364. *Relations between Electrostatic Potentials and Reaction Velocities.*

By H. O. Jenkins.

In the alkaline hydrolysis of a series of benzoic esters, a linear relation has been discovered between the energy of activation and the electrostatic potential at the carbon atom to which the carbethoxy-group is attached. The slope of the line is approximately given by Ne, Faraday's constant, where N is the Avogadro number, and e is the electronic charge, thus offering a real proof that the electrical interpretation of the reaction is the correct one. Reactions are discussed in which the permanent mesomeric effect is directly proportional to the inductive effect.

The general problem of the influence of substitution on reaction veloctity has received much attention. Since $k = PZe^{-E/RT}$ it is usual to analyse the velocity coefficient into its component parts PZ and E and attempt to correlate either of these with some property of the substituent. In the event that series of reactions exist with constant PZ or E, then log k is a legitimate function to use for correlation. It is probable that relations will be discovered if only one of the variables in the Arrhenius equation varies systematically.

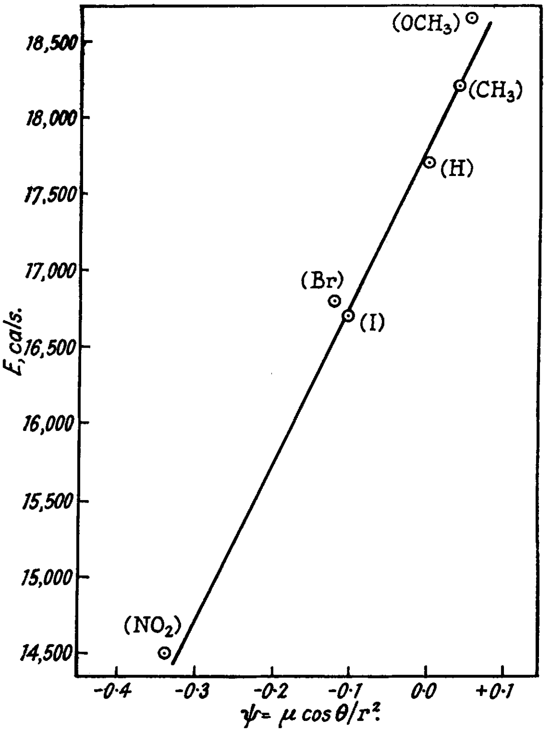
The first quantitative attempt to link the polarity of the substituent with changing velocity constant was made by Watson and his collaborators. (Mention should, however, be made of the work of Waters, J., 1933, 1551.) Evans (J., 1933, 890; *Trans. Faraday Soc.*, 1938, **34**, 165) and Morgan and Watson (J., 1935, 1174), following on the work of Nathan and Watson (J., 1933, 890, 1248), found that, in three cases for series of *m*- and *p*-substituted benzene derivatives undergoing reaction, the expression $E = E_0 - c(\mu + b\mu^2)$ held, where μ was the electric dipole moment of the corresponding monosubstituted benzene. Again, since the non-exponential term of the Arrhenius equation did not vary seriously, this was equivalent to $\log k = \log k_0 + y(\mu + x\mu^2)$. This equation has the following limitations.

First, since electric dipole moments are vector quantities, it cannot be strictly correct to correlate simply the moment of the monosubstituted benzene derivative with the reaction velocity or energy of activation without taking account of distance or direction. Secondly, no attempt was made to deal with *o*-derivatives.

Ingold and Nathan (J., 1936, 222) studied the bimolecular reaction between hydroxyl ion and substituted derivatives of ethyl benzoate and confined themselves to *p*-compounds. Here, in contradistinction to Watson, Moelwyn-Hughes (*Trans. Faraday Soc.*, 1938, **34**, 94) believes that an approximate linear relation exists between E and μ. It may be pointed out that the interpolation performed by the last author at that point of the graph where the substituent is hydrogen, gives, not the moment of the $C_{ar.}$–H link as 0·27 ± 0·13, but this value for the moment of benzene. A novel method for calculating this moment has not been found. It should be remembered also that NH_2 and OCH_3 are inclined groups.

Brönsted and Pedersen (*Z. physikal. Chem.*, 1924, **108**, 185) were the first to demonstrate that a relation existed between the rate constant of a base-catalysed reaction and the equilibrium constant of the base. Their equation was $\log k = x \log K + C$. Hammett (*J. Amer. Chem. Soc.*, 1937, **59**, 96) has very largely extended this work and has generalised the relation to the equation $\log K = \log K^0 + \sigma\rho$, where K is a rate or equilibrium constant for a substituted reactant, K^0 the corresponding quantity for the unsubstituted compound, σ a substituent constant, and ρ a reaction constant. Hammett's equation holds for *m*- and *p*-derivatives only. It is believed that a substituent in the *o*-position exerts an influence whose governing laws and mechanism are entirely different from those concerned in the effect of more distant substituents. Recently, relations have been shown to exist between the electrostatic potential due to the substituent dipole, at the carbon atom to which a hydroxy-, amino-, or carboxy-group is attached, and the basicities or acidities of the corresponding phenols, anilines, or carboxylic acids (H. O. Jenkins, this vol., pp. 640, 1137). The normality of the strengths of some *o*-substituted anilines, phenols, and acids was demonstrated, and a proof given in the aniline and phenol series of the proportionality, as between one nuclear position and another, of the mesomeric to the inductive effect. On account of the Brönsted–Pedersen, Hammett, and Watson relations, it seems natural to seek for correlations between the electrostatic potential $\psi = \mu \cos \theta / r^2$ and some component of the Arrhenius equation. Typical reactions are considered.

FIG. 1.

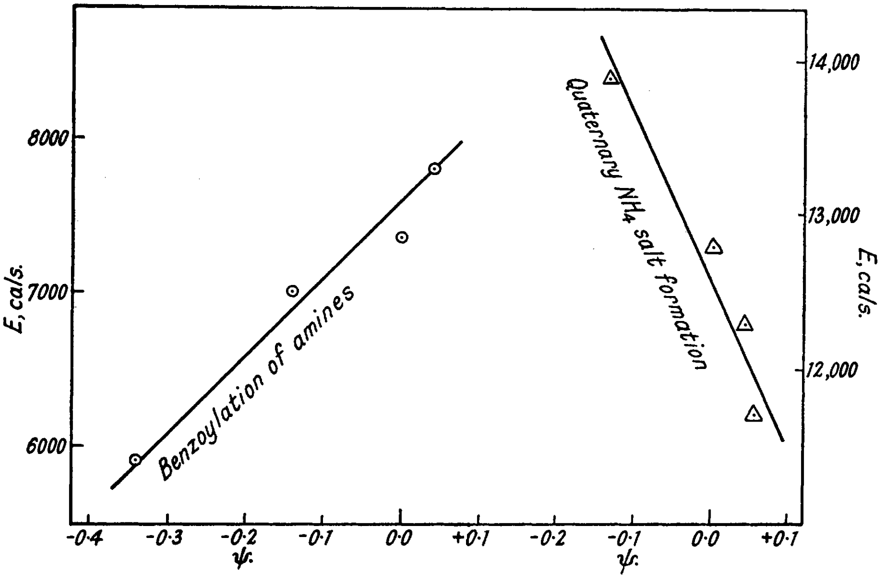


Alkaline Hydrolysis of Benzoic Esters.—The results of Ingold and Nathan (*loc. cit.*) in 60% aqueous-alcoholic solution are given below, together with the calculated electrostatic potentials at the carbon atom to which the carbethoxy-group is attached. As in previous papers (H. O. Jenkins, *loc. cit.*), r values have been obtained by using Pauling and Huggins' table of interatomic distances (*Z. Krist.*, 1934, **87**, 205) and Brockway's values (*Ann. Reports*, 1937, **34**, 197); θ has in each case been calculated trigonometrically. The calculated potential is a constant, the same for every reaction. It will be seen that a plot of these results (Fig. 1) indicates that a linear relation exists between E and ψ which can be expressed in the form $E = a + b\psi$. Linearity would also be expected if a mesomeric effect were present proportional to the inductive effect (H. O. Jenkins, *loc. cit.*). An attempt has been made to deal with ethyl *p*-methoxybenzoate by special treatment. It is well known that in the hydrolysis and in determining the strength of the acid, the powerful mesomeric effect takes control. Now, if this effect can be calculated, its potential can be evaluated in an exactly similar manner. Groves and Sugden (J., 1937, 1995) have given a method for calculating μ_{Me} in anisole which acts through the plane of the benzene ring along the X axis. Using their nomenclature, we have $\mu_x = \mu_{Me} + 1{\cdot}45$ with $\mu_{Me} = -0{\cdot}40$ and $-2{\cdot}50$. Taking the larger value, since clearly the mesomeric effect takes control, we have $\mu_x = -1{\cdot}05$. This value can be used to calculate ψ, and since the dipole must be located, it is arbitrarily put at the oxygen atom. The C–O distance has been taken as 1·38 A. It is not claimed that great accuracy is achieved by this calculation, although it is seen the *p*-methoxy-point falls on the same straight line as that given by the other compounds.

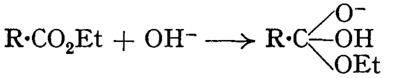
p-Substituent	OCH_3	CH_3	H	Br	I	NO_2
E (cals.)	18,650	18,200	17,700	16,800	16,700	14,500
ψ (D.)	+0·058	+0·040	±0·000	−0·122	−0·103	−0·339

The slope of the line, when Napierian logarithms are used, is $10{,}500 \times 2{\cdot}3 \times 4{\cdot}2 \times 10^7 \times 10^2 = 10{\cdot}1 \times 10^{13}$ ergs/mol./abs. unit of potential.

FIG. 2.



This gives the decrease in activation energy per mole in ergs when a substituent is introduced which alters the electrostatic potential at the carbon atom to which the carbethoxy-group is attached, by one absolute unit of potential. Now the alkaline hydrolysis of an ester depends on the slow reaction

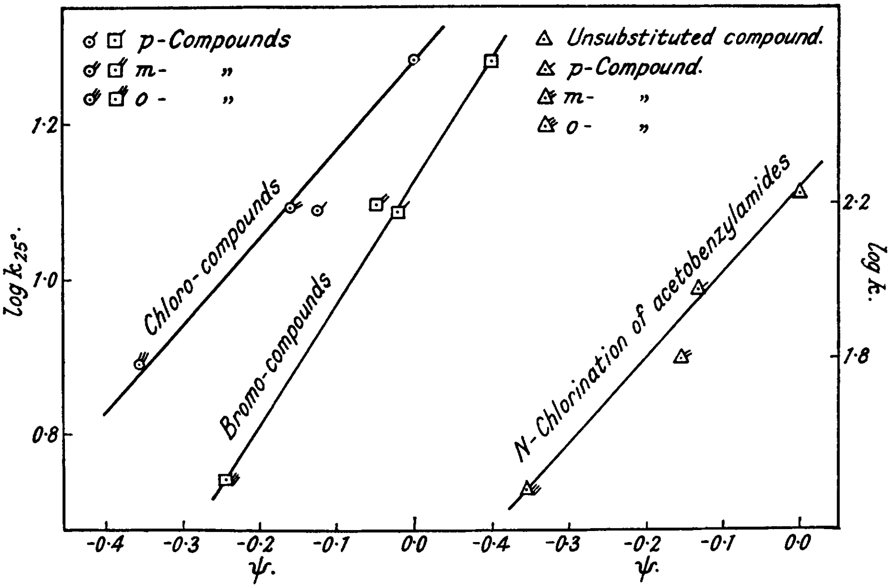


$$R{\cdot}CO_2Et + OH^- \longrightarrow R{\cdot}C\begin{cases}O^-\\OH\\OEt\end{cases}$$

which is facilitated by electron-attracting groups. The work done in bringing up 1 g.-mol. of hydroxyl ions through one absolute unit of potential is $\boldsymbol{Ne}$ (Faraday's constant) where $\boldsymbol{N}$ is the Avogadro number and $\boldsymbol{e}$ is the electronic charge ($4{\cdot}77 \times 10^{-10}$ e.s.u.). On evaluation we have $\boldsymbol{Ne} = 28{\cdot}9 \times 10^{13}$ ergs/mol./abs. unit potential. This is of the same order of magnitude as the experimental slope of the energy of activation–potential line, indicating that the change in the energy of activation is almost entirely accounted for by the work term in bringing up the hydroxyl ion against the dipole field. This is a real proof that the electrical interpretation of the reaction is the correct one. Fig. 2 shows similar plots for the benzoylation of amines (Williams and Hinshelwood, J., 1934, 1079) and for quaternary ammonium salt formation (Laidler, J., 1938, 1786). In each case, a linear relation exists between E and ψ. *o*- and *p*-Compounds have not been included in the above correlations. The results of Timm and Hinshelwood (J., 1938, 862) for the acid hydrolysis of esters can be interpreted in a similar manner, since they found $E_{\text{acid}} = \alpha \Delta E_{\text{alkaline}}$.

Hydrion-catalysed Esterification of Substituted Benzoic Acids.—Hartman and Borders (*J. Amer. Chem. Soc.*, 1937, **59**, 2107) have studied the effects of polar groups on esterification velocities, and interpreted their results in the light of the Hammett relation without considering the *o*-derivatives; E appears to be roughly constant in the halogeno-series, but an inspection of the velocities indicates that it is the inductive effect that matters, although no real proof of this has been offered. Doubt is sometimes cast on the polar mechanism of esterification in aliphatic series because the hydrion-catalysed esterifications of both trichloroacetic and trimethylacetic acids are slower than that of acetic acid. If we assume that either PZ or E is constant, it is legitimate to plot log k_{25° against $\psi = \mu \cos \theta / r^2$, and this has been done for the chloro- and bromo-series in Fig. 3. It is clear that a linear relation exists between log k_{25° and ψ which extends to the *o*-acids, also indicating some small systematic variation of the probability factor or energy of activation with dipole potential.

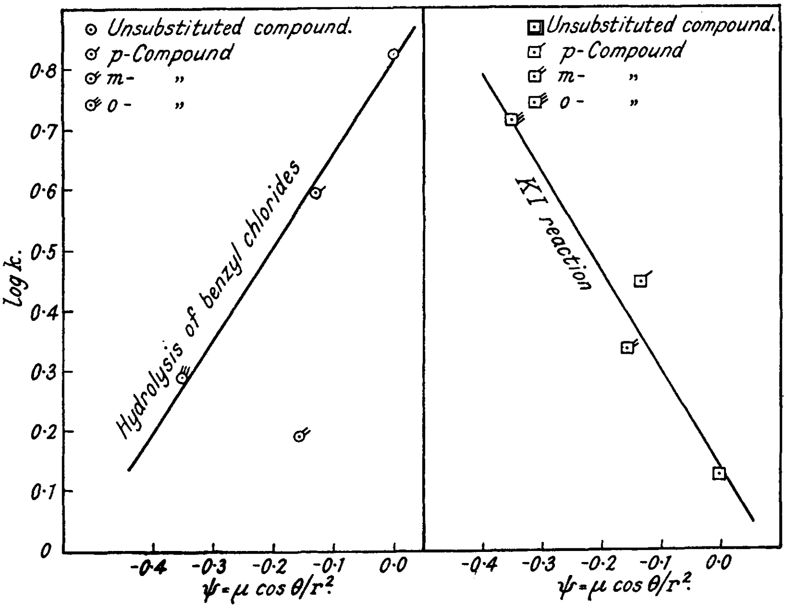
FIG. 3.



Reactions with Substituted Benzyl Chlorides.—Bennett and Jones's data (J., 1935, 1815) for the acid hydrolysis of chloro-substituted benzyl chlorides in 50% aqueous acetone, and for the reactions of the same compounds with potassium iodide are plotted in Fig. 4. These two series of reactions are of opposed polar type or are reciprocal processes. The speed of the acid hydrolysis depends on the rate of elimination of a chlorine ion, and the speed of the potassium iodide reaction on the rate of attachment of a negative iodine ion to the benzyl chloride molecule (Bennett and Berry, *loc. cit.*, and J., 1927, 1676). It is to be noticed that the *o*-compounds react quite normally. Since the slopes of the log k–ψ lines should be proportional to the work gained or done in removing a chlorine ion or attaching an iodine ion against the dipole field of the substituent, they should be approximately the same in the two series of reactions : Fig. 4 shows that this expectation is obeyed. Bennett and Jones (*loc. cit.*) discerned the operation of the mesomeric effect in the hydrolytic reactions, and this permanent mesomeric effect is clearly seen in Fig. 4, where the linearity is obeyed only by *o*-, *p*-, and unsubstituted benzyl chlorides. This means that there is a direct proportionality of the mesomeric to the inductive effects, as between one nuclear position and another

(H. O. Jenkins, *loc. cit.*). This proportionality no doubt holds in many other reactions, and another instance is seen in the *N*-chlorination of acetobenzylamides (Williams, J., 1930, 37) (see Fig. 3).

FIG. 4.



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