241. *The Separation of Polar and Steric Effects. Part II.*[1] *The Basic and the Acidic Hydrolysis of Substituted Methyl Benzoates.*

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Rate coefficients at several temperatures for the basic hydrolysis of a series of ring-substituted methyl benzoates (mainly *o*-alkyl, with alkyl = Me, Et, Pr^i, or Bu^t; and *o*-halogeno-derivatives) in 80% v/v methanol–water and in 60% dioxan–water (for the *o*-alkyl derivatives) have been determined. Arrhenius parameters and the related magnitudes of transition-state theory have been evaluated. Rate coefficients for the acidic hydrolysis at 100° in 80% v/v methanol–water of most of the compounds and of a few in 60% v/v dioxan–water have also been measured. Values of Taft's parameters σ^* and E_s have been calculated for the halogens and for methyl and ethyl.

The influence of *ortho*-substituents on the entropies of activation for basic hydrolysis is discussed in terms of the interplay between two opposed steric effects: a " bulk effect " and " steric inhibition of solvation "; and, in the case of *o*-halogen, increase of solvation in the transition state, due to polar influences. The same factors influence the heats of activation, together with polar and secondary steric effects. For acidic hydrolysis it appears that the Hammett ρ-value may reasonably be taken as zero.

The values of the parameters σ^* and σ_p imply that for the halogens polar effects are equivalent from *ortho*- and *para*-positions, but this conclusion is strongly at variance with that reached on the basis of the work described in Part I.[1] The assumptions made in deriving the Taft–Ingold equations are therefore re-examined, and it is concluded that the effect of solvation of the transition state in relation to the initial state invalidates the assertion that steric effects in acidic and basic hydrolysis are equivalent. Other experimental evidence is adduced in favour of this view.

The first paper[1] in this series dealt with the separation of polar and steric effects in the reactions of substituted benzoic acids with diazodiphenylmethane. The present paper records a study of the acidic and the basic hydrolysis of ring-substituted methyl benzoates, the object being a separation of polar and steric effects by the Taft–Ingold analysis.[2] The results of the two investigations may then be compared and the assumptions made in the derivation of the Taft–Ingold equation may be tested. At present, only scanty kinetic data relating to both basic and acidic hydrolysis of benzoates in the same solvent are available. Results of this kind are necessary for a strict application of the Taft–Ingold equation. In addition, the kinetics of hydrolysis of *ortho*-alkylbenzoates, except *o*-toluates, have not been studied previously.

EXPERIMENTAL

Substituted Methyl Benzoates.—Substituted benzoic acids, prepared as described in Part I,[1] were esterified with diazomethane.

Purity. The methyl esters, with the exception of methyl *m*-nitrobenzoate, were analysed by vapour-phase chromatography. With one exception a stationary phase of 10% Apiezon L on Celite 100—120 was used, with a column temperature of 150°. Methyl *o*-t-butylbenzoate was analysed on a stationary phase of 1% of propylene sebacate on Celite 100—120 at 100°.

No impurities were detected except for methyl *o*-isopropylbenzoate which contained one (2·6%) of a lower b. p. than the main product and a second (3·4%) of a higher b. p. The equivalent weight of the parent acid, determined by titration, was 164·3 (calc. 164·20); this, together with a consideration of the method of preparation, is strong evidence that the impurities are the isomeric *m*- and *p*-isopropylbenzoic acid.

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[1] Part I, *J.*, 1962, 1824.

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

It was also thought desirable to confirm that the major product was in fact the *ortho*-isomer. The following evidence was obtained. (*a*) The ester is resistant to side-chain oxidation by chromic oxide in acetic acid or by alkaline potassium permanganate. (*b*) The ester showed no olefinic unsaturation (no reaction with bromine in carbon tetrachloride). (It was necessary to show that the compound was fully saturated as " *o*-isopropylbenzoic acid " prepared by Elsner, Strauss, and Forbes's method [3] contained an unsaturated compound, probably *o*-isopropenylbenzoic acid.) (*c*) The infrared spectrum of the ester showed peaks at 1387, 1365, and 802 cm.$^{-1}$, characteristic of an *o*-isopropyl group, and at 763 cm.$^{-1}$, characteristic of *ortho*-disubstituted benzene derivatives. If the impurities are the *meta*- and *para*-isomers the stoicheiometry of basic and acidic hydrolysis will not be affected. As the *ortho*-substituted ester is not very reactive compared with the *meta*- or *para*-isomer it is possible to eliminate the effect of these impurities from the reaction by delaying measurement of the initial ester and base or acid concentrations. The consistent kinetics observed when using this technique justify this assumption.

Dioxan was purified as described by Cavell, Chapman, and Johnson [4] and had b. p. 101·5°/760 mm., m. p. 11·8°, n_D^{22} 1·4212.

Commercial methanol was purified by treatment with aqueous silver nitrate and sodium hydroxide, followed by filtration through Celite and fractional distillation from silver nitrate under nitrogen. The pure methanol was stored under nitrogen and over anhydrous calcium sulphate for 24 hr. before use.

Kinetic Procedure.—Solutions. 60% v/v Dioxan–water, 80% v/v methanol–water, and solutions of sodium hydroxide in both systems were prepared by weighing the appropriate amount of organic component, adding a suitable volume of N-sodium hydroxide (carbonate-free) for the base solutions, and making up to 1 l. with boiled-out distilled water. For the acidic hydrolysis, solutions of hydrochloric acid in 60% v/v dioxan–water, and of benzenesulphonic acid in 80% v/v methanol–water were prepared analogously.

Measurement of Rate Coefficients.—Basic hydrolysis. Modifications of Evans, Gordon, and Watson's method [5] with equal concentrations of ester and base were employed. Stainless-steel reaction vessels were used for the basic hydrolysis at elevated temperatures of methyl *o*-t-butylbenzoate in both solvent systems. Polythene reaction vessels were used when measuring basic hydrolysis of methyl *o*-isopropylbenzoate in 60% v/v dioxan–water. All hydrolyses were carried out under nitrogen.

The equation used to calculate the rate coefficient k (l. mole^{-1} min.$^{-1}$) was the second-order expression with the reactants present in equal concentrations, *i.e.*, $k = x/at(a - x)$, where t is the time in minutes, a the initial concentration, and x the concentration of the reactants (mole l.$^{-1}$) at time t. Rate coefficients were corrected for solvent expansion at high temperatures.

There is evidence that the position of equilibrium in the system [6]

$$\mathrm{OH^- + EtOH \rightleftharpoons EtO^- + H_2O} \quad \text{(i)}$$

lies significantly to the right even in moderately aqueous solutions. It is important therefore to consider the implications of the equilibrium

$$\mathrm{OMe^- + H_2O \rightleftharpoons OH^- + MeOH} \quad \text{(ii)}$$

for the kinetic experiments carried out in 80% v/v methanol–water.

The second-order rate coefficient as ordinarily evaluated is an apparent rate coefficient k_a. It can be shown that this is related to the true rate-coefficient k_t for the reaction between OH$^-$ and ester by the expression $k_a = k_t\alpha$, where $\alpha = K/(1 + K)$, and K is the equilibrium constant $[\mathrm{OH^-}]/[\mathrm{OMe^-}]$ for reactions (ii). This means that comparison of the apparent rate coefficients for the hydrolysis of a series of esters in aqueous methanol is meaningful and that valid conclusions may be drawn, since k_a is proportional to k_t at constant temperature.

A relation between the apparent energy of activation, E_a, and the true energy of activation, E_t, can also be derived, namely, $E_t = E_a - \Delta H\ (1 - \alpha)$, where ΔH is the heat change of the forward reaction in the reversible reaction (ii) above. It is also possible to derive a similar

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[3] Elsner, Strauss, and Forbes, *J.*, 1957, 578.

[4] Cavell, Chapman, and Johnson, *J.*, 1960, 1413.

[5] Evans, Gordon, and Watson, *J.*, 1937, 1413.

[6] Caldin and Trickett, *Trans. Faraday Soc.*, 1953, **49**, 772.

expression relating the observed log A values of the Arrhenius equation with true values, and it is found that

$$\ln A_t = \ln A_a - [\ln \alpha + \Delta H(1 - \alpha)/\boldsymbol{R}T].$$

It is expected that the value of ΔH will be small and nearly independent of temperature, as for other acid–base equilibria in which the number of charges is unaltered by reaction, so that the variation of α with temperature will be small. The observed energy of activation is thus seen to differ from the true value by a term that will be constant over the temperature range involved in the experimental determinations. As we do not know the temperature-dependence of K in these systems it is not possible to correct E_a to give E_t. It has been assumed therefore that, although the rate coefficients and Arrhenius parameters determined in aqueous methanol are not absolute values, they are suitable for comparison with each other.

Acidic hydrolysis. In aqueous dioxan the measurements were straightforward and the method used was that of Hinshelwood and Timm [7] in which the catalyst (hydrochloric acid) and ester are in equal initial concentration (~0·0500N). The reaction was followed by titration of samples (from sealed bulbs) with standard sodium hydroxide. The reaction obeys the first-order expression,

$$kt = (2{\cdot}303/[H^+]) \log a/(a - x),$$

where a is the initial ester concentration and x is the amount of ester consumed at time t. From the slope of a plot of t against log $(a - x)$, k was calculated in l. mole^{-1} min.$^{-1}$ units.

In aqueous methanol two serious problems are encountered: reversibility of the reaction and the instability of the solvent system at high temperatures. The sealed-bulb technique was again used, and the rate coefficients for the forward and the backward reaction were separated by Guggenheim's [8] method.

The catalyst used in aqueous methanol was benzenesulphonic acid and at 100° it undergoes the following reactions:

$$\mathrm{Ph{\cdot}SO_3H + MeOH \xrightleftharpoons{H^+} Ph{\cdot}SO_3Me + H_2O}$$
$$\mathrm{Ph{\cdot}SO_3Me + MeOH \longrightarrow Ph{\cdot}SO_3H + Me_2O}$$

This side reaction limited the duration of kinetic runs that could be followed and thus it was possible to measure the rates of acid-catalysed hydrolysis of methyl *o*-isopropylbenzoate and methyl *o*-t-butylbenzoate.

TABLE 1.

Summary of rate coefficients (l. mole^{-1} min.$^{-1}$) for the basic hydrolysis of substituted methyl benzoates.

Subst.	Rate coefficient (temperature in parentheses)			
	In 80% v/v *methanol–water*			
H	0·0833 (34·8°)	0·226 (44·8°)	0·325 (49·8°)	0·546 (55·2°)
o-Me	0·0122 (35·0°)	0·0340 (45·0°)	0·0835 (55·0°)	0·328 (70·2°)
o-Et	0·0161 (45·0°)	0·0410 (55·0°)	0·172 (70·2°)	0·436 (80·4°)
o-Pr^{i}	0·154 (71·6°)	0·255 (78·4°)	0·595 (89·9°)	1·320 (100·2°)
o-Bu^{t}	0·0190 (119·8°)	0·0415 (129·8°)	0·0614 (134·0°)	0·905 (140·0°)
o-F	0·0573 (15·4°)	0·160 (25·5°)	0·397 (35·0°)	0·977 (44·8°)
o-Cl	0·169 (35·0°)	0·402 (44·8°)	0·573 (50·0°)	0·917 (55·2°)
o-Br	0·120 (34·9°)	0·281 (45·0°)	0·441 (50·0°)	0·668 (55·2°)
o-I	0·0832 (34·8°)	0·197 (44·8°)	0·276 (49·0°)	0·469 (54·9°)
m-NO$_2$	0·158 (4·6°)	0·505 (15·0°)	1·34 (25·0°)	3·24 (34·5°)
m-Cl	0·0781 (15·0°)	0·230 (25·4°)	0·553 (34·5°)	1·41 (45·2°)
m-Me	0·0439 (30·1°)	0·120 (40·7°)	0·292 (50·0°)	0·665 (59·8°)
	In 60% v/v *dioxan–water*			
H	0·209 (10·0°)	0·707 (25·0°)	1·49 (35·0°)	
o-Me	0·0876 (25·0°)	0·285 (40·2°)	0·584 (50·4°)	
o-Et	0·0496 (30·0°)	0·113 (40·0°)	0·234 (50·0°)	
o-Pr^{i}	0·0825 (40·9°)	0·168 (49·2°)	0·306 (60·0°)	0·613 (69·9°)
o-Bu^{t}	0·047 (114·6°)	0·111 (124·1°)	0·187 (133·7°)	0·383 (144·3°)

Individual rate coefficients are usually accurate to ±2%.

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[7] Hinshelwood and Timm, *J.*, 1938, 862.

[8] Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

All experiments on acidic hydrolysis were carried out under nitrogen. Rate coefficients were corrected for solvent expansion at high temperatures.

Results.—Results are summarised in Tables 1 and 2.

TABLE 2.

Summary of rate coefficients (l. mole^{-1} min.$^{-1}$) for the acidic hydrolysis of substituted methyl benzoates.

In 80% v/v *methanol-water at* 100·8°

Subst.	H	*o*-Me	*o*-Et	*o*-F	*o*-Cl	*o*-Br	*o*-I	*m*-Me	*m*-Cl	*m*-NO_2
10^3k_2	11·3	2·21	1·23	11·1	3·67	2·87	1·66	8·36	9·18	7·75

In 60% v/v *dioxan-water at* 100°

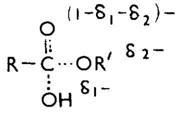
Subst.	H	*o*-Me	*o*-Et
10^3k_2	9·03	2·55	1·16

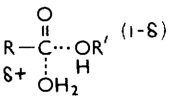
Individual rate coefficients are usually accurate to ±5%.

DISCUSSION

The Transition States in Ester Hydrolysis.—It is generally accepted that basic hydrolysis of esters proceeds through an intermediate complex [R·CO(OH)·OR′]$^-$ of some stability.[9] The overall rate coefficient, k, is a composite quantity, but it is probable that the effect of the structure of R on it reflects mainly that on the rate coefficient, k_1, for the formation of the intermediate complex from the reactants. In discussing the effect of structure on k we shall therefore assume that the transition state to be considered is that for the formation of the intermediate complex, which we may represent as (I).

(I)





(II)

Acidic hydrolysis proceeds through the formation of an intermediate complex [R·CO(H_2O)·OHR′]$^+$ produced by attack of a water molecule on the protonated form of the ester.* The overall rate coefficient, k, is again a composite quantity, involving in particular the equilibrium constant K for the protonation of the ester, and the rate coefficient, k_1', for the formation of the complex from protonated ester and water, as the terms sensitive to changes in the structure of R. Polar effects on these almost cancel (see p. 1297). The influence of primary steric effects on k reflects that on k_1', the protonation not being subject to steric influences. Hence the transition state to be considered in discussing the influence of primary steric effects on k is that for the formation of the intermediate complex, which we may represent as (II).

Substituent Effects on $\Delta S^‡$ *in Basic Hydrolysis* (Table 3).—The results of the present work are in accord with those of earlier workers for *o*-halogen substituents,[10] $\Delta S^‡$ being decreased substantially for all except fluorine. $\Delta S^‡$ is not lowered to a similar extent by *o*-alkyl substituents except for the isopropyl group. The t-butyl substituent apparently causes a significant increase in $\Delta S^‡$ for the reaction in aqueous dioxan.

* Aksnes and Prue (*J.*, 1959, 103) suggest, on the basis of experiments with esters containing a quaternary ammonium pole, that in acid-catalysed hydrolysis the carbonyl-oxygen atom is protonated. The general validity of this view is not yet certain but, in any case, the point is not of great importance for the present discussion.

[9] Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626; Bender and Thomas, *ibid.*, 1961, **83**, 4189.

[10] Ref. 5; also Tommila and Hinshelwood, *J.*, 1938, 1801; Tommila, *Ann. Acad. Sci. Fennicae*, 1941, *A*57, No. 3; *A*59, Nos. 3, 4, 5, 9, and 10.

ortho-Substituents in this system may cause a competition between two effects: the "bulk effect" and "steric inhibition of solvation." Bulky substituents near the reaction centre will reduce the number of energy levels available to the transition state relative to those in the initial state and will make $\Delta S^\ddagger$ more negative;[11] this is the bulk effect. A bulky substituent may also hinder the orientation of solvent molecules round the reaction site in the transition state more than in the initial state and thus make $\Delta S^\ddagger$ more positive; this is steric inhibition of solvation.

"Solvent sorting"[12] must also be considered when discussing solvation in binary solvent systems. Solvation is essentially an electrostatic phenomenon and in a binary solvent system the more dipolar (or polarisable) component will predominate at the solvated site. For both methanol–water and dioxan–water, it is reasonable to assume that most of the solvation will be by water molecules. It follows that as the water content of the solvent increases so will the degree of solvation of the transition state relative to the initial state. In accordance with this the values for $\Delta S^\ddagger$ (Table 3) for the reaction in 60% dioxan–water are more negative than those in 80% methanol–water; also the values of $\Delta H^\ddagger$ are lower in the former medium.

TABLE 3.

Basic hydrolysis of substituted methyl benzoates.

Subst.	E (kcal. mole^{-1})	$\Delta H^\ddagger$ (kcal. mole^{-1})	log A (A in sec.)	$\Delta S^\ddagger$ (cal. mole^{-1} deg.$^{-1}$)
	In 80% v/v *methanol–water*			
H	18·4	17·8	10·2	−13·6
o-Me ...	19·5	18·8	10·1	−14·0
o-Et ...	20·8	20·2	10·7	−11·5
o-Pr^i ...	19·4	18·8	9·7	−16·4
o-Bu^t ...	24·8	24·1	10·3	−13·6
o-F	17·6	17·0	10·3	−13·4
o-Cl ...	16·6	16·0	9·2	−18·4
o-Br ...	17·1	16·5	9·4	−17·4
o-I	17·1	16·5	9·3	−18·1
m-NO_2	17·2	16·5	10·9	−10·6
m-Cl ...	17·5	16·9	10·4	−13·2
m-CH_3	18·4	17·8	10·1	−14·4

Subst.	E (kcal. mole^{-1})	$\Delta H^\ddagger$ (kcal. mole^{-1})	log A (A in sec.)	$\Delta S^\ddagger$ (cal. mole^{-1} deg.$^{-1}$)
	In 60% v/v *dioxan–water*			
H	13·6	12·9	8·0	−23·9
o-Me ...	14·3	13·7	7·7	−25·5
o-Et ...	15·2	14·6	7·9	−24·5
o-Pr^i ...	14·5	13·9	7·2	−27·4
o-Bu^t ...	22·2	21·6	9·4	−16·9
2,6-Me_2 *	21·8	—	9·2	—

* Goering, Rubin, and Newman, *J. Amer. Chem. Soc.*, 1954, **76**, 787. Values of E and $\Delta H^\ddagger$ are accurate to ±300 cal., of log A to ±0·2 unit, and of $\Delta S^\ddagger$ to 1·0 e.u.

Steric inhibition of solvation will increase as the series Me to Bu^t is traversed, and this increase will make $\Delta S^\ddagger$ more positive. In opposition is the bulk effect, which also increases as the series is traversed. It seems evident that in 80% v/v methanol–water the effects are finely balanced at the extremes of the series. In the middle, steric inhibition of solvation predominates for the ethyl substituent and the bulk effect is more important when the size of the substituent is increased to that of isopropyl. Solvation (mainly by water) is probably greater in 60% aqueous dioxan than in 80% aqueous methanol, thus increasing the effective radius of the solvation shell of the alkoxycarbonyl group. This must enhance both the bulk effect and the effect of steric inhibition of solvation and it appears that the former is predominant for methyl, ethyl, and isopropyl, but that with the very bulky t-butyl and 2,6-dimethyl substituents[13] inhibition of solvation is very marked and a sharp increase in $\Delta S^\ddagger$ is observed.

To explain the results obtained with *o*-halogen substituents a further factor must be postulated. It is suggested that the carbon–halogen dipole facilitates solvation of the reaction site by virtue of the negative end of the dipole, augmenting the negative field of the reaction centre in the transition state. The increase in solvation will increase the effective

[11] Ivanoff and Magat, *J. Chim. phys.*, 1950, **47**, 914.

[12] Hyne, *J. Amer. Chem. Soc.*, 1960, **82**, 5129.

[13] Goering, Rubin, and Newman, *J. Amer. Chem. Soc.*, 1954, **76**, 787.

radius of the reaction site, and this will alter the bulk effect on $\Delta S^\ddagger$. The bulk effect produced by the halogens will thus be greater than that produced by alkyl groups of the same size. This will act to make $\Delta S^\ddagger$ more negative. The experimental findings are in accordance with this: in aqueous methanol *o*-halogen substituents, except fluorine, decrease $\Delta S^\ddagger$. The behaviour of fluorine is presumably due to its small bulk. The electron-repelling *o*-alkyl substituents might be supposed to inhibit solvation of the reaction site, since the positive ends of dipoles will be disposed towards the reaction site. Such an effect should be much smaller than that caused by the halogens. While it may be real (see below) it need not be introduced to explain the influence of *o*-alkyl groups on $\Delta S^\ddagger$.

The difference between the effects in the two series of substituents may be summarised by comparing the effects of methyl and bromine. These two substituents have approximately the same bulk; methyl is weakly electron-repelling but bromine is quite strongly electron-attracting. In 80% v/v methanol–water, methyl has no effect on $\Delta S^\ddagger$, but bromine depresses $\Delta S^\ddagger$ by 3·76 e.u.

Substituent Effects on $\Delta H^\ddagger$ (Table 3).—In basic hydrolysis of esters, electron-withdrawing substituents decrease $\Delta H^\ddagger$, and electron-repelling substituents increase $\Delta H^\ddagger$. There are also primary steric effects on $\Delta H^\ddagger$. An increment in $\Delta H^\ddagger$ will result from any additional compression energy between the reaction centre, the hydroxyl ion, and the *ortho*-substituent that arises in passing from the initial to the ransition state. Steric inhibition of solvation is another factor that will tend to raise $\Delta H^\ddagger$, for solvation stabilises the transition state and, therefore, an effect inhibiting solvation will increase the enthalpy term. Polar facilitation of solvation would decrease $\Delta H^\ddagger$.

A secondary steric effect must also be considered. A bulky substituent near the reaction centre will inhibit conjugation between the carboxyl group and the benzene ring and thus reduce the electron density at the carbonyl-carbon atom. Such conjugation is less important in the transition state than in the initial state. This will decrease $\Delta H^\ddagger$.

The results of the present investigation relating to changes in $\Delta H^\ddagger$ may be explained in terms of the effects described above. All electron-withdrawing substituents lower $\Delta H^\ddagger$ and all electron-repelling substituents increase $\Delta H^\ddagger$, as predicted. The primary steric effect on $\Delta H^\ddagger$ is also observed and is demonstrated by the results for *o*-alkyl compounds. In this case both the polar and the primary steric effects will act to increase $\Delta H^\ddagger$ but, whereas there is only a small change in polarity in the series methyl to t-butyl, the bulk of these groups increases sharply as the series is traversed. The increase in $\Delta\Delta H^\ddagger$ from 1·0 to 6·3 kcal./mole in aqueous methanol, and from 0·8 to 8·7 kcal./mole in aqueous dioxan, is much greater than would be expected on polar grounds alone. This sharp increase must be a reflection of the differences in bulk between methyl and t-butyl. This point is emphasised when 2,6-dimethyl substitution is considered. The polar effect of two *o*-methyl substituents should not exceed twice that of a single *ortho*-group. An increase in $\Delta H^\ddagger$ of over ten times that produced by monosubstitution is actually observed and seems best explained in terms of the great increase in primary steric interaction resulting from the introduction of a second *ortho*-substituent.

The effect of *o*-isopropyl substitution is, however, anomalous, and it is difficult to explain the small increase in $\Delta H^\ddagger$ satisfactorily. Models of methyl *o*-alkylbenzoates show that without solvation little interaction between the carboxylate function and the substituent is observed, except with the isopropyl and t-butyl groups. This suggests that the secondary steric effect may not become important until isopropyl is reached. If this is so, then *o*-isopropyl substitution initiates the competition of three factors: the polar and primary steric effects tending to increase $\Delta H^\ddagger$, and the secondary steric effect which decreases $\Delta H^\ddagger$. The observed increase in $\Delta H^\ddagger$ should therefore be less than expected from considering polar and primary steric effects alone. This is a tentative explanation put forward in the absence of a more satisfactory one.

The overall effect of *o*-halogen substitution corresponds to the polar characteristics of the substituents. The fact that $\Delta H^\ddagger$ for the *o*-fluorine and *o*-chlorine differs by 1 kcal./mole is, however, noteworthy. The electron-attracting power of *p*-chlorine is considerably greater than that of *p*-fluorine, owing to the large mesomeric effect of the latter, and this difference appears to be in some measure carried over to the *ortho*-position.

Acidic Hydrolysis of Esters.—The results under discussion confirm the view that polar influences on the rate of acidic hydrolysis of esters are small. The rate coefficients range from 0·00775 l. mole^{-1} min.$^{-1}$ to 0·0113 l. mole^{-1} min.$^{-1}$ for *meta*-substituents with such different polar properties as H and NO_2 (Table 2). This implies that the Hammett ρ-value may be taken as zero.

Taft Parameters.—The Taft parameters σ^* and E_s at ~100° were obtained by substituting the appropriate kinetic results in the Taft–Ingold equations, (1) and (2):

$$\sigma^* = [\log (k/k_0)_B - \log (k/k_0)_A]/(\rho_B - \rho_A) \tag{1}$$

The subscripts A, B, and 0 refer to acidic and basic hydrolysis and to the unsubstituted compound, respectively. The steric parameter is given by

$$E_s = \log (k/k_0)_A \tag{2}$$

The Hammett ρ-values for the reactions in aqueous methanol were obtained from our experimental results on the reactions of *meta*-substituted compounds, as suggested by van Bekkum, Verkade, and Wepster.[14] A plot of log k_B (at 100°) against σ gave $\rho_B = +1{\cdot}94$. No linear relation was found between log k_A and σ, so ρ_A was taken as zero. A ρ-value for the basic hydrolysis of benzoate esters in 60% v/v dioxan–water was obtained from results of Goering, Rubin, and Newman[13] at 125° on methyl *para*-substituted 2,6-dimethylbenzoates, by using Jaffé's[15] σ-values for *p*-Me, *p*-Br, and *p*-NO_2. (Goering, Rubin, and Newman's conclusion that the mechanism for these esters involves alkyl–oxygen fission has been disproved.[16]) This value of ρ, +1·47, was converted into a value of +1·57 for 100° by use of the approximate relation $\rho_1/\rho_2 = T_2/T_1$. ρ_A was assumed to be zero as for the methanolic solvent. It is emphasised that the σ^* values of the present work (Table 4) are obtained from results relating to the same conditions of temperature, solvent, and alkyl group in the ester function, whereas Taft's values were obtained in most cases from experimental results for which these conditions vary.

TABLE 4.

Taft parameters.

Subst.	This work σ^*	This work E_s	Taft § σ^*	Taft § E_s	van Bekkum *et al.*† σ_p
	In 80% v/v *methanol–water at* 100·8°				
Me	+0·003	−0·709	−0·17	−0·49	−0·129
Et	+0·036	−0·963	—	—	—
F	+0·291	−0·008	+0·24	0·00	+0·12 ‡
Cl	+0·219	−0·488	+0·20	−0·31	+0·238
Br	+0·296	−0·595	+0·21	−0·49	+0·265
I	+0·341	−0·833	+0·21	−0·69	+0·299
	In 60% v/v *dioxan–water at* 100°				
Me	−0·157	−0·549	−0·17	−0·49	−0·129
Et	−0·135	−0·891	—	—	—

§ Ref. 2. † Ref. 14. ‡ For ester hydrolysis. For this work σ^* values are accurate to ±4·5%, and E_s values to ± 7%.

In the halogen series $\sigma^* \approx \sigma_p$, implying that polar effects are equivalent from *ortho*- and *para*-positions. A notable exception, however, is fluorine, the polar effect of which is

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[14] van Bekkum, Verkade, and Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.
[15] Jaffé, *Chem. Rev.*, 1953, **53**, 191.
[16] Bender and Dewey, *J. Amer. Chem. Soc.*, 1956, **78**, 317.

much greater from the *ortho*-position. Taft's σ^* values for chlorine, bromine, and iodine are approximately equal, whereas σ_p values increase steadily along the series. The σ^* values from the present work increase more than σ_p from chlorine to iodine.

Where comparison is possible between parameters determined for the two solvents, agreement is poor. Qualitative agreement is found; that is methyl is " smaller " and more electron-releasing than ethyl in both solvents. In aqueous methanol, however, methyl and ethyl are apparently slightly electron-withdrawing, a point not capable of easy explanation. The steric parameters also differ for the two media, E_s values being numerically larger for aqueous methanol.

It is difficult to reconcile the conclusions drawn from these results with those drawn from the work on esterification with diazodiphenylmethane, described in Part I,[1] where it was concluded that in halogenobenzoic acids polar effects are greater from the *ortho*- than from the *para*-position by a factor of about 3. That σ^* is approximately equal to σ_p for the halogens is, therefore, unexpected. Consequently we now re-examine the assumptions made in deriving the Taft–Ingold equations.[2]

It has been confirmed that the rate of acidic hydrolysis is almost unaffected by the introduction of highly polar substituents (Table 2). The argument that resonance effects are small and similar in basic and acidic hydrolysis is also acceptable, as there seems little doubt that the structures of the transition states [2] preclude resonance interaction. The fundamental assumption, however, is that steric effects are the same in the basic and the acidic hydrolysis. Taft claims that since the transition states for the two reactions differ only by a pair of protons this assumption is reasonable. For this assumption to be valid, however, the solvation shells round the reaction centres must be the same in the transition states of both basic and acidic hydrolysis of esters. The electrical structures of the transition states differ by two units of charge and it is unlikely that the solvation patterns will be similar to the extent that $\log (k/k_0)_A$ will represent the steric effect on the kinetics of the corresponding basic hydrolysis. An indication that steric effects in basic and acidic hydrolysis are not always equal has been obtained as follows. In this laboratory the kinetics of the basic and the acidic hydrolysis of methyl *cis*- and *trans*-4-t-butylcyclohexanecarboxylate have been studied.[17] A Taft–Ingold analysis of the results indicates that in the basic hydrolysis the polar effect of the 4-t-butyl group, necessarily equatorial, is 3·4 times greater when the alkoxycarbonyl group is axial than when it is equatorial. The t-butyl group has a low dipole moment and its electrostatic influence on the reaction centre is likely to be small and certainly not very different in the two cases. The inductive polar effect is also unlikely to differ as a result of change of conformation and it seems more likely that the assumption concerning the equivalence of steric effects in acidic and basic hydrolysis is not applicable in this case.

Chapman, Shorter, and Toyne [17] have suggested that solvation is more important in governing steric effects in basic hydrolysis than in acidic hydrolysis for the cyclohexanecarboxylic esters with which they were concerned, *i.e.*, E_s underestimates the steric effect in basic hydrolysis. Application of this idea to the basic hydrolysis of the *o*-halogenobenzoates would explain why σ^* values (except for *o*-F) are much lower than expected. In the Taft–Ingold analysis, if the steric effect in basic hydrolysis is underestimated, then the substituents appear to be less electron-attracting than they actually are. Presumably the analysis gives a high polar effect of *o*- compared with *p*-fluorine because the steric effect of *o*-fluorine is very small in both basic and acidic hydrolysis, so that differences in the part played by solvation are of little importance. However, the above idea will not account for the anomalous σ^* values of *o*-methyl and *o*-ethyl in aqueous methanol. These could be explained on the supposition that E_s overestimates that steric effect in basic hydrolysis. Further, the influence of polar effects on the solvation pattern (see p. 1295) must be considered when the relevance of E_s to basic hydrolysis is being discussed.

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[17] Ref. 4 and Chapman, Shorter, and Toyne, *J.*, **1961**, 2543.

For basic hydrolysis it was suggested that *o*-halogen facilitates solvation markedly by a polar effect, whereas *o*-alkyl might produce some inhibition of solvation by a polar effect of opposite sign. There is, as yet, no evidence regarding similar effects in acidic hydrolysis and their occurrence need not be postulated now. The polar effect on solvation in basic hydrolysis would have the following influence: for *o*-halogen-substituted esters it would tend to make solvation more important in governing steric effects in basic than in acidic hydrolysis; the reverse would hold for *o*-alkyl-substituted esters, *i.e.*, for *o*-halogen E_s would tend to be an underestimate of the steric effect in basic hydrolysis, while for *o*-alkyl E_s would tend to be an overestimate of the steric effect in basic hydrolysis. This polar phenomenon would be superimposed on that postulated by Chapman, Shorter, and Toyne,[17] and would account for the apparent electron-attracting influence of *o*-methyl and *o*-ethyl that emerges from the Taft analysis of the results for aqueous methanol. In aqueous dioxan solvation is presumably so strong that polar facilitation and inhibition of solvation are less important than in aqueous methanol. E_s is then a better measure of the steric effect in basic hydrolysis, so that *o*-methyl and *o*-ethyl appear to be somewhat electron-releasing in nature, as would be expected.

The E_s values of *o*-methyl and *o*-ethyl are numerically smaller for 60% dioxan–water than for 80% methanol–water. Since the solvating power of the former solvent is greater than of the latter (see p. 1295) this result is surprising. Further work on the solvent dependence of E_s is in progress.

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