The relative solvolysis rates [11,12] of the naphthylmethyl and phenanthrylmethyl chlorides

[11] Dewar and Sampson, *J.*, 1956, 2789; 1957, 2946, 2952.

[12] Fierens, Hannaert, Rysselberge, and Martin, *Helv. Chim. Acta*, 1955, **38**, 2009.

in a given medium illustrate the latter point (Figs. 3*B* and *C*, Table 3), but the derivatives with the larger delocalisation energies are all *peri*-compounds, and it is possible that there is steric hindrance between the methyl and *peri*-CH groups in the carbonium ion.[11] Such a steric effect is not evident in the S_N2 reaction with potassium iodide in acetone, even for the *meso*-compounds (Fig. 3*A*, Table 3), though gross hindrance, as in the case of the *peri*-2-aryl-2-chloropropanes, does lead to marked retardation of solvolysis.[11] In general, the tetracyclic arylmethyl chlorides are solvolysed[11,12,13] faster than might be expected from the values of their delocalisation energies (Figs. 3*B* and *C*, Table 3). In particular, 2-triphenylenylmethyl chloride is solvolysed some 40% faster than 2-naphthylmethyl chloride in formic acid,[11] the corresponding carbonium ions having the same delocalisation energies, and 3 : 4-benzo-2-phenanthrylmethyl chloride is solvolysed 3—16 times as rapidly as 1-naphthyl- and 9-phenanthryl-methyl chloride in water–formic acid–dioxan mixtures,[12,13] the corresponding carbonium ions having very similar delocalisation energies (Table 3). However, 3 : 4-benzophenanthrene is an overcrowded nucleus, and the non-planarity of the system[14] may increase the reactivity of the 2-chloromethyl derivative by relieving *peri* steric hindrance in the carbonium ion.

It may be noted that the total resonance energies (E_R, equation 1) of the monoarylmethyl ions increase with the delocalisation energy components expressed in terms of the carbon–carbon resonance integral, $E_D\beta^{-1}$, according to a general trend which gives β the approximate apparent value of —120 kcal./mole (Table 2). The apparent β values obtained from correlation of $E_D\beta^{-1}$ with the relative rates of reaction of the arylmethyl chlorides are smaller (*ca.* —60 kcal./mole for the solvolysis in moist formic acid, *ca.* —40 kcal./mole for solvolysis in water–formic acid–dioxan, and *ca.* —10 kcal./mole for reaction with potassium iodide in acetone), illustrating the effects of the incomplete separation of charge between the carbonium and the chloride ion in the transition state (equation 12),

TABLE 4. *Logarithms of the probability factors* (log *PZ*) *for the reactions* : (a) *Of arylmethyl chlorides, as follows* : I, S_N2 *reaction with potassium iodide in acetone*; II, *solvolysis in water* (6·1%)*-formic acid* (54·1%)*-dioxan* (39·8%); III, *solvolysis in water* (5·8%)*-formic acid* (34%)*-dioxan* (80·2%); IV, *solvolysis in water* (20·5%)*-dioxan* (79·5%); V, *solvolysis in water* (49·3%)*-dioxan* (50·7%). (b) *Of* 1*-arylethyl chlorides, as follows* : VI, *Solvolysis in water* (20%)*-acetone* (80%); VII, *solvolysis in water* (10%)*-acetone* (90%). *Also the summed squares of the Hückel charges* ($\sum_r q_r^2$) *of the corresponding carbonium ions.*

		log *PZ*							
No.	Aryl	I [a]	II [a]	III [a]	IV [a]	V [a]	VI [b]	VII [b]	$\sum_r q_r^2$
1	Phenyl	10·07	8·61	—	7·02	8·26	10·1	—	0·387
2	2-Phenanthryl	9·94	10·80	—	—	—	11·3	—	0·351
3	2-Naphthyl	9·42	10·86	—	—	—	11·3	—	0·350
4	4-Diphenylyl	—	—	—	—	—	11·2	—	0·319
5	2-Fluorenyl	—	—	—	—	—	11·8	10·2	0·319
6	3-Phenanthryl	9·94	10·51	—	9·38	10·20	11·7	—	0·315
7	4-Phenanthryl	10·84	12·88	—	—	—	—	—	0·311
8	2-Anthryl	—	—	—	—	—	—	10·2	0·310
9	9-Phenanthryl	10·79	11·82	10·04	8·72	11·84	11·8	—	0·297
10	1-Naphthyl	11·26	11·77	9·67	8·29	10·45	11·4	—	0·290
11	1-Phenanthryl	10·79	13·07	10·08	—	—	—	—	0·282
12	3 : 4-Benzo-2-phenanthryl	11·38	10·03	11·81	10·68	14·27	—	—	0·278
13	1-Anthryl	—	—	—	—	—	—	10·4	0·248
14	2-Chrysenyl	—	—	—	—	—	12·1	10·5	0·247
15	9-Anthryl	10·55	—	3·35	11·18	—	—	9·5	0·194
16	3-Pyrenyl	10·42	—	8·61	—	—	—	10·2	0·190
17	1 : 2-Benz-10-anthryl	11·27	—	7·55	10·61	13·89	—	—	0·185

[a] Refs. 12, 13, and 16. [b] Berliner and Shieh, *J. Amer. Chem. Soc.*, 1957, **79**, 3849.

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[13] Brandli, Dujardin, Fierens, Martin, and Planchon, *ibid.*, 1956, **39**, 1501.

[14] Herbstein and Schmidt, *J.*, 1954, 3302.

and the decrease in the solvation energy of a carbonium ion with increasing resonance energy (equation 11, Tables 2 and 3).

The importance of the solvation energy of the carbonium ion as a determinant of the reactivity of arylmethyl chlorides is shown by the relative values of the pre-exponential factors for the various reactions of these compounds (Fig. 4, Table 4). The solvation energy due to the Born charging, ΔG_S, is the only free-energy term on the right-hand side of equation (12), the components of the resonance energy being internal-energy terms. Thus the relative entropies of activation, $\Delta S^{\ddagger}$, of arylmethyl chlorides for a given reaction may be equated to the relative entropies of the solvation of the carbonium ions due to the Born charging, which are given by the derivative of the right-hand side of equation (11) with respect to temperature:

$$\Delta S^{\ddagger} = \sum_r q_r^2 \alpha^2 e^2 (\mathrm{d} \ln D/\mathrm{d}T)/2RD + \text{Constant} \quad . \quad . \quad . \quad . \quad (13)$$

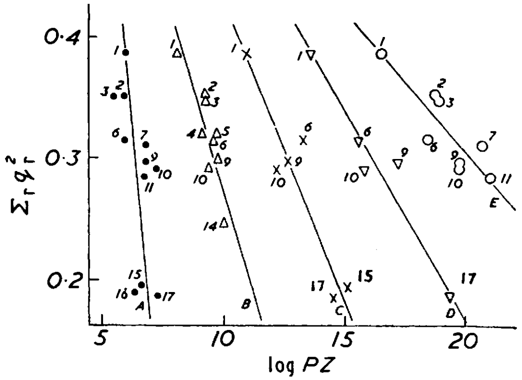

FIG. 4. *Relations between* $\sum_r q_r^2$, *the parameter governing the entropy of solvation of the carbonium ions due to the Born charging, and the pre-exponential factor,* log PZ.

A (●) S_N2 *reaction of arylmethyl chlorides with potassium iodide in acetone.*

B (△) *Solvolysis of* 1-*arylethyl chlorides in* 80% *acetone.*

C (×) *Solvolysis of arylmethyl chlorides in water* (20·5%)-*dioxan* (79·5%).

D (▽) *Solvolysis of arylmethyl chlorides in water* (49·3%)-*dioxan* (50·7%).

E (○) *Solvolysis of arylmethyl chlorides in water* (6·1%)-*formic acid* (54·1%)-*dioxan* (39·8%).

(*Numbers refer to the compounds in Table* 4.)

It is found that for five (Fig. 4) of the seven reactions for which information is available (Table 4) the pre-exponential factor, log PZ, increases as the Born charging parameter, $\sum_r q_r^2$, decreases, in conformity with equation (13), since (d ln D/dT) is invariably a negative quantity.[15] Moreover, log PZ varies more widely with $\sum_r q_r^2$ the greater the ionising power of the reaction medium (Fig. 4), that is, the larger the degree of ionisation in the transition state, α, again as equation (13) requires. From the slope of the relation between log PZ and $\sum_r q_r^2$ for a given reaction medium a value may be obtained for R/α^2, the ratio of the effective radius of a charged centre in a carbonium ion to the square of the separation of charge in the transition state. The temperature coefficients of the dielectric constants of mixed solvents are uncertain, but acetone and water, and presumably their mixtures, have the same value[15] for d ln D/dT, namely, $-4{\cdot}63 \times 10^{-3}$. By using this value it is found from the observed pre-exponential factors for the solvolysis of the 1-arylethyl chlorides in 80% acetone (Fig. 4*B*, Table 4) by equation (13) that R/α^2 has the value of 0·4 Å. This value is too small, but it may be of the correct order of magnitude as it has been shown[10] for the solvolysis of *tert.*-butyl bromide in 90% acetone that the degree of ionisation in the transition state is approximately 0·5.

The pre-exponential factors for the reactions of 3 : 4-benzo-2-phenanthrylmethyl chloride, in which the aromatic nucleus is non-planar,[14] do not fit the observed correlations (Fig. 4) at all well, and those for the solvolysis of the 1-arylethyl chlorides in 90% acetone and arylmethyl chlorides in water (5·8%)-formic acid (34%)-dioxan (60·2%) show no obvious correlation with the Born charging parameter of the carbonium ions, $\sum_r q_r^2$ (Table 4). In the last series, for the most part, the more reactive members, which have the smaller $\sum_r q_r^2$ values, have the smaller log PZ factors (Table 4), in apparent contradiction to equation (13). However, it has been suggested[11,16] that the more reactive arylmethyl

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[15] Pearson, *J. Chem. Phys.*, 1952, **20**, 1478.

[16] Fierens and Berkowitch, *Tetrahedron*, 1957, **1**, 129.

chlorides are ionised more completely in the transition state than their less reactive analogues in reaction media of low ionising power. Such a change of mechanism, an increase in α when $\sum_r q_r^2$ is small, would lead (equation 13) to smaller pre-exponential factors for the solvolysis of the more reactive arylmethyl chlorides in these media.

The author is indebted to Dr. H. O. Pritchard for the Hückel coefficients and energy levels of the 9-anthrylmethyl radical.

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[*Received, May* 20*th*, 1957;
revised, August 19*th*, 1957.]