333. *The Activation Energy of Organic Reactions. Part IV. Transmission of Substituent Influences in Ester Hydrolysis.*

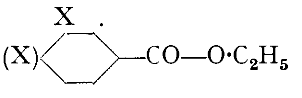
By E. Tommila and C. N. Hinshelwood.

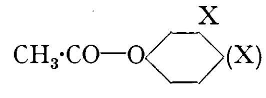
The constants of the Arrhenius equation have been measured for the alkaline and the acid hydrolysis in aqueous acetone of a large number of substituted esters belonging to the following series, and chosen so that a wide range of velocities was covered: $X\cdot C_6H_4\cdot CO\cdot OEt$, $X\cdot C_6H_4\cdot CO\cdot OMe$, $CH_3\cdot CO\cdot O\cdot CH_2\cdot C_6H_4X$, $CH_3\cdot CO\cdot O\cdot C_6H_4X$. In each series for the alkaline hydrolysis *PZ* is nearly constant, the changes due to the substituents being measured by ΔE. In the acid hydrolysis the influence of the substituents is smaller and less regular. For the former, the values of ΔE provide a quantitative measure (*a*) for the relative influence of the different substituents in a given series, which proves to be fairly constant from one series to another, and (*b*) of the relative transmissibility of the electronic effect of a given substituent through the different structures: this transmissibility also appears to be fairly constant for different substituents, so that relative transmission coefficients for different types of structure can be determined.

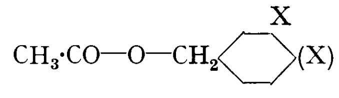
One of the most important effects of a substituent group in a reacting molecule is to modify the activation energy. In some series of reactions the members of which differ only in the substituents present, the changes in velocity are wholly accounted for by the changes, ΔE, in the activation energy. In others the term PZ of the Arrhenius equation changes as well as E, sometimes showing small random variations but more often a regular functional correlation with E itself. The first type of behaviour seems to be the more characteristic (Part I, Hinshelwood, Laidler, and Timm, this vol., p. 848), and is exemplified in the alkaline hydrolysis of substituted benzoic esters, studied in 85% alcohol by Ingold and Nathan (J., 1936, 222) and by Evans, Gordon, and Watson (J., 1937, 1430), and in 56% aqueous acetone by Newling and Hinshelwood (J., 1936, 1357), whereas in the acid hydrolysis of benzoic esters, PZ tends to increase as E increases (Timm and Hinshelwood, this vol., p. 862).

The same set of substituents does not produce equal effects in different reactions; and if ΔE_1 is the change caused by any given substituent in reaction 1 and ΔE_2 that caused by the same substituent in reaction 2, then it may be found that $\Delta E_1 = \alpha \Delta E_2$, where α is approximately constant for the whole set of substituents. For the series, α might conveniently be called the relative *transmission coefficient* of the effect of the substituent from the substituent to the actual reaction centre in the molecule. It will depend upon the structures concerned, and is a quantity of importance in the ultimate physical interpretation of electronic theories of the reactivity of organic compounds.

In the present paper the relative values of the transmission coefficients have been determined for the influence of various electron-attracting or -repelling groups in the *m*- and *p*-position of the benzene ring on the hydrolysis by acids and alkalis respectively in aqueous acetone of the following series of esters:







Besides the investigations cited above, of reactions concerning these series, the acid hydrolysis of phenyl acetate has been studied in alcohol by Waters (J., 1936, 1014) and in aqueous acetone by Newling and Hinshelwood (*loc. cit.*).

Another question of interest from the standpoint of electronic theories is how far the ratios $\Delta E^a_1/\Delta E^b_1$, $\Delta E^a_2/\Delta E^b_2$ . . . . , of the influences of two given substituents are constant from reaction to reaction; and, if they are approximately constant for various series of reactions, what are the mean values of the several ratios. In particular, it is interesting to inquire how far the ratio of the effects of meta- and para-substituents is dependent upon the nature of the substituent itself.

The present paper also contributes observations bearing upon these questions.

EXPERIMENTAL.

Reactants.—Benzyl acetate, phenyl acetate, ethyl and methyl benzoates, nitrobenzoates, and *p*-aminobenzoate, and methyl anisate were commercial products, which were purified, the liquid esters by distillation at reduced pressure, and phenyl acetate further by freezing out from the melt, and the nitrobenzoates, *p*-aminobenzoate and methyl anisate by recrystallization to correct m. p. from light petroleum or from alcohol. Methylbenzyl acetates were prepared from corresponding monobromoxylenes by boiling in glacial acetic acid, first with an excess of lead acetate, and finally for a short time with a little silver acetate. *m*-Nitrobenzyl acetate, which seems not to have been prepared before, was obtained from *m*-nitrobenzyl alcohol and acetyl chloride by the usual esterification process and purified by repeated fractionating in a vacuum; it was an oil (b. p. 177°/10 mm.) of a slightly yellowish colour, without any smell. All attempts to crystallise it failed. *p*-Nitrobenzyl acetate was prepared by nitrating benzyl acetate, separated from the *o*-compound and unchanged benzyl alcohol by suction and crystallised from alcohol (Beilstein and Kuhlberg, *Annalen*, 1867, **147**, 340). All substituted phenyl acetates were prepared by the elegant method of Chattaway (J., 1931, 2495) from the corresponding phenols and purified by distillation at reduced pressure and freezing out (tolyl acetates) or by crystallisation from alcohol. In the preparation of *p*-aminophenyl acetate the method of Galatis (*Ber.*, 1926, **59**, 848) was used, consideration being paid to the remarks of Ruggli and Constin (*Helv. Chim. Acta*, 1932, **15**, 103), but with the difference that benzylidene-*p*-aminophenyl acetate was prepared by the much preferable method of Chattaway. The m. p. of the pure product was 76° (Galatis, 75°). *m*-Aminobenzyl acetate is difficult to get pure, so its hydrochloride, which was obtained by esterifying the acid in alcohol with hydrogen chloride as catalyst, was carefully purified by repeated precipitation from alcohol with ether, before the ester was liberated by sodium carbonate solution. Finally, the ester was fractionated in a vacuum.

All fractionations were carried out at least twice, often three times. Crystallisations were continued to constant m. p. The purity of the esters was further checked by total hydrolysis with an excess of alkali. The physical properties of the esters were in good agreement with those given in Beilstein's "Handbuch" or in the papers mentioned. Besides the special values recorded above, it may be mentioned that the m. p. of *m*-acetoxybenzoic acid was considerably higher than that found before, *viz.*, 132° (125—129° in Beilstein).

The solvent chosen was aqueous acetone, containing 400 c.c. of water made up to 1 l. with acetone (56% of acetone by weight). This contains so much water that we may assume that $[H_2O]$ is constant during the course of the hydrolysis, and that alkali and acid catalysts are completely ionised. For the solvent, commercial acetone was dried over potassium carbonate for several days and then slowly fractionated through a 4-ft. column. The water was ordinary distilled water, which was freed from carbon dioxide by boiling. In alkaline hydrolysis, sodium hydroxide, and in acid hydrolysis benzenesulphonic acid, was used as catalyst. Benzenesulphonic acid was prepared from its barium salt by adding the equivalent of sulphuric acid.

Method.—The experiments were carried out by using both ester and catalyst in equal concentration. Where possible, N/10-solutions were used, so that, after mixing, the initial concentrations of each were N/20. In the alkaline hydrolysis of nitrophenyl acetates and methyl nitrobenzoate, where the reaction is very fast, 2- or 5-fold diluted solutions were used, as also at 25° with all phenyl acetates. For the alkaline hydrolysis of *m*- and *p*-carboxyphenyl acetates, a neutral solution of the semi-ester was first prepared by addition of an equivalent of alkali before the composition of the solvent was finally adjusted. The catalyst was prepared by diluting 40 c.c. of N/4-stock solution to 100 c.c. with acetone, and, for more dilute solutions, with acetone–water. In the alkaline hydrolysis, freshly prepared solutions were always used. Although the solvent, in principle, is unstable to alkali, it was verified that even during the slowest reactions the constitution of the solution underwent no changes which affected the velocity constants.

The electrically regulated thermostats for 15°, 25°, 40°, 60°, and 80° could be controlled to within 0·05°. Experiments at low temperatures were carried out in a Dewar vessel which contained, for 0° crushed ice and water, for − 10° a mixture of sodium thiosulphate and ice, and for − 20° salt and ice. The temperature could be kept constant to within about 0·2°. All thermometers were checked against N.P.L. standards.

The rate of hydrolysis was measured by the ordinary titration methods, cresol-red being used as indicator. All acids formed in the hydrolysis, including *m*- and *p*-aminobenzoic acids, gave sharp titration points. Also it was verified that even in the hydrolysis of phenyl acetates the titration of the acetic acid formed could be accurately carried out. For *m*-nitrophenyl acetate, however, bromothymol-blue was used as indicator, and for the *p*-compound methyl-red had to be adopted, and the titration carried to a standard tint.

The procedure for following the acid hydrolysis was that described by Timm and Hinshelwood (*loc. cit.*). In the alkaline hydrolysis several methods were used depending on the reaction velocity. In the hydrolysis of benzoates (except nitrobenzoates), where the reaction velocity is low, the reaction was carried out in glass-stoppered bottles, and the course of hydrolysis was followed by removal of 10 c.c. samples. For the more rapid reactions, 5 c.c. of the 0·1N-ester solution were run into a small thin bulb with a long neck fitted in a cork, and placed in a test-tube containing 5 c.c. of N/10-catalyst. The bulb was broken with a glass rod, and the time recorded by using a stop-watch. At 40°, however, a closed tube containing 5 c.c. of each solution in separate bulbs was used, the reactants being mixed by shaking the tube. In all cases the reactants were kept in the thermostat until they had acquired its temperature before the reaction was started. At and above 60°, sealed Pyrex-glass tubes were always used. The reaction was stopped by an excess of N/50-hydrochloric acid, and the acid titrated with N/50-baryta solution. Constants were determined at four, often at five, temperatures. Glassware was standardised. Results were corrected for change of concentration due to thermal expansion of solvent.

In the alkaline hydrolysis, the velocity constants were calculated from the ordinary bimolecular formula. For phenyl acetates, where the liberated phenols themselves react with and remove catalyst, this formula gives values of k which decrease with the time. In this case, therefore, rather better constancy was obtained by using the formula $dx/dt = k(a - x)(a - 2x)$, which, however, is valid only in so far as formation of alkaline phenoxide is complete. The velocity constants for phenyl acetates were calculated from both formulæ and extrapolated to zero reaction. The values so obtained were in good agreement. In the acid hydrolysis, the reaction always went practically to completion, so that the simple formula $dx/dt = k[H^+][a - x]$ could be used. The Arrhenius equation was followed within the limits of experimental error in every case.

Since the object of the experiments was to measure small changes in activation energy as accurately as possible, the preparation of the solvent and all other operations were carefully standardised. All the measurements were made by one of the authors (E. T.) so that personal factors should be eliminated as fully as possible. The accuracy of the results in the alkaline hydrolysis is, of course, higher for the benzyl acetate and benzoate series than for the phenyl acetate series, where the reaction is very rapid and the results are extrapolated. On account of the rapidity of the hydrolysis of nitro-esters, the accuracy of the values for their activation energies is in each series less than that of the other members of the series. For each series the relative values of the activation energies will be more accurate than their absolute values. The earlier results of Newling and Hinshelwood (*loc. cit.*) on the alkaline hydrolysis of the benzoic esters were repeated (except those with ethyl anisate), so that there would be no need to take differences between sets of figures not as fully comparable as possible in every way. The values for the two nitrobenzoic esters agree well with the earlier ones, but, for an unexplained reason, the value for the benzoic ester is now found to be several hundred calories higher. The original value did not lie well on the line showing the relation of log k and E, but the new one does, and is therefore assumed to be the correct one; the error in the older value must be attributed to a slightly incorrect composition of one of the solvents used—or possibly to the presence of some methyl alcohol in the acetone, to which the reaction rate might be rather sensitive. For the acid hydrolysis of phenyl acetate a slightly higher value for E was obtained than before. With the ethyl aminobenzoates a very large difference was found between the *p*- and the *m*-compound. The position of the former in the series corresponded to the result obtained by Ingold and Nathan (*loc. cit.*) in alcohol–water solvent; therefore some of the measurements with the *m*-compound were repeated with another specimen, purchased from B.D.H. and carefully purified: the result, however, was the same as before. Indeed, the ratio of the reaction velocities of the two compounds was in good agreement with that found by Kindler (*Annalen*, **1926**, **450**, 1) in alcohol–water. The present results are used in direct comparison with those recently obtained by Timm for the acid hydrolysis of benzoic esters, since the differences involved are quite large, and errors of a few hundred calories would not matter.

DISCUSSION.

General.—The results are tabulated in Tables I and II. Table I contains the observed velocity constants in l.g.-mol.$^{-1}$sec.$^{-1}$ and Table II values for $k_{25°}$ (calculated from the Arrhenius equation), $\log_{10}PZ$, and E.

In Fig. 1, log $k_{25°}$ is plotted against E. The results for ethyl anisate are those of Newling and Hinshelwood (*loc. cit.*). In Fig. 2 the values for $\Delta E = E_H - E_X$ in the different series are plotted against the corresponding values for the ethyl benzoate series, E_H being the activation energy for the unsubstituted ester and E_X that for the same type of ester with a substituent X. The slope of the straight lines gives the relative transmission coefficients for the various series, the coefficient for the ethyl benzoate series being taken as unity. The values for the acid hydrolysis of ethyl benzoates are those of Timm and Hinshelwood (*loc. cit.*).

In the case of alkaline hydrolysis, log k_{25° plotted against E gives, for all three series, lines the slope of which approximates to $-2{\cdot}303\boldsymbol{R}T$, showing that PZ is nearly constant and that the substituents exert their principal influence on the activation energy.

For acid hydrolysis, the benzoic esters show a well-marked correlation of PZ and E (Timm and Hinshelwood, *loc. cit.*), while with the phenyl acetates and the benzyl acetates the changes are too small and irregular to allow a definite conclusion to be reached.

TABLE I.

A. *Alkaline Hydrolysis.*

(a) *Benzyl acetates.* Values of 10^3k.

Temp.	Benzyl acetate.	*m*-Methyl-.	*p*-Methyl-.	*m*-Nitro-.	*p*-Nitro-.
−10·0°	4·349	3·315	2·950	—	—
0·0	10·22	7·782	7·170	35·30	45·9
15·05	34·40	26·34	23·60	108·4	137·2
24·9	69·95	54·64	48·76	209·1	266·0
40·13	189·9	150·0	137·0	565·3	696·1

(b) *Phenyl acetates.* Values of 10^2k.

Temp.	Phenyl acetate.	Temp.	*m*-Methyl-.	Temp.	*p*-Methyl-.	Temp.	*p*-Amino-.
−20·0°	1·26	−20·0°	0·82	−20·0°	0·65	−18·8°	0·74
−12·0	2·53	−10·0	1·95	−10·0	1·75	−10·0	1·49
0·0	7·48	0·0	5·22	0·0	4·50	0·0	3·80
15·05	25·0	15·05	18·0	15·05	15·4	15·0	14·0
24·9	57·6	24·9	38·0	24·9	31·0	24·9	27·2

Temp.	*m*-Nitro-.	Temp.	*p*-Nitro-.	Temp.	*m*-Carboxy-.	Temp.	*p*-Carboxy-.
−20·0	18·3	−20·0	29·0	−20·8	1·90	−21·0	2·52
−10·0	41·0	−10·0	70·0	− 9·5	5·50	−10·5	5·80
0·0	97·0	0·0	140·0	0·0	13·3	0·0	13·0
15·05	280·0	15·05	430·0	15·0	39·5	15·0	48·8
				28·9	73·0	24·9	95·0

(c) *Ethyl benzoates.* Values of 10^4k.

Temp.	Ethyl benzoate.	*m*-Methyl-.	*p*-Methyl-.	*m*-Nitro-.	*p*-Nitro-.	*m*-Amino-.	Temp.	*p*-Amino-.
0·0°	3·02	1·640	1·060	185	358	1·59	24·9°	0·840
15·0	12·74	7·224	4·77	666	1212	7·26	40·13	3·412
24·9	28·68	17·10	11·56	1370	2442	16·47	60·0	17·37
40·13	95·60	55·60	39·00	3863	6867	56·00	80·0	71·39

(d) *Methyl benzoates.* Values of 10^3k.

Temp.	Methyl benzoate.	*p*-Methoxy-.	*p*-Nitro-.
0·0°	1·000	0·200	91·68
15·0	4·043	0·904	311·2
24·9	9·007	2·218	640·2
40·13	28·88	7·70	1697·0

B. *Acid Hydrolysis.*

(a) *Benzyl acetates.* Values of 10^5k.

Temp.	Benzyl acetate.	*m*-Methyl-.	*p*-Methyl-.	*m*-Nitro-.	*p*-Nitro-.
15·05°	1·153	1·081	—	1·075	1·070
24·9	2·988	2·830	2·983	2·550	2·723
40·13	12·30	10·43	12·36	10·31	10·75
60·0	57·98	49·67	57·13	49·40	50·81
80·0	227·9	201·7	226·0	186·5	197·9

(b) *Phenyl acetates.* Values of 10^5k.

Temp.	Phenyl acetate.	*m*-Methyl-.	*p*-Methyl-.	*m*-Nitro-.	*m*-Carboxy-.	*p*-Carboxy-.
15·05°	1·047	1·008	—	0·700	—	—
24·9	2·700	2·656	2·930	1·940	2·285	2·422
40·13	11·44	10·97	11·80	7·615	10·02	9·82
60·0	58·13	57·49	61·90	37·95	49·56	50·10
80·0	268·0	257·0	284·4	157·6	220·4	218·6

TABLE II.

A. *Alkaline Hydrolysis.*

Ester.	$k_{25^\circ} \times 10^3$.	$\log_{10} PZ$.	E (cals.).
Benzyl acetate	6·960	7·91	12,320
m-Methylbenzyl acetate	5·415	7·88	12,420
p-Methylbenzyl acetate	4·894	7·88	12,480
m-Nitrobenzyl acetate	21·27	7·91	11,650
p-Nitrobenzyl acetate	26·85	7·87	11,470
Phenyl acetate	53·70	8·97	12,550
m-Tolyl acetate	37·83	9·04	12,860
p-Tolyl acetate	31·91	8·99	12,890
m-Nitrophenyl acetate	549*	9·06	11,310
p-Nitrophenyl acetate	805*	9·00	11,000
p-Aminophenyl acetate	28·15	8·97	12,930
m-Carboxyphenyl acetate	77·62	8·77	12,070
p-Carboxyphenyl acetate	92·93	8·81	12,010
Ethyl benzoate	0·2891	8·18	14,560
Ethyl *m*-methylbenzoate	0·1686	8·17	14,870
Ethyl *p*-methylbenzoate	0·1142	8·22	15,160
Ethyl *m*-nitrobenzoate	13·65	8·56	12,800
Ethyl *p*-nitrobenzoate	24·63	8·55	12,400
Ethyl *m*-aminobenzoate	0·1658	8·25	14,980
Ethyl *p*-aminobenzoate	0·00864	8·23	16,700
Methyl benzoate	0·9012	8·38	14,160
Methyl anisate	0·2192	8·70	15,420
Methyl *p*-nitrobenzoate	62·62	8·84	12,290

* Extrapolated.

B. *Acid Hydrolysis.*

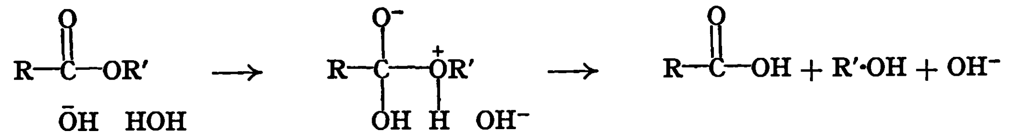
Ester.	$k_{25^\circ} \times 10^5$.	$\log_{10} PZ$.	E (cals.).
Benzyl acetate	3·078	7·58	16,400
m-Methylbenzyl acetate	2·786	7·35	16,200
p-Methylbenzyl acetate	3·162	7·40	16,200
m-Nitrobenzyl acetate	2·683	7·29	16,100
p-Nitrobenzyl acetate	2·757	7·39	16,200
Phenyl acetate	2·767	8·10	17,200
m-Tolyl acetate	2·685	8·08	17,200
p-Tolyl acetate	2·934	8·09	17,200
m-Nitrophenyl acetate	1·945	7·61	16,700
m-Carboxyphenyl acetate	2·374	7·94	17,100
p-Carboxyphenyl acetate	2·460	7·81	16,900

In each series E for the alkaline hydrolysis is much lower than E for the acid hydrolysis, and the difference accounts for much more of the difference in velocity than do the relatively small changes in PZ. In the ethyl benzoate series the activation energies in 56% acetone are about 3000 cals. lower than those found by Ingold and Nathan (*loc. cit.*) and Evans, Gordon, and Watson (*loc. cit.*) in 85% aqueous alcohol.

The Transmission Coefficients.—From Fig. 2 it is evident that the transmission coefficient for the influence of the substituent to the reaction centre is greatest in the case of the alkaline hydrolysis of benzoic esters, and then decreases in the order: benzoic esters (alkaline) > phenyl acetates (alk.) > benzyl acetates (alk.) > benzoic esters (acid) > phenyl acetates (acid), benzyl acetates (acid), the results in the case of the last two being irregular, but leaving no doubt that the transmission coefficient is very small. Approximate numerical values for the transmission coefficient in the alkaline hydrolysis are 1 in the ethyl benzoate series, 0·71 in the phenyl acetate series, and 0·36 in the benzyl acetate series. For acid hydrolysis of the benzoic esters a very rough value may be taken as 0·2, and with the remaining two series the value is nearly zero. For alkaline hydrolysis of methyl benzoates, where only two points are available, the transmission coefficient seems to be about the same as for ethyl benzoates.

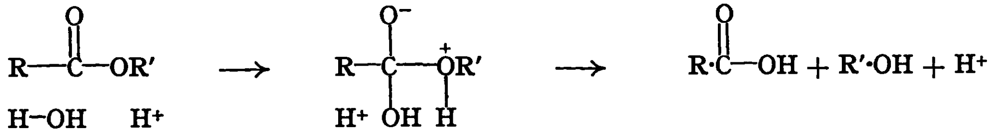
In interpreting these results, we must again consider the generally accepted mechanism of hydrolysis which is represented in the equations:

Alkaline hydrolysis.



$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OR' \quad \bar{O}H \quad HOH \longrightarrow R{-}\overset{\displaystyle O^-}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}{-}\overset{+}{\underset{\displaystyle H}{\underset{|}{O}}}R' \quad OH^- \longrightarrow R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH + R'{\cdot}OH + OH^-$$

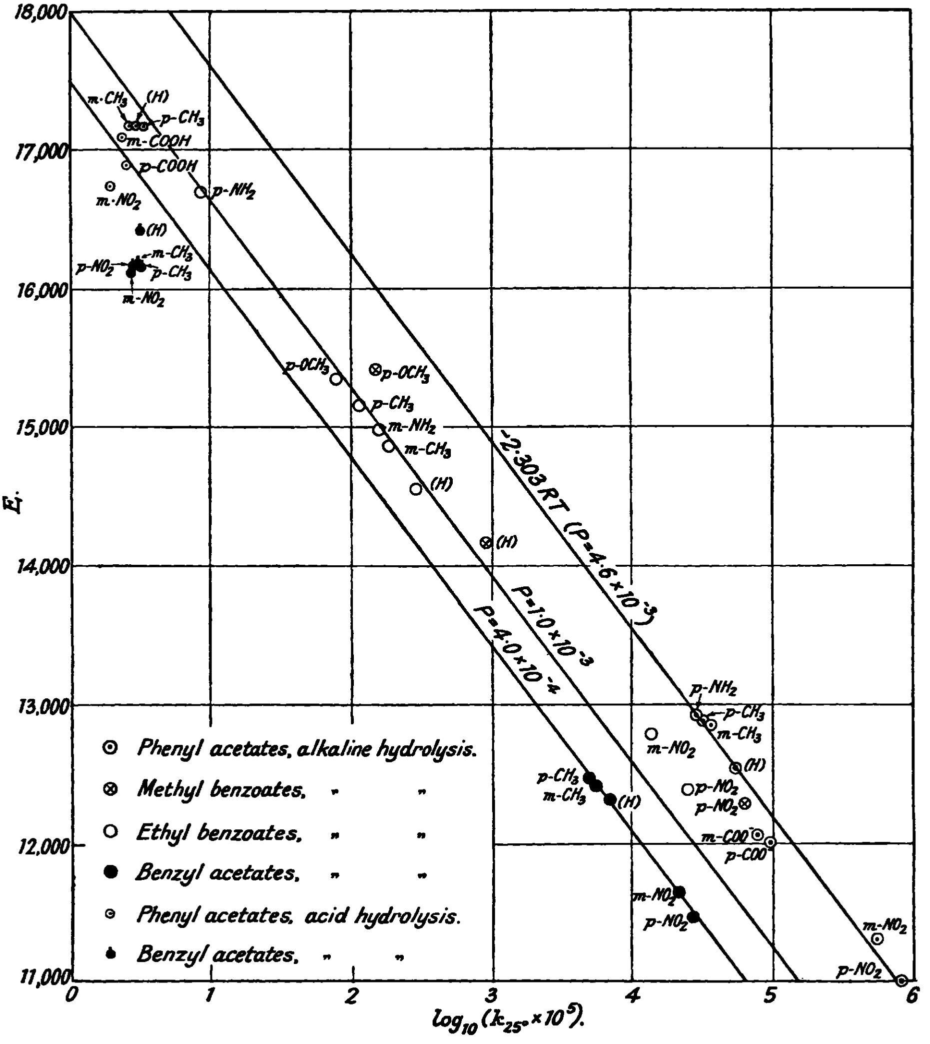
Acid hydrolysis.



$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}OR' \quad H{-}OH \quad H^+ \longrightarrow H^+ \; R{-}\overset{\displaystyle O^-}{\overset{|}{\underset{\displaystyle OH}{\underset{|}{C}}}}{-}\overset{+}{\underset{\displaystyle H}{\underset{|}{O}}}R' \longrightarrow R{\cdot}\overset{\displaystyle O}{\overset{\|}{C}}{-}OH + R'{\cdot}OH + H^+$$

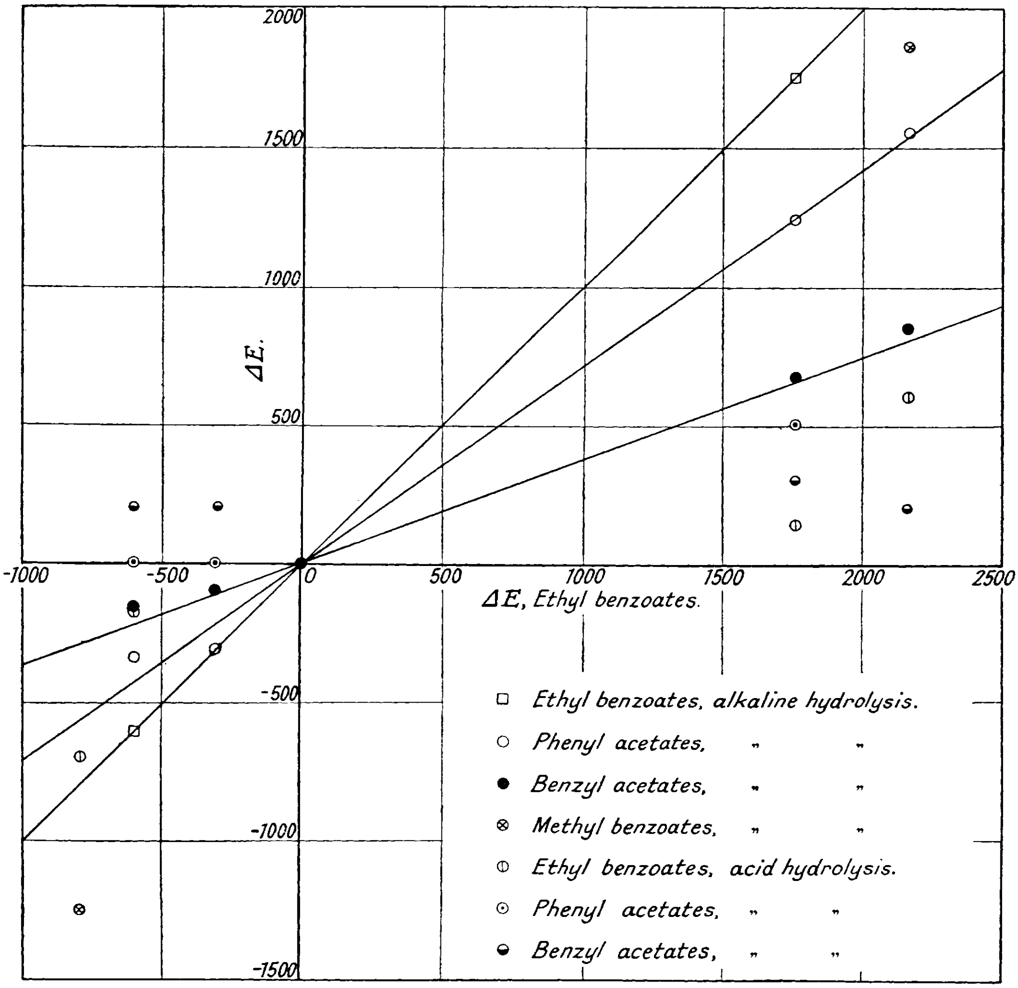
That the transmission should be greatest in the case of the alkaline hydrolysis of the benzoic esters is readily understandable. The reaction is of the type in which the influence of the substituent follows its influence on the approach of the reagent. In alkaline hydrolysis the

FIG. 1.



charged hydroxyl ion approaches the carbonyl carbon, and this is the nearest atom to the benzene ring which carries the substituents. With phenyl acetate, which shows the next most effective transmission, the nearest atom to the benzene ring is the ethereal oxygen, which receives a proton from an approaching water molecule: this process is impeded by electronic influences which facilitate the approach of hydroxyl to the carbon. A group, therefore, which facilitates the hydrolysis of benzoic esters, will have an adverse influence at the ethereal oxygen to which the water molecule with its feeble effective charge approaches, and a favourable influence at the carbonyl carbon to which the fully-charged hydroxyl ion comes. The question therefore arises whether the oxygen atom conducts the effect of the substituent well enough to the carbonyl carbon to leave the total effect of the same sign as before, or whether the adverse effect at the ethereal oxygen predominates because the oxygen is nearer to the substituent. The fact that the value of α for the phenyl acetates compared with the benzoates is about 0·71 shows that the influence of the substituent is still measured by its effect on the electron availability at the carbonyl carbon, even though the oxygen atom is interposed. This means either that the oxygen must be regarded as rather a good conductor, or that the adverse effect due to an unfavourable charge on the ethereal oxygen is rather unimportant; or perhaps that both statements are true. The anomalous behaviour of the semi-esters is referred to later.

FIG. 2.



The comparison of the phenyl and benzyl acetates is simple—the relative values of α measure the damping of the effect by the interposition of a methylene group. The reduction is from 0·71 to 0·36.

The acid hydrolysis is a little more difficult to interpret. Here the reagent with the highest effective charge is the hydrogen ion which approaches the ethereal oxygen. Substituents which facilitate approach to the carbonyl oxygen of hydroxyl must oppose the approach of hydrion to the ethereal oxygen, so that in the acid hydrolysis of benzyl and phenyl acetates, since the ethereal oxygen is not only nearer than the carbonyl carbon to the substituent but is also the centre which is attacked by the most highly charged reagent, we might expect the influence of the substituents to be the opposite of what it is in the case of the alkaline hydrolysis. What is actually found is that the influence of the substituents is very small. This is clearly due to the balancing of the opposing influences at the two reaction centres, carbonyl and ethereal oxygen. The sign of the effect is sometimes the same as in alkaline hydrolysis and sometimes the reverse, and in some cases the small differences appear positive or negative according as they are judged by the activation energy or by the velocity. The irregularity of the effect is not of much significance, since the effect itself is so small. What is of greater interest is that no marked reversed effect appears when we pass from alkaline to acid hydrolysis, in spite of the fact that the sign of the charge on the reagent which attacks the atom nearest to the substituent is reversed. This shows that the electron availability at the carbonyl carbon always remains of greater significance than the effective charge of the ethereal oxygen, whether this carbonyl carbon is attacked by a " strong " or by a " weak " reagent. The tendency to a reversal is, however, clearly shown by the reduction of α to a value of nearly zero, and perhaps also by the fact that in acid hydrolysis the actual velocities for the nitrophenyl acetates and nitrobenzyl acetates are smaller than those for the unsubstituted compounds—in contrast with what is found for the alkaline hydrolysis.

Relative Influence of the Different Substituents.—The relative influence of the different substituents in a given series of reactions appears to be fairly constant throughout the three series of alkaline hydrolyses (the effects in the acid hydrolysis being too small to make a reliable comparison possible). The results are summarised in Table III, which contains the ratios $\Delta E_X/\Delta E_{p\text{-NO}_2}$ for each series.

TABLE III.

Relative influence of the different substituents in a given series in the alkaline hydrolysis.

	NO_2.		CH_3.		NH_2.		OCH_3.	COO^-.	
	m-.	*p*-.	*m*-.	*p*-.	*m*-.	*p*-.	*p*-.	*m*-.	*p*-.
Ethyl benzoates	0·81	*1·00*	−0·14	−0·28	−0·19	−0·99	−0·37	—	—
Methyl benzoates ...	—	*1·00*	—	—	—	—	−0·67	—	—
Phenyl acetates	0·80	*1·00*	−0·20	−0·22	—	−0·25	—	0·31	0·35
Benzyl acetates	0·79	*1·00*	−0·12	−0·19	—	—	—	—	—
Average	0·80	*1·00*	−0·15	−0·23	−0·19	—	−0·52	(0·31)	(0·35)

The points of interest which this table reveals are as follows. The effect of the various groups appears in the order which the electronic theory would lead us to expect, except that the group COO^- appears to function as an electron-attracting group like the undissociated carboxyl group. Doubtless, the electron attraction has been diminished by the ionisation, but there is no basis of comparison by which the extent of this can be judged, and it is remarkable that the effect has not been completely reversed. Further work on the comparison of the electronic effect of the ionised carboxyl group with that of other groups will be of interest.

With regard to the quantitative measure of the effects in terms of activation energy changes, it may be said that the results for different series show in general an accordance which is as close as could be expected. The *p*-amino-group is an exception. The effect of a meta-substituent is always smaller than that of a para-substituent, the ratio varying from 65% to 90% (except for the *p*-amino benzoate).

The Values of PZ.—In the alkaline hydrolysis, the values of *PZ* are very nearly constant for any given series, the mean being slightly greater than that for the corresponding series in acid hydrolysis, where, however, the values obtained at far less constant. For alkaline hydrolysis the values decrease in the order phenyl acetates > methyl benzoates > ethyl benzoates > benzyl acetates, and for acid hydrolysis where comparison is possible the same relative order is found (see Table IV).

TABLE IV.

	Average value of $\log_{10} PZ$.		$P \times 10^4$.	
	Alkaine hydrolysis.	Acid hydrolysis.	Alkaline hydrolysis.	Acid hydrolysis.
Benzyl acetates	7·890	7·402	4·0	1·4
Ethyl benzoates	8·295	7·739*	10	3·0
Methyl benzoates	8·640	—	22	—
Phenyl acetates	8·951	7·938	46	4·7

* Timm and Hinshelwood, *loc. cit.*

In the estimate of the absolute values of P, Z is calculated by the usual kinetic-theory formula, and a value of 4×10^{-8} cm. assumed for the diameters. The differences may be partly explained by geometrical factors, but other conditions, probably connected with the internal energy distributions, must also be playing their part.

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