CCLXXVI.—*The Mechanism of, and Constitutional Factors controlling, the Hydrolysis of Carboxylic Esters. Part V. The Effect of Alkyl Groups on Hydrolytic Stability Maxima.*

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IT has long been known that the speed with which carboxylic esters hydrolyse under the influence of a single catalyst is a highly complicated function of structure, and in Part I (J., 1930, 1032) it was shown that a certain simplification results from considering, not the simple speeds, but the hydrogen potentials of minimal speed (p_H^*) in relation to constitution; the matter was further illustrated in Part IV (preceding paper). On the basis of data relating to specially simple cases, the original complexity was ascribed in Part I to the duplex control of velocities, by polar and spatial factors; and, reasons were given for the assumption that, on the contrary, p_H^* is primarily a function only of polar variables. In Part III (J., 1930, 1375) a possible form for this function was indicated inasmuch as it was shown that in the case of an ionic group (the primary electric constant of which is its net charge), the externally propagated polar effect, which for a large class of structures is the only polar effect of importance, is expressed in a linear relation between p_H^* and the net charge on the group. By an analogous argument it follows that, for similarly situated non-ionic groups (whose primary electric constants are their electric moments), there will be a similar linear relation between p_H^* and the electric moment.

These and other special cases may be generalised by taking, as a measure of the polar effect of the substituent, that charge, q, which, if conferred by the substituent on the reactive group would give rise to the observed effect of the substitution on any essentially polar function of velocity. This definition possesses the advantage that it has a meaning which can be visualised in relation to molecular polarisability as well as in relation to molecular polarisation. If the measuring charge, q, is located at a distance r_i from the ith charge in the catalyst at the collision-distance, then a combination of the methods of Parts I and III yields the relation

$$\log (k_1'k_2''/k_1''k_2') = (q_1 - q_2)\Sigma\{(e_i''/r_i'') - (e_i'/r_i')\}/DJRT$$

where the dashes distinguish catalysts and the numerical suffixes esters. Remembering the mass-law connexion between p_H^*, k_H, and k_{OH}, it follows that p_H^* and q are linearly related.

The very direct polar significance which this inference appears to confer on p_H^* illuminates consideration of the results, recorded in Parts II and IV (J., 1930, 1039; preceding paper), for the hydro-catalytic hydrolysis of the two series of esters $C_2H_3(OH)_2 \cdot CO \cdot OR$ and $R' \cdot CO \cdot O \cdot C_3H_5(OH)_2$, where R and R' are variable alkyl groups. These data are shown graphically in Figs. 1 and 2, inspection of which yields the following conclusions : (*a*) That two methyl groups in the same situation relatively to $\cdot CO_2 \cdot$ in $R' \cdot CO_2 \cdot R$ displace p_H^* by roughly equal amounts. (*b*) That the displacement of p_H^* by a

FIG. 1.
Number and position of methyl groups.

FIG. 2.
Number and position of methyl groups.
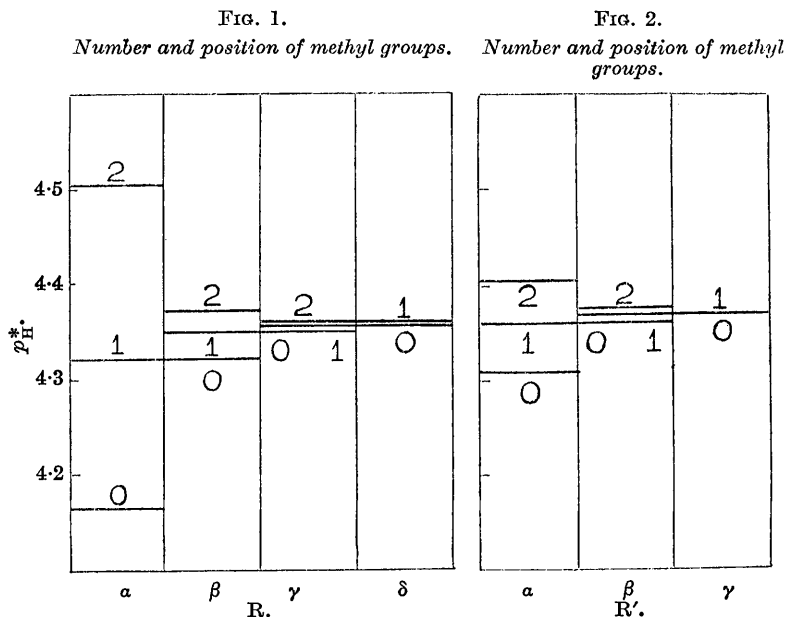
methyl group or by a *gem*-dimethyl group decreases approximately geometrically as successive carbon atoms are included normally between the group and the carboxyl nucleus. (*c*) That the displacement of p_H^* caused by any group in R' bears a nearly constant ratio to the displacement produced by the same group in R.

The degree of precision with which this last relation holds may be exhibited by plotting the values of p_H^* for each ester $C_2H_3(OH)_2 \cdot CO \cdot O \cdot R$ against that of the ester $R' \cdot CO \cdot O \cdot C_3H_5(OH)_2$ for which R' = R. The points (Fig. 3) lie on or about a straight line, and similar lines result from analogous comparisons of the p_H^* values of each of the above series with those of the series $CH_3 \cdot CO \cdot O \cdot R''$, for which the requisite data are taken from the literature. The lines show that the displacement of p_H^* by a group is given by the

product of two numerical factors separately dependent on the nature of the group and on its position.
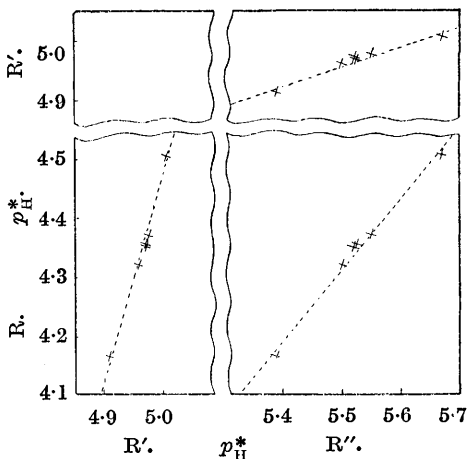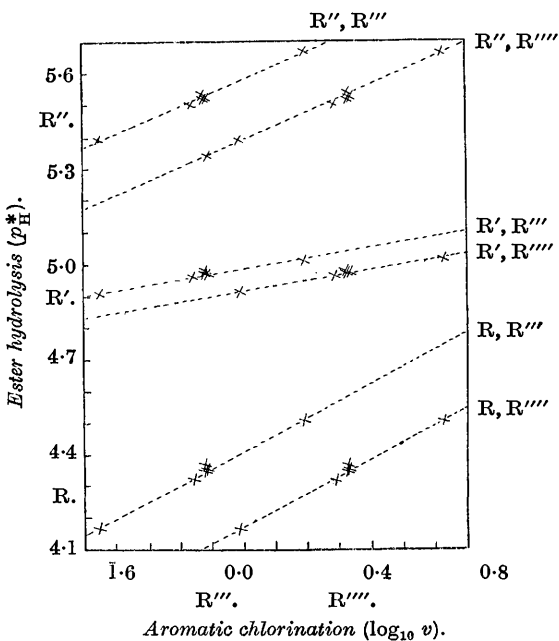
FIG. 3.

FIG. 4.

Aromatic chlorination ($\log_{10} v$).

The suggested relation between p_H^* and q, together with the wider interpretation of q already given, encourages the tentative generalis-

3 x 2

ation of the above conclusion to embrace, as correlatives, reactions other than ester hydrolysis. As an illustration, we will attempt to collate p_H^* for the hydrolysis of each of the series $C_2H_3(OH)_2 \cdot CO_2R$, $R' \cdot CO_2 \cdot C_3H_5(OH)_2$, and $CH_3 \cdot CO_2R''$, with Bradfield and Jones's data (J., 1928, 1006, 3073) for the speeds of chlorination of the phenol ethers $R''' \cdot O \cdot C_6H_4 \cdot CO_2H$ and $R'''' \cdot O \cdot C_6H_4Cl$, on the assumption that for these nuclear substitutions the steric effect of R''' and R'''' is unimportant and that $\log v$ may therefore be taken as the measure of q. The comparison, shown graphically in Fig. 4, exhibits relations so closely similar to those shown in Fig. 3 as to implement considerably the above conception of the possibility of reaching the same quantitative measure of polarity from the dynamics of independent reactions.

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