999. *The Separation of Polar and Steric Effects. Part III.*[1] *The Kinetics of the Reactions of Arylaliphatic Carboxylic Acids with Diazodiphenylmethane, and of the Acid-catalysed Esterification of the Acids in Methanol.*

By K. BOWDEN, N. B. CHAPMAN, and J. SHORTER.

Rate coefficients have been determined for the reactions of diazodiphenylmethane with the following acids in toluene at 15°, and in 2-n-butoxyethanol at 25°: acetic, phenylacetic, diphenylacetic, αα-diphenylpropionic, αα-diphenylbutyric, triphenylacetic, 9-X-fluorene-9-carboxylic (X = H, Me, Et, Pr^i, Bu^t, or Ph), and 9,10-dihydroanthracene-9-carboxylic acid. The free energies of activation for the reactions in the two solvents at the above temperatures conform well with a linear relation. Taft polar substituent constants, σ^*, have been determined by assuming, as is reasonable, that the reactions obey the relation $\log k/k_0 = \rho^*\sigma^*$; and the additivity of substituent effects has been examined.

Rate coefficients have been determined for the acid-catalysed esterification of the above-mentioned acids in methanol at 60°, with toluene-*p*-sulphonic acid as catalyst. Taft steric substituent constants, E_S, have been evaluated and are discussed.

PARTS I and II of this series have been concerned with the separation of polar and steric effects in the reactions of *ortho*-substituted benzoic acids with diazodiphenylmethane[2] and in the alkaline and the acidic hydrolysis of the *ortho*-substituted methyl benzoates.[1] In this work the separation of polar and steric effects as attempted by Taft[3] was critically assessed. The present work extends this study to highly substituted arylaliphatic systems, whose reactivity may be studied relative to that of acetic acid as standard. The series chosen includes substituents of varying polarity and steric requirement; it also demonstrates the effect of two different interannular links.

If the influence of change of molecular structure on the free energy of activation is considered to be the sum of polar, steric, and resonance contributions, it is necessary to estimate these factors independently in order to interpret the results for a reaction in which two or more of them are important, *e.g.*, the alkaline hydrolysis of the methyl esters in 80% v/v methanol–water (Part IV, to be published). This was accomplished by studying a reaction involving only polar effects, *i.e.*, esterification of the acids with diazodiphenylmethane[2] (in this case in toluene or in 2-n-butoxyethanol), and one involving only steric effects, *i.e.*, acid-catalysed esterification in methanol.[3] The present paper describes this work. The transition states of these reactions are described in the earlier papers.[1,2] (In connection with the determination of the factors controlling reactivity in alkaline ester hydrolysis, to be discussed in Part IV, results for acid-catalysed hydrolysis of esters in 80% v/v methanol–water are ideally desirable. The Taft analysis strictly requires the use of results obtained for the same solvent for alkaline and acidic hydrolysis. Unfortunately, acid-catalysed hydrolysis of hindered esters is prohibitively slow even at high temperatures. Acid-catalysed esterification may be used to evaluate Taft E_S values instead of ester hydrolysis, because the transition states are the same and the reactions are similarly insensitive to polar effects.[3] Any changes in E_S values as between 80% v/v methanol–water and methanol should not be very great, but they might in certain circumstances be significant.) The dissociation constants of the carboxylic acids were also measured to discover whether polar effects alone are of importance in the ionisation equilibria of the acids (Part IV).

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[1] Part II, Chapman, Shorter, and Utley, *J.*, 1963, 1291.

[2] Chapman, Shorter, and Utley, *J.*, 1962, 1824.

[3] Taft, " Steric Effects in Organic Chemistry," ed. Newman, John Wiley and Sons, Inc., New York, 1956 Ch. 13.

Taft and Smith,[4] and Hoefelmeyer and Hancock,[5] have studied the reaction in ethanol and in toluene, respectively, between substituted acetic acids and diazodiphenylmethane, the rate of disappearance of the latter being measured. Taft and Smith did not allow for possible variations in the extent of esterification in the solvent ethanol, in which a competitive acid-catalysed ether-formation also occurs. Roberts and Regan [6] state that the proportion of esterification changes significantly as between acetic acid (87% esterification) and benzoic acid (60% esterification). Roberts and his co-workers [7] also find that the reaction is not of integral order with respect to acid in benzene and similar solvents. Presumably this is because the degree of association of the acid varies with concentration. Hoefelmeyer and Hancock,[5] however, applied a rate expression to the reaction in toluene in which the order with respect to acid was assumed to be unity.

The acid-catalysed esterification of aliphatic and arylaliphatic carboxylic acids has been studied previously by Hinshelwood and Legard,[8] Smith and Burn,[9] and Newman and his co-workers.[10]

EXPERIMENTAL

Materials.—Arylaliphatic acids not available commercially were synthesised by one of the following methods: (*a*) alkylation of methyl diphenylacetate in ether, with sodium amide in liquid ammonia to generate the conjugate base, (*b*) alkylation of methyl fluorene-9-carboxylate with sodium methoxide in methanol similarly, or (*c*) metallation of the appropriate hydrocarbon with n-butyl-lithium, followed by carbonation with solid carbon dioxide.

The acids were recrystallised to constant m. p. (see Table 1), usually from benzene–light petroleum (b. p. 40—60°), benzene, or acetic acid. Each carboxylic acid was esterified with diazomethane in ether or tetrahydrofuran. The solution was kept at room temperature overnight and the solvent was evaporated. The residue was analysed by vapour-phase chromatography. The stationary phases used were 1% or 10% of polypropylene sebacate, or 10% of

TABLE 1.

Physical constants of acids.

Acid	M. p. (corr.)	M. p. in lit.	Ref.	Synthetic method (see text)
Acetic	16·5°	16·6°	*a*	*
Phenylacetic	76·5—77	76·7	*b*	*
Diphenylacetic	147·5—148	148·2—148·7	*c*	*
αα-Diphenylpropionic	170—172	172—174	*d*	(*a*)
αα-Diphenylbutyric	173	173—174	*e*	(*a*)
Triphenylacetic	264—266	265—266	*c*	(*c*)
Fluorene-9-carboxylic	226—228	228—230	*f*	(*c*)
9-Methylfluorene-9-carboxylic	169—170	170—171	*g*	(*b*)
9-*Ethylfluorene*-9-*carboxylic* †	154—156	—	—	(*b*)
9-*Isopropylfluorene*-9-*carboxylic* ‡	208·5—210	—	—	(*b*)
9-t-Butylfluorene-9-carboxylic	233—235	233—235	*g*	(*b*)
9-Phenylfluorene-9-carboxylic	189—190·5	189—190·5	*h*	(*c*)
9,10-Dihydroanthracene-9-carboxylic	202—204	201·5—203·5	*i*	(*c*)

* Commercially available. † Found: C, 80·7; H, 6·0. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%. ‡ Found: C, 81·1; H, 6·6. $C_{17}H_{16}O_2$ requires C, 80·9; H, 6·4%.

a, Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950. *b*, Smith, *J. Amer. Chem. Soc.*, 1939, **61**, 1176. *c*, Smith and Burn, *ibid.*, 1944, **66**, 1494. *d*, Bateman and Marvel, *ibid.*, 1927, **49**, 2914. *e*, Cope and McElvain, *ibid.*, 1932, **54**, 4319. *f*, Burtner and Cusic, *ibid.*, 1943, **65**, 262. *g*, Bavin, *Analyt. Chem.*, 1960, **32**, 554. *h*, Gilman, Meikle, and Morton, *J. Amer. Chem. Soc.*, 1952, **74**, 6282. *i*, May and Mosettig, *ibid.*, 1948, **70**, 1077.

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[4] Taft and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 305.

[5] Hoefelmeyer and Hancock, *J. Amer. Chem. Soc.*, 1955, **77**, 4746.

[6] Roberts and Regan, *J. Amer. Chem. Soc.*, 1952, **74**, 3695.

[7] (*a*) Roberts and Regan, *Analyt. Chem.*, 1952, **24**, 360; (*b*) Roberts, Watanabe, and McMahon, *J. Amer. Chem. Soc.*, 1951, **73**, 760.

[8] Hinshelwood and Legard, *J.*, 1935, 587.

[9] Smith and Burn, *J. Amer. Chem. Soc.*, 1944, **66**, 1494.

[10] Loening, Garrett, and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 3929.

Apiezon L on " Celite 100—120." Except with very volatile esters a column temperature of 200° was used. No significant impurity was found in any sample of the methyl esters and hence in the acids themselves, subsequently used for measurements. Neutralisation equivalents were determined for all acids and were well within 1% of the theoretical values in every case.

Diazodiphenylmethane was prepared by Smith and Howard's method,[11] and methanol was purified by Lund and Bjerrum's method [12] and had b. p. 64·5°/760 mm., d_4^{20} 0·7924 (lit.,[13] 64·5°, 0·7914). Commercial 2-n-butoxyethanol was dried over anhydrous potassium carbonate. It was then fractionally distilled (b. p. 170—171°/760 mm.; lit.,[14] 171·2°), and was stored in the dark. Toluene (commercial " pure " grade, sulphur-free) was dried with anhydrous magnesium sulphate and fractionally distilled from sodium wire; it had b. p. 109—110°/749 mm., d_4^{20} 0·8675 (lit.,[13] 110·1°, 0·8669). All solvents were stored under nitrogen. The purity of each solvent was determined by vapour-phase chromatography, in conditions similar to those employed in examining the esters. Only minor impurities ($<0·1\%$) were present and the water content was found to be less than 0·08% by Karl Fischer titration. The anhydrous toluene-*p*-sulphonic acid was of Microanalytical Reagent Grade (Hopkins and Williams Ltd.) and was dried in a vacuum-desiccator; it had m. p. 106—107° (lit.,[15] 106—107°).

Measurements.—Diazodiphenylmethane reaction. Rate coefficients for reactions in 2-butoxyethanol and in toluene of diazodiphenylmethane with the acids listed in Table 1 were measured as described [2] previously, by using a Unicam S.P. 500 spectrophotometer. In most cases a ten-fold excess of acid (0·0300M) was used and the reaction was studied as a first-order process. For the sparingly soluble fluorene-9-carboxylic and triphenylacetic acid reacting with diazodiphenylmethane in toluene, the reaction was studied as a second-order process. Diazodiphenylmethane reacts with 2-butoxyethanol in the presence of acid, as well as with the acid itself.[6,7] The ratio (R) of the amount of diazodiphenylmethane consumed in the reaction with each arylaliphatic acid to the total amount consumed was determined as described previously.[2] The true second-order rate coefficient (k) for the reaction of each acid with diazodiphenylmethane is given by $k = k_1{}^{a}/R[\text{Acid}] = k_2{}^{a}R$, where $k_1{}^{a}$ is the apparent first-order rate coefficient and $k_2{}^{a}$ is the second-order rate coefficient uncorrected for the competing reaction. For toluene $k = k_1{}^{a}/[\text{Acid}]$. The molar extinction coefficients at 525 mμ for diazophenylmethane in 2-butoxyethanol and in toluene were found to be 93·4 ± 0·4 and 103·1 ± 0·7 l. mole^{-1} cm.$^{-1}$, respectively. These values were required for determining R for 2-butoxy·ethanol, and for studying the second-order process in toluene.

Acid-catalysed esterification in methanol. The method was essentially that of Smith and Reichardt,[16] the acid catalyst being toluene-*p*-sulphonic acid (0·0200M). (Earlier workers used hydrogen chloride but its rate of reaction with methanol above 40° makes its use as a catalyst undesirable.) Solutions of toluene-*p*-sulphonic acid in methanol were found to be stable for long periods at 60°.

Under the conditions of temperature (60°) and initial concentration of arylaliphatic acid (0·0200M) the Goldschmidt equation [16] reduces to the simple first-order equation $k_1 = \ln\,[a/(a - x)]/t$ and $k = k_1/[\text{Catalyst}]$.

DISCUSSION

Esterification of Arylaliphatic Acids with Diazodiphenylmethane.—The rate coefficients for the reactions of diazodiphenylmethane with the acids are shown in Table 2. We have not yet measured the rate coefficients over a range of temperatures, but unpublished experiments by Mr. A. Buckley have shown that, for the closely related reactions of alkyl- and halogeno-benzoic acids with diazodiphenylmethane, the pattern of the results is unaltered when the temperature is varied over a range of 30°, and it is reasonable to assume that the present reactions will be similar in this respect. The effect of substitution upon

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[11] Smith and Howard, *Org. Synth.*, 1944, **24**, 53.

[12] Lund and Bjerrum, *Ber.*, 1931, **64**, 210.

[13] Weissberger, " Technique of Organic Chemistry," Vol. VII, Interscience Publ., Inc., New York, 2nd Edn., 1955.

[14] Beilstein's " Handbuch der Organischen Chemie," 4th Edn., 3rd Suppl., Springer-Verlag, Berlin, 1958, p. 2081.

[15] " The Merck Index of Chemicals and Drugs," Merck and Co., Rahway, N.J., 6th Edn., 1952.

[16] Smith and Reichardt, *J. Amer. Chem. Soc.*, 1941, **63**, 605.

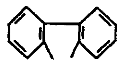
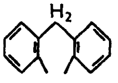
the rates of reaction is best discussed in terms of log k/k_0, where k and k_0 are the true second-order rate coefficients, and k_0 refers to acetic acid. Log k/k_0 is proportional to the change in free energy of activation, $\Delta\Delta G^\ddagger$, at the reaction temperature. The results are presented in this form also in Table 2, with σ^* values (in the footnote) calculated by Taft.[3] In 2-butoxyethanol the proportion of esterification to etherification was found to be approximately constant. Although the corrected rate coefficient has been considered to be of greater significance, there is the possibility that the rate-determining step may be the formation of a complex involving acid, solvent, and diazodiphenylmethane. This complex could then decompose in a fast step in either of two ways. The first way would give the ester, the second the ether. If this is so, the total rate coefficients should strictly be used in the discussion, but this would make no significant difference to the following conclusions.

The linear free-energy relation for this series of reactions in toluene (a) and in 2-butoxyethanol (b) as solvent is very good; the equation log $(k/k_0)_a = 2{\cdot}165$ log $(k/k_0)_b$ is closely obeyed except for the reaction of fluorene-9-carboxylic acid (7), which shows a small but significant deviation. The rates of reaction of this acid and of triphenylacetic acid (6) in toluene were determined at a low acid concentration (~0·003M), whereas the other results were obtained with a standard concentration (0·0300M). As the rate coefficients for reactions in toluene have been found to vary with initial concentration of acid, the rate coefficients for the reactions of these two acids (6 and 7) in toluene are not strictly comparable with those of the other acids. Changing the concentration will change the extent of association (mostly dimerisation) which has been shown to affect the order with respect to acid.[7] As such a good relationship is found between the results obtained with 2-butoxyethanol and with toluene as solvent with the acids at a standard concentration, we conclude that the variation in the extent of association for a series of acids at the standard concentration does not affect the relative rates of esterification. This may be because all the acids exist almost entirely as dimers at this concentration, so that variations with structure in the dimerisation constants of the acids are not important. Data compiled by Allen and Caldin [17] for dimerisation of carboxylic acids in benzene support this view. The results for the reactions of fluorene-9-carboxylic and of triphenylacetic acid in toluene are not used in the following discussion.

TABLE 2.

Esterification of arylaliphatic acids with diazodiphenylmethane.

	R in acid $R\cdot CO_2H$ ‡	k	log k/k_0	$k_2{}^a$	R (%)	k	log k/k_0
		In toluene † at 15°			In 2-butoxyethanol † at 25°		
1	Me	0·115	0·0	0·103	75·6	0·0779	0·0
2	$Ph\cdot CH_2$	0·449	+0·590	0·199	74·1	0·147	+0·275
3	Ph_2CH	1·54	+1·125	0·347	74·4	0·258	+0·520
4	Ph_2CMe	0·636	+0·745	0·233	73·5	0·171	+0·340
5	Ph_2CEt	0·447	+0·590	0·195	74·4	0·145	+0·270
6	Ph_3C	4·00	+1·540	0·551	73·3	0·404	+0·715
7	FlCH	2·19	+1·280	0·471	72·4	0·341	+0·640
8	FlCMe	0·857	+0·870	0·276	72·7	0·201	+0·410
9	FlCEt	0·588	+0·710	0·227	73·6	0·167	+0·330
10	$FlCPr^i$	0·399	+0·540	0·188	74·5	0·140	+0·255
11	$FlCBu^t$	0·307	+0·425	0·162	74·8	0·121	+0·190
12	FlCPh	4·80	+1·620	0·604	72·6	0·439	+0·750
13	AnCH	1·49	+1·110	0·339	73·8	0·250	+0·505

Fl =  (o-biphenylyl). An = .

The rate coefficients (l. mole^{-1} min.$^{-1}$) are accurate to ±2% or better. Values of log k/k_0 are given to ±0·005 unit.

‡ Values of σ^* (ref. 3): Me, 0·00; $Ph\cdot CH_2$, +0·215; Ph_2CH, +0·405 (acids 1,2, and 3, respectively).

† ρ^* for reaction in toluene at 15° is +2·77; in 2-butoxyethanol at 25°, +1·28.

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[17] Allen and Caldin, *Quart. Rev.*, 1953, **7**, 255.

As the reaction rates of carboxylic acids with diazodiphenylmethane appear to be almost entirely governed by polar effects,[2] the reaction may be interpreted in terms of the Taft " polar free energy " relation,[3] *viz.*, $\log k/k_0 = \rho^*\sigma^*$. A value of the reaction constant, ρ^*, for each solvent can be found by use of results for the three acids (1, 2, and 3) for which polar substituent constants are known from Taft's work. Ideally more values are desirable in obtaining ρ^*, but we are limited in this respect by the availability of independently determined σ^* values. This value of ρ^* can then be used to derive the σ^* values for the other acids in the series. This procedure is essentially a means of bringing the results for the two solvents on to the same scale; most of the ensuing discussion could be carried out, but less conveniently, in terms of $\log k/k_0$ values for the separate solvents. The mean values of σ^* (as between the two solvents) are shown in the first column of Table 3.

In discussing the σ^* values hyperconjugative effects may be neglected. The reaction mechanism [7b] does not involve a rate-determining step in which the unsaturation of the carbonyl-carbon atom changes. Thus hyperconjugative influences, if present, will be constant in the change from the initial to the transition state and will not affect the free energy of activation. The very close similarity of rates for $CD_3{\cdot}CO_2H$ and $CH_3{\cdot}CO_2H$ in this reaction, found by Roberts and Regan,[6] is in accord with the absence of hyperconjugative effects.

Polar substituent constants. All substituents used in this study accelerate the reaction relative to that of acetic acid and give rise to positive σ^* values, *i.e.*, they are electron-withdrawing relative to the methyl group. The effect of successive substitution and of substitution in relation to position is summarised in Table 4. In aliphatic systems the effect of an α- or a β-methyl substituent on the polar substituent constant, σ^*, is $\Delta\sigma^* =$ −0·100 or −0·020, respectively.[3] Considerably exalted values (disregarding sign) of $\Delta\sigma^*$, *viz.*, −0·155 and −0·065, are observed in this study. In this case the methyl groups are situated near powerfully electron-withdrawing aromatic groups, which evidently promote electron-release by methyl. The reduction factor for the polar effect of methyl

TABLE 3.

Polar substituent constants.

	R	σ^* (obs.)	σ^* (additive)	σ^* (compensated)
1	Me	0·0	—	—
2	$\mathrm{Ph{\cdot}CH_2}$	+0·215	—	—
3	$\mathrm{Ph_2CH}$	+0·405	+0·430	+0·400
4	$\mathrm{Ph_2CMe}$	+0·270	+0·330	+0·250
5	$\mathrm{Ph_2CEt}$	+0·210	+0·290	+0·190
6	$\mathrm{Ph_3C}$	+0·560	+0·645	+0·555
7	FlCH	+0·500	—	—
8	FlCMe	+0·320	+0·400	+0·340
9	FlCEt	+0·255	+0·360	+0·275
10	$\mathrm{FlCPr^i}$	+0·195	+0·320	+0·210
11	$\mathrm{FlCBu^t}$	+0·150	+0·280	+0·150
12	FlCPh	+0·585	+0·715	+0·645
13	AnCH	+0·400	—	—
	Mean deviation from observed values:		+0·092	±0·020

For key to Fl, An, see Table 2.

The values of σ^* (obs.) are accurate to about ±0·01 unit; individual values for the two solvents agree within ~0·005 unit.

TABLE 4.

Effect of substitution.

Change in structure	$\Delta\sigma^*$	Ratios	
First α-Ph substitution	+0·215	$\sigma^*\ (\mathrm{Ph_2CH})/\sigma^*\ (\mathrm{Ph{\cdot}CH_2})$	1·88
Second α-Ph substitution	+0·190	$\sigma^*\ (\mathrm{Ph_3C})/\sigma^*\ (\mathrm{Ph{\cdot}CH_2})$	2·60
Third α-Ph substitution	+0·155	$\Delta\sigma^*$ (β-Me)/$\Delta\sigma^*$ (α-Me)	~0·4
α-Me substitution	−0·155 †		
First β-Me substitution	−0·065 †		
Second β-Me substitution	−0·060		
Third β-Me substitution	−0·045		

† Mean value from interannular-linked and unlinked series.

transmitted through a methylene group obtained in this study (0·4) is similar to that usually observed for the transmission of polar effects; values in the range 0·3—0·5 have been suggested for various substituents in different systems.[18] However, the factor normally observed for methyl groups is much lower (about 0·20).[19] The decreasing effectiveness of successive introduction of α-phenyl groups is another example of the " saturation " effect observed by earlier workers.[20] (There are also slight indications of this effect with β-methyl groups.) Taft has recently stated[21] that the σ^* values for disubstituted groups (X_2CH) and trisubstituted groups (X_3C) are, respectively, about 1·7 and 2·2 times the σ^* value for a monosubstituted group (XCH_2), these factors being evaluated from the relevant σ^* values with halogen atoms only as X.

Ritchie[19] has suggested that, for multisubstitution, the Taft " polar free energy " relation should be applicable, in the forms:

$$\log k/k_0 = \rho^*[\sigma_1^* + \sigma_2^* + q(\sigma_1^*\sigma_2^*)] \text{ for } X^1X^2CH,$$

and $$\log k/k_0 = \rho^*[\sigma_1^* + \sigma_2^* + \sigma_3^* + q(\sigma_1^*\sigma_2^* + \sigma_2^*\sigma_3^* + \sigma_1^*\sigma_3^*)] \text{ for } X^1X^2X^3C,$$

where q is a factor expressing the importance of interaction terms relative to additive terms. The numerical magnitude of q, in contrast to the constant fractional " fall-off " for multisubstitution by a given substituent proposed by Taft, is dependent on the magnitude of the polar substituent constants involved.

This relation has been applied to the polar substituent constants obtained in this work. In Table 3 are shown the observed σ^* values and values calculated on a simple additive basis, by using the following $\Delta\sigma^*$ values: α-Ph, +0·215; α-Me, −0·100; β-Me, −0·04; *o*-biphenylyl, +0·500. (For α-Me, −0·100 is used, because this is the value generally observed in aliphatic systems;[3] for β-Me, −0·04 is used to give a reduction factor of 0·4 for the polar effect of methyl transmitted through methylene, as for polar substituents in general.[18]) Values of σ^* have then been calculated by employing relations of the above type, with values of q of −0·65 and +1·20, respectively, for the interaction of two electron-withdrawing substituents one with another, and of an electron-releasing with an electron-withdrawing substituent. Whereas values of σ^* (additive) show poor agreement with those of σ^* (observed), the compensated values agree well with those observed.

Interannular links. The polar effects of the two interannular links are as follows: for a simple interannular link (fluorene), $\Delta\sigma^* = +0{\cdot}095$; for a methylene interannular link (dihydroanthracene), $\Delta\sigma^* = -0{\cdot}005$. A simple interannular link between two phenyl groups thus increases the ability of the substituent system to accommodate electrons. This is consistent with the ability of fluorene, as a cyclopentadiene derivative, readily to form a carbanion. In the 9,10-dihydroanthracene system the very slight electron-release due to the methylene link can be ascribed to the polar character of the methylene group itself. This effect would be similar to that shown in the weakening of phenylacetic acid by an *o*-methyl group.[22]

Acid-catalysed Esterification of Arylaliphatic Acids in Methanol.—Earlier workers,[8,9] have studied extensively the acid-catalysed esterification of aliphatic and arylaliphatic acids in methanol with hydrogen chloride as the catalyst. Extrapolated rate coefficients (l. mole^{-1} min.$^{-1}$) for esterification at 60° can be calculated from data in the literature for three of the acids studied in the present work; *viz.*, acetic acid 20·9, 21·8, (22·0); phenylacetic acid 9·10, (9·43); and diphenylacetic acid 0·794, 0·816, (0·825). The first value in each case is due to Smith and Burn,[9] the second (not in parentheses) to Hinshelwood and

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[18] McGowan, *J. Appl. Chem.*, 1960, **10**, 312.

[19] Ritchie, *J. Phys. Chem.*, 1961, **65**, 2091.

[20] Branch and Calvin, " The Theory of Organic Chemistry," Prentice-Hall, New York, 1941, Ch. VI.

[21] Taft, quoted by Ritchie, ref. 19.

[22] Kortüm, Vogel, and Andrussow (I.U.P.A.C.), " Dissociation Constants of Organic Acids in Aqueous Solution," Butterworths, London, 1961.

TABLE 5.

Acid-catalysed esterification in methanol at 60·0°.

	R in acid $R{\cdot}CO_2H$	k	E_s	Recorded E_s †
1	Me	22·1	0·0	0·0
2	$Ph{\cdot}CH_2$	9·43	−0·37	−0·38 (−0·36, −0·25, −0·51)
3	Ph_2CH	0·825	−1·43	−1·76 (−1·51, −1·82, −2·96)
4	Ph_2CMe	0·00627	−3·55	—
5	Ph_2CEt	0·00101	−4·34	—
6	Ph_3C ...	0·000459	−4·68	—
7	FlCH ...	1·77	−1·10	—
8	FlCMe ...	0·412	−1·73	
9	FlCEt ...	0·236	−1·97	
10	$FlCPr^i$ ...	0·0110	−3·30	
11	$FlCBu^t$ ...	0·00168	−4·12	
12	FlCPh ...	0·0183	−3·08	
13	AnCH ...	1·13	−1·29	

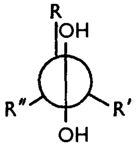
For key to Fl, An, see Table 2.
Values of k (l. mole^{-1} min.$^{-1}$) are accurate to ±2% or better.
Values of E_s are accurate to ±0·02 unit.

† Value given by Taft,[3] 25°; those in parentheses calculated from results in refs. 9 (esterification in methanol at 25°), Sudborough and Lloyd, *J.*, 1899, 467 (esterification in ethanol at 15°), and Smith and Myers, *J. Amer. Chem. Soc.*, 1942, **64**, 2362 (hydrolysis of ethyl esters in 70% aqueous acetone at 25°).

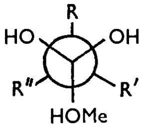
Legard;[8] and the figures in parentheses are those obtained in the present study with toluene-*p*-sulphonic acid as catalyst. Smith and Burn[9] attempted to measure the rate coefficient for triphenylacetic acid, but found no significant reaction at 60°. The rate coefficients for the acid-catalysed esterification of the acids in methanol are shown in Table 5. From scanty data in the literature it seems likely that the pattern of the rate coefficients will be unaltered by a limited change in the temperature of the reactions. This point, however, is to be investigated.

Effect of substitution. The effect of substitution is best discussed in terms of the Taft steric substituent constant, E_s.[3] This parameter is proportional to the relative free energy of activation, $\Delta\Delta G^{\ddagger}$, at the reaction temperature, thus: $\log (k/k_0)_A = E_s$. Polar effects are considered to be almost entirely absent in this reaction, but a resonance effect is to be considered in the esterification of benzoic acids.[3] The formation of the transition state involves a loss of resonance stabilisation, for the initial state is unsaturated whereas the transition state is saturated. Hancock and his co-workers[23] have similarly postulated an α-hydrogen or hyperconjugative resonance effect in aliphatic systems. The formation of the transition state will destroy this type of resonance. Hancock has suggested that a "true" steric substituent constant, $E_s{}^c$, can be found by using the equation: $E_s{}^c = E_s + h(n - 3)$, where h is calculated as 0·283 for 60° and n is the number of α-hydrogen atoms. These considerations do not affect the following discussion of E_s. The hyperconjugative contribution serves only to reinforce the steric effects accompanying α-hydrogen replacement.

The results are shown in the form of E_s values in Table 5, together with Taft's E_s values for the first three substituents. E_s values for these substituents can also be calculated directly from results in the literature for the esterification of the acids in methanol or in ethanol, and for the acid-catalysed hydrolysis of the ethyl esters in 70% aqueous acetone; these values are shown in parentheses. The observed solvent- and reaction-dependence of E_s values makes any averaging undesirable as it is liable to obscure important relations.



(I)



(II)

For the esterification of the acid $RR'R''C{\cdot}CO_2H$ the initial and the transition state may be formulated approximately as (I) and (II), respectively, by use of Newman's projection

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[23] Hancock, Meyers, and Yager, *J. Amer. Chem. Soc.*, 1961, **83**, 4211.

formulæ; the structures (I) and (II) carry positive charge but this is omitted from the diagrams for simplicity.

The observed steric retardation can be seen as the result of a combination of two effects. The steric strain effect increases the relative energy of activation owing to repulsive interactions between the substituent and the reaction centre, and an increase in the internal repulsive interactions. Further the entropy of activation will be decreased by a decrease in the number of stable, low-energy conformations available in the transition state relative to the initial state. The relative importance of these effects cannot be assessed until Arrhenius parameters for acid-catalysed esterification of these acids have been determined. For the present, however, the E_s values may be profitably discussed in very simple terms.

If it can be assumed that the degree of steric interaction or crowding present in the initial state gives an indication of the increase in these interactions in forming the transition state, the E_s values can be discussed by reference to scale models of the acids. The E_s values can then be easily understood in terms of hindrance of the approach of methanol to the protonated carboxylic acid.

The observed values differ widely from those expected on an additive basis and this accords with a similar observation by Taft.[3] The increase in E_s caused by further substitution is dependent both on the bulk of the substituent and on the bulk of the substituent groups already present. The large increase observed for the third substituent in the groups without an interannular link (acids 4, 5, and 6) can be understood as a " buttressing " effect on the two phenyl groups. This effect causes the phenyl groups to twist to relieve the interaction due to crowding and results in an increase in the effective bulk, in addition to the increase due to the third substituent itself.

Only a small increment in the E_s value is observed when the first β-methyl group is introduced into the fluorene acid (9), relative to the previous acid (8). This may be attributed to the existence of a preferred conformation of the group for minimum interaction. Models of these acids show that the β-methyl group can be accommodated in a position distant from the reaction site and below the plane of the fluorene ring. Models of the isopropyl- and t-butyl-substituted fluorene acids (10 and 11) show clearly that no such preferred conformations exist. The increase in bulk gives rise to the large increment in E_s observed on introducing the second and the third β-methyl group (acids 10 and 11).

The marked similarity and the order of the E_s values of the substituents with acids 3, 7, and 13 can be attributed to their similar size and to the extent to which interannular linking reduces the steric interaction. The coplanarity of the phenyl rings in fluorene and their near-coplanarity in dihydroanthracene[24] reduces the " steric size " of the substituent. If the observed effect is due only to coplanarity, the E_s values for acids 7 and 13 should be the same. The less negative value of E_s observed for the fluorene acid, 7, must be due to a reduction in the forward projection of the parts of the aromatic nuclei in the vicinity of the reaction centre.

TABLE 6.

Subst. (X)	$E_s(X{\cdot}CH_2)$ †	$E_s(X_2CH)/E_s(X{\cdot}CH_2)$ †	$E_s(X_3C)/E_s(X{\cdot}CH_2)$ †
Me	−0·07	6·7	22·0
Et	−0·36	5·5	10·6
Ph	−0·37	4·0	12·6
F	−0·24	2·8	4·8
Cl	−0·24	6·4	8·6
Br	−0·27	6·9	9·0

† Ref. 3 or present study.

Some of the observations are not adequately explained by discussion in the above simple terms but require detailed consideration of the transition state. Thus in Table 6

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[24] Iball and Young, *Acta Cryst.*, 1958, **11**, 476.

are shown the ways in which the build-up of the total steric effect occurs for different types of substituent. The van der Waals radii of the substituents methyl and bromine, for example, are about the same.[3] The reason for the large difference in the increments for successive substitution probably lies in the type of interactions caused when the transition state is formed. Substitution by "symmetrical-top" halogen atoms should be very effective in making the entropy of activation more negative because of steric hindrance to the internal motions. This should tend to a limit and the steric effect will then not have a major contribution from an increase in steric strain. The influence of alkyl and aryl groups may follow a different pattern. Steric hindrance to internal motions should be small for limited α-substitution because of the possibility of low-energy conformations even in the transition state. However, for crowded substitution of this type, an intense rise in the steric strain effect will result from the greatly increased internal interactions in the groups. Determination of Arrhenius parameters should test these ideas.

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UNIVERSITY OF HULL.

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