105. *Relationships between Reaction Velocities and Ionisation Constants.*

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IN 1933, Hammett and Pfluger (*J. Amer. Chem. Soc.*, **55**, 4079) observed a roughly linear relationship between the logarithms of the velocity coefficients (k) for the reactions of certain methyl esters with trimethylamine and those of the dissociation constants (K) of the corresponding acids. The variations in log K and log k represent the changes of the free energy of ionisation and of the energy of activation respectively, provided, in the latter case, that the value of the non-exponential term in the Arrhenius equation does not vary seriously. The close similarity between Hammett and Pfluger's reaction and the process of ionisation is obvious from the equations (referring to benzoic acids and esters) :

$$C_6H_4X{\cdot}CO_2Me + NMe_3 = C_6H_4X{\cdot}COO^- + NMe_4^+$$
$$C_6H_4X{\cdot}CO_2H + H_2O \rightleftarrows C_6H_4X{\cdot}COO^- + H_3O^+$$

A reagent removes a positively charged methyl group or a hydrogen ion respectively, and the position of the variable substituent X with respect to the ion removed is identical in the two cases. The approximate proportionality between the increments of energy due to the same substituent is not surprising, therefore, since polar effects of any character, whether they be induced polarisations, direct field effects, or electromeric displacements, have equal opportunity of transmission in each of the three reactions represented above. In a later contribution, Hammett (*Chem. Reviews*, 1935, **17**, 125) noted a similar connexion between the ionisation constants of bases $C_6H_4X{\cdot}NH_2$ and the velocity coefficients of several reactions of the type

$$C_6H_4X{\cdot}NR_2 + R{\cdot}Hal = C_6H_4X{\cdot}NR_3^+ + Hal^-$$

which is clearly comparable with

$$C_6H_4X{\cdot}NH_2 + H{\cdot}OH \rightleftharpoons C_6H_4X{\cdot}NH_3^+ + OH^-.$$

Finally, similar remarks are found to apply (Hammett, *loc. cit.*) to a third type of reaction, represented by the alkaline hydrolysis of *m*- and *p*-substituted benzoic and phenylacetic esters, where the plot of log k against log K for the *corresponding* acid (benzoic or phenylacetic) is approximately linear. In all these examples, the substituent is situated in the same position with respect to the point of reaction as it is in the acid or base with which comparison is made, and hence all effects have equal chances of transmission in the two cases. Hammett further cites instances of reactions where a comparable connexion exists between oxidation potentials and velocities of oxidation or reduction.

Burkhardt, Ford, and Singleton (this vol., p. 20; cf. Burkhardt, *Nature*, 1935, **136**, 684) have recently sought to extend Hammett's relationship between reaction velocities and dissociation constants of acids, and have obtained, for a number of side-chain reactions, a roughly linear plot of log k (and also of log K for a series of substituted phenylacetic acids) against log K for the corresponding benzoic acids. They include, however, certain systems where all the effects originating at the substituent group are not likely to be transmitted to the same extent as in the benzoic acids employed as reference series.

Very shortly before the appearance of Hammett and Pfluger's original observation, Nathan and Watson (J., 1933, 893) pointed out that an accurate connexion exists between the dissociation constants of a series of substituted acetic acids and the dipole moments of the corresponding methanes; the plot of log K against μ gives a smooth curve of the form

$$\log K = \log K_0 - x(\mu + a\mu^2) \qquad \qquad (1)$$

where K and K_0 refer to the substituted and the unsubstituted acids respectively, and x and a are constants. The relationship was extended by Dippy and Watson (*Chem. and Ind.*, 1935, **54**, 735) to *m*- and *p*-substituted benzoic and phenylacetic acids (using the older " classical " constants in the former case), where certain reservations were necessary, as would be anticipated. In a saturated aliphatic compound the dipole moment is a measure of the inductive effect of the substituent, but when the group is attached to the aromatic nucleus, resonance phenomena (mesomeric effects) are also included (Ingold, *Ann. Reports*, 1926, **23**, 149; J., 1933, 1120; *Chem. Reviews*, 1934, **15**, 253; Sutton, *Proc. Roy. Soc.*, 1931, **133**, *A*, 668; Bennett, *Ann. Reports*, 1929, **26**, 132; Bennett and Glasstone, *Proc. Roy. Soc.*, 1934, **145**, *A*, 71). Nevertheless, the dipole moment is the best measure of the permanent polarisation set up by a group, and, since the dissociation constants of the saturated aliphatic acids are related in a simple manner to the dipole moments of substituted methanes, the application of the same expression to aromatic acids and the corresponding benzene derivatives is likely to provide useful evidence regarding electromeric or other variable effects which operate when the group is in aromatic combination. The plot of dissociation constant against dipole moment should, in fact, illustrate very clearly the peculiarities of certain groups, and it is satisfactory to note that, when such a plot was prepared (Dippy and Watson, *loc. cit.*), the anticipated divergences were found. Accurate thermodynamic constants for a further number of substituted benzoic acids (in water at 25°) have recently become available as the result of work in these laboratories, and a better test of the relationship is now possible. The graph (Fig. 1) is very similar to that obtained by use of the older classical constants. The special features of the groups which cause deviations have already been discussed (Dippy, Watson, and Williams, J., 1935, 346).

A quantitative relationship between dipole-moment values and a suitable function of reaction velocities was also observed by Nathan and Watson (J., 1933, 890, 1248; *Nature*, 1934, **133**, 379). Continuing this work, Evans, Morgan, and Watson (J., 1935, 1174) found that, in three cases where energies of activation were known for the same reaction of a whole series of *m*- and *p*-substituted benzene derivatives, the expression $E = E_0 - C(\mu + b\mu^2)$ is applicable except for substituents which give rise to effects not included in the measured moment (the constant C may have either a positive or a negative sign, according as the reaction is of Type A or B). Further, when it is assumed that log k is a measure of E (the changes in the collision term due to variations of molecular weights and diameters are inappreciable), a number of other reactions, for which data at one temperature only are available, conform to the same formula. Hence, for a given reaction of a series of *m*- or *p*-substituted compounds, where the non-exponential term of the Arrhenius equation does not vary seriously, the connexion between velocity coefficients and the dipole moments of the appropriate substituted benzenes is

$$\log k = \log k_0 - y(\mu + b\mu^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the reservations noted above being necessary for some groups.

FIG. 1.

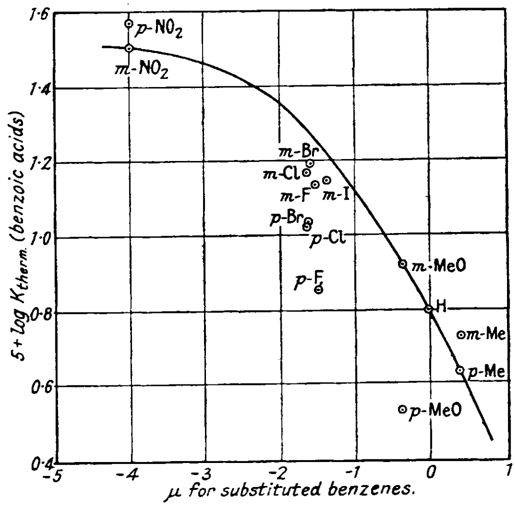
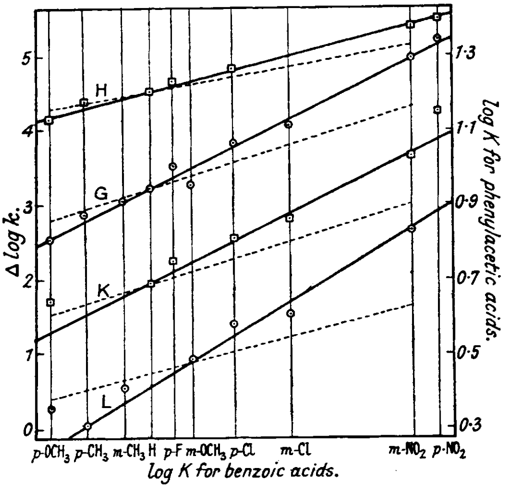


FIG. 2.



Values of K are due to Dippy and Williams (J., 1934, 1888; 1935, 343) and Dippy and Lewis (in the press); μ values are from tables in *Trans. Faraday Soc.*, Sept. 1934; all were obtained by the optical method in benzene at about 20°. The " effective moment " for $-OCH_3$ is taken as $\mu \times \cos 105^\circ$ (compare Nathan and Watson, *Nature*, 1934, **133**, 379; Evans, Morgan, and Watson, J., 1935, 1177).

It is interesting to consider whether the relationship between reaction velocities and dissociation constants, as observed by Hammett, and extended by Burkhardt, Ford, and Singleton, follows as a deduction from equations (1) and (2). These equations being written in the form $\Delta \log K = -x(\mu + a\mu^2)$ and $\Delta \log k = -y(\mu + b\mu^2)$, combination of the two gives

$$\Delta \log k = (y/x)\,\Delta \log K + y(a - b)\mu^2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

This equation refers to polar effects of a permanent nature only, and it is evident that, if only these effects are operative, equations (1) and (2) indicate a linear relationship between log k and log K if $a = b$, *i.e.*, if the coefficients of the μ^2 term are the same for the process under consideration as for the acids of the reference series. We have calculated the following values from the data for dissociation constants of benzoic acids in water at 25° (Dippy and Williams, J., 1934, 1888; 1935, 343; Dippy and Lewis, in the press), alkaline hydrolysis of benzoic esters in 88% alcohol at 30° (G; Kindler, *Annalen*, 1926, **450**, 1; 1927, **452**, 90; 1928, **464**, 278), alkaline hydrolysis of cinnamic esters under the same conditions (H; Kindler, *ibid.*), dissociation constants of phenylacetic acids in water at 25° * (K;

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* The remarks concerning the velocity coefficients of the other processes are equally applicable here : Δ log k in equation (3) becomes Δ log K', where K' is the dissociation constant of a substituted phenylacetic acid.

Dippy and Williams, J., **1934**, **161**, **1888**; **1935**, **343**), and the prototropy of the $\alpha\gamma$-diphenylmethyleneazomethine system in alcohol at 82° catalysed by sodium ethoxide (L; Shoppee, J., **1931**, **1225**; **1932**, **696**):

Benzoic acids $\log K = \log K_0 - 0{\cdot}402\,(\mu + 0{\cdot}14\mu^2)$
G $\log k = \log k_0 - 0{\cdot}625\,(\mu + 0{\cdot}069\mu^2)$
H $\log k = \log k_0 - 0{\cdot}356\,(\mu + 0{\cdot}096\mu^2)$
K $\log K = \log K_0 - 0{\cdot}125\,(\mu + 0{\cdot}076\mu^2)$
L $\log k = \log k_0 - 0{\cdot}504\,(\mu + 0{\cdot}0096\mu^2)$

Although the coefficients of the μ^2 term are of the same order of magnitude, there is an appreciable variation.

If, however, the Hammett relationship is to be general, there must also be *either* the absence of *or* a strict proportionality between effects not included in the dipole moment. The operation of electromeric effects is proved by the deviation from the dipole-moment expression (and even sequence) of acids and other compounds having substituents such as *p*-OCH_3; the proportionality or otherwise of these effects in the different systems considered will be indicated by the extent to which Hammett's relationship applies to such cases.

Both Hammett and Burkhardt employed the older classical values for the dissociation constants of substituted benzoic acids; these are, of course, not accurate, and sometimes are not comparable. It might be thought, therefore, that the appreciable and sometimes even serious deviations from the linear relationship, as found by Hammett and by Burkhardt, are due to the uncertainty of the values of the dissociation constants. Any doubt arising from this cause can now be removed, however, by constructing a plot using our accurate thermodynamic constants, all obtained by an identical procedure; relationships observed under such conditions may be regarded with confidence. In Fig. 2 the relevant data for processes G, H, K, and L are plotted against these values. These particular sets of data have been selected for the test because (*a*) there is every reason to believe that they are accurate, (*b*) the differences between the highest and lowest values of the velocities (or equilibrium constants in case K) are suitably large, and (*c*) data for a whole series of substituted derivatives are available. It is clear from the figure that, when the accurate constants are used, a number of the points fall very near to straight lines (the continuous lines in Fig. 2), but also that there are still serious divergences. It might be urged that, in G, H, and L, these *could* be attributed to variations in the non-exponential term of the Arrhenius equation, or differences of temperature or medium, but this is certainly not the case in K, where the points refer to the dissociation constants of substituted phenylacetic acids, obtained by a technique and under conditions identical with those employed for the benzoic acids. The linear relationship is clearly only a rough approximation.

The positions of the points referring to *p*-methoxy-substituted compounds show that in some cases (G and H), as would be expected, the electromeric effects are almost proportional to those operating in the benzoic acid series, while in others (K and L) they are not, as would again be anticipated from the different possibilities of transmission. It may be pointed out that Hammett plotted velocities of hydrolysis of phenylacetic esters against the dissociation constants of the *same* acids and not against benzoic acids.

The broken lines in Fig. 2 are those which would be obtained if the coefficients of μ^2 were the same in all cases; these are quite different from the lines (continuous in Fig. 2) which pass most closely to the points for any given reaction. The arrangement of the points round straight lines is thus not an obvious deduction from the dipole-moment relationship.

The use of accurate dissociation constants for the acids of the reference series enables us, therefore, to state the following conclusions with some degree of certainty:

1. A connexion of a roughly linear character exists, in a number of cases, between the values of log *k* for the same reaction of a series of *m*- or *p*-substituted benzene derivatives and those of log *K* for the corresponding benzoic acids.

2. This connexion does not follow from the known relationships of velocity coefficients

and dissociation constants with dipole moments; it may, perhaps, arise from the approximate balancing of opposing effects.

3. In some reactions electromeric effects cause divergence from the linear relationship, exactly as they do from the dipole-moment expression; clearly, this must occur except in cases where identical paths are available, in the compounds compared, for the transmission of these effects.

4. The relationship of reaction velocities either with dissociation constants or with dipole moments is no doubt conditional upon the absence of serious variations in the non-exponential term of the Arrhenius equation.

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