**INTRODUCTION**

Organic compounds can be prepared with structural variation in the vicinity of a reaction centre and thus it is possible to allow an almost continuous variation in its electrophilic or nucleophilic character. This capacity may then be used as a delicate probe into the effects caused by electronic perturbation upon reaction and from which the electronic demands of the reaction may be inferred. Many rate constants and equilibrium constants for organic reactions in solution have been measured and the spectra ( IR, UV, NMR etc. ) of thousands of organic compounds have been recorded. As this body of quantitative results has been enormous, it becomes important to summarize and analyse data. The summarizing has involved the development and application of empirical correlations by means of which one body of data can be related to another. At the same time, the data may be analysed to reveal the fundamental factors underlying the phenomena in question. This general approach is commonly known as correlation analysis.

One of the most successful and intensively investigated empirical relationships towards quantitative exploration of reactivity in organic chemistry is the famous Hammett equation.1-15 The Hammett equation describes linear relationship involving log k or log K of substituted benzoic acids. Such correlations may be described as rate-rate, equilibrium-equilibrium or rate-equilibrium relationships. These relationships are usually referred to as Linear Free Energy Relationships (LFER). The term LFER has often been used to cover the whole correlation analysis in organic chemistry. A brief account of correlation analysis is given below:

**The Hammett equation**

The Hammett equation3,12,14,15 is usually expressed in the form of equations (1) and (2), where k or K is the rate or equilibrium constant respectively for a side-chain reaction of *meta*- or *para*-substituted benzene derivative.

log k = log ko + ρσ (1)

log K = log Ko + ρσ (2)

The symbol ko or Ko denotes the statistical quantity approximating to k or K for the unsubstituted or parent compound. The empirical constant σ, known as substituent constant, measures the polar effect relative to hydrogen as a substituent in the *meta*- or *para*- position and is, in principle, independent of the reaction. The other constant ρ, known as reaction constant, depends on the nature of the reaction and measures the susceptibility of the reaction to polar effects. The value of ρ is determined by the reaction and its condition such as reagent, solvent, catalyst and temperature and is independent of the nature of the substituents. The ionization of benzoic acids in water at 25o C is taken as the standard reaction for which ρ is defined as 1.00. The value of σ for a given substituent is thus log (ka/kao), where ka is the ionization constant of the substituted benzoic acid itself. The magnitude of ρ measures the extent of transmission of the electronic effect of substituents. The validity of the above equations (1) and (2) is restricted to substituents in the *meta*- and *para-* positions of the benzene ring. These equations (1) and (2) were tested by Hammett15 on fifty-two reaction series, and found to express a large body of experimental data with a mean deviation of about ±15 percent.

The electron density at the reaction site is determined by the ability of the substituent to withdraw or donate electrons and is measured by σ constants. Electron-attracting substituents have positive values of σ and electron-releasing substituents have negative values of σ . The σ scale covers roughly the numerical range 0 ± 1.0.

A reaction which is facilitated by reducing the electron density at the reaction centre has a positive value of ρ and one facilitated by increasing the electron density at the reaction centre has a negative value. The ρ scale covers roughly 0 ± 4. The sign of ρ in radical reactions cannot easily be predicted. However, the electron distribution in the transition state of radical reactions can be inferred from the experimental value. The dependence of ρ on temperature has the form16,17 of equation (3).

ρ = constant (1- β/T) (3)

The slope of ρ vs T-1 plot is usually positive,8 so that ρ decreases with temperature. The slope is usually small even almost zero18,19 but steep dependence20 and even reversal ones8 have also been described.

The dependence of ρ on solvent21-23 is very marked but is not well understood theoretically. It seems that the effect of solvent cannot be described by a single parameter equation.

Of the factors controlling the absolute values of ρ, the distance of the substituents from the reaction centre is the most important, more exactly it is the length and nature of the side chain. When the side-chain is extended by inserting in it a group Y, the constant ρ decreases in the ratio ЛY (the transmission factor) defined in equation (4)

ЛY = ρYZ / ρZ (4)

Where ρYZ is the reaction constant for the compound of the type Ar-Y-Z and ρZ is the reaction constant for the compound of the type Ar-Z.

The value of Л indicates the ability of the chain to transmit polar effects;24-27  however, in order to obtain results of general validity, π must be independent of the reaction centre chosen (Z), as indicated in (5).

ρYZ / ρZ = ρYZ ’ / ρZ ’ (5)

The equation (5), the so called ρ – ρ relationship, has been shown to hold in the dissociation of carboxylic acids, their reactions with diazodiphenylmethane and hydrolysis of their esters.25-29 For the insertion of a CH2 group in Ar-Z, π corresponds to the value of about 0.419,30 and with two CH2 groups it decreases to ca. 0.2.8,27,29 Replacing one CH2 group by a hetero atom (oxygen27,31,32 or Sulphur31,33,34 ), a sulphoxy,31,33 a sulphonyl group31,33 or an amino group35,36 has little effect on the value of π.

Conjugated chains transmit polar effects much better than saturated chains. A CH=CH group is approximately equivalent to one CH2 group.25,27,37,38

Transmission through the C≡C group is similar39 to that of the C=C bond but it is weaker than through the CH=CH group.27,40,41 Even longer conjugated chains transmit electronic influence effectively.42-45

As early as 1953, Jaffe8 examined the application of the Hammett equation to about 400 reaction series and on the basis of correlation coefficient concluded that about 70% of the correlations were satisfactory (r > 0.95) or excellent (r > 0.99). This suggests that about 30 % of the rate or equilibrium data are outside the scope of the Hammett equation in its original form and mode of application.

Deviations are commonly shown by *para*-substituents of cconsiderable +R or -R effect. When σ values based on the ionization of benzoic acids are used, deviations may occur with highly electron-withdrawing *para*-substituents (+R substituents) for reactions involving -R electron-rich reaction centres are with highly electron-releasing substituents (-R substituents) for reactions involving +R electron-poor reaction centers. These deviations, have been explained in terms of ‘cross conjugation’ i.e., conjugation involving substituent and reaction center. In each case ‘exalted’ σ values are required for conformity to the Hammett equation. The special substituent constants for +R substituents are denoted by σ – and those for -R substituents are denoted by σ +.46 The values of σ – are based on the ionization of either anilinium ions or phenols in water. The values of σ + are based on the rates of solvolysis of t-cumyl chlorides in 90 % acetone-water at 25o C.

The use of σ + and σ –  greatly extends the range of applicability of the Hammett equation.47-49 However, the contribution of the resonance effect of a substituent relative to its inductive effect must, in principle, vary continuously as the electron-demanding quality of the reaction center varies, i.e., demanding upon whether it is electron-rich or electron-poor. Hence for each substituent having a resonance effect, a sliding scale of substituent constants would be expected and not just a pair of discrete values of σ + and σ for -R substituents or σ –  and σ for +R substituents. This tends towards the situation in which the substituent constant becomes reaction dependent. Therefore, various multimeter extensions of the Hammett equation appeared, notably the Yukawa-Tsuno equation,50,51 the Taft-Lewis equation,52-56 and the Swain-Lupton equation.57

**Multiparameter extensions of the Hammett equation**

Yukawa and Tsuno50 proposed a method for dealing with -R substituents in their influence on reactions which are more electron-demanding than the ionization of benzoic acids. They suggested that values of ( σ+-σ ) would provide a scale of enhanced resonance effects and they modified the Hammett equation as

log k = log ko + ρ[σ +r ( σ+-σ ) ] (6)

The equation (6) implies the multiple linear correlation of log k with σ and ( σ+-σ ). The quantity r is a proportionality constant giving the contribution of the enhanced resonance effect for -R substituents. If r = 0 the equation is reduced to the simple Hammett equation and if r = 1, it corresponds to a straight forward correlation with σ +.

A corresponding equation with σ – constants to deal with the influence of +R substituents on reactions which are less electron-demanding than the ionization of benzoic acids was formulated by Yoshika *et al*.51

log k = log ko  + ρ[σ +r ( σ --σ ) ] (7)

According to Taft52-54 the Hammett σ values are quantitatively separable into inductive and resonance contributions through the following equations:

σm = σI + ασR (8)

σp = σI + σR (9)

The inductive effect given by σI, is assumed to operate equally from the *meta*- and *para*-positions. The resonance effect given by σR, contributes to σm indirectly, α being the “ relay coefficient”. Taft and Lewis53,54 set up a σI scale based on alicyclic and aliphatic reactivities. Based on the ionization of benzoic acid, a value for σ of 0.33 was suggested.

Exner58 carried out a modified analysis based on the following equations:

σm = σI + 0.33 σR  (10)

σp = λσI + σR (11)

The coefficient λ expresses any differences in the operation of the inductive effect as between the *meta*- and the *para*- position. Exner58 was in favour of λ = 1.14 i.e., the inductive effect operates more powerfully from the *para-*position. The dissection of parameters into σI and σR- type contributions gives the possibility of a ‘dual substituent parameter’ treatment for reaction series through an equation.53,54

log (k/ko) = ρI σI + ρR σR (12)

In Taft’s treatment, each substituent is characterized by position-independent σI  and σR values, but the susceptibility to inductive and to resonance effect is to be expressed separately through position-dependent ρI  and ρR values. The separation into inductive and resonance effects has been performed for σ+, σ- and σo (based on ‘insulated’ system) constants to give σR+, σR- and σRo respectively.

Swain and coworkers57,59 have expressed the polar effect of any given substituent in terms of two basic characteristics: a field constant, F, and a resonance constant, R. All the various σ constants are the linear combinations for F and r of the form (13)

σ = f F + Rr (13)

The field, f, and resonance, r, are weighting factors which give the blend of field and resonance effects for the systems used to define the particular σ scale. This treatment has found extensive application in the correlation analysis of NMR data. Application to chemical reactivity seems to be restricted to a few instances.

**Correlation with spectroscopic data**

Though correlation of the substituent constant σ was originally proposed to equilibria and reaction rates, the substituent constants have also been applied to optical spectroscopy,60 NMR spectroscopy6,7 and to mass spectroscopy of organic compounds.61 Thus correlations of infrared frequencies62-65 with substituent constants and also of 1H and 13C NMR substituent-induced chemical shifts (SCS)66-74  have received considerable attention. Substituent effects in the mass spectra of organic compounds are also often explained with the Hammett σ constants.61,75-78

**Correlation with electrochemical properties**

The free energy relationship obtained by polarographic studies differs from that obtained from most other physical methods.85,86 The half-wave potentials of reversible systems are equivalent to logarithms of equilibrium constants, whereas those of irreversible systems are proportional to logarithms of rate constants. Hence the application of half-wave potentials in extra thermodynamic relationships is not merely empirical but is a logical extension of the treatment of kinetic and equilibrium data.

Cyclic voltammetry, a popular tool in the **last thirty years** for studying electrochemical reactions has been employed by organic chemists in the study of biosynthetic reaction pathways87 and studies of electrochemically generated free radicals.88 An increasing number of inorganic chemists have been using cyclic voltammetry to evaluate the effects of ligands on the oxidation/reduction potentials of the central metal ion in complexes and multinuclear clusters.89 This type of information plays an integral part in many of the approaches directed toward solar energy conversion90 and in model studies of enzymatic catalysis.91 Knowledge of the electrochemistry of a metal complex can be useful in the selection of the proper oxidizing agent to put the metal complex in an intermediate oxidation state.92 Electrochemical methodology has also been exploited as a novel means of introducing functional groups and removing blocking agents.93

In the reaction series of the type x-Ar-R, if R is the electroactive group and X is the substituent in *meta*- of *para*- position, it is possible to write the equation (14)94

( E1/2 )XR = ρR σX + ( E1/2 ) HR (14)

In the equation (14), ( E1/2 )XR  is the half-peak potential of the substituted compound and ( E1/2 ) HR is that of the parent compound. ρR is the proportionality constant, called the reaction constant, expressed in volts, that characterizes the susceptibility of the electroactive group R on a benzenoid ring to the effect of substituents placed in *meta*- or *para*- positions on the ring. Its value is dependent on the nature of the electroactive group, R, on the composition of the supporting electrolyte, on temperature and on other experimental conditions. It is independent of the kind and position of the substituent. σX is the Hammett substituent constant.3

There are many articles that deal with the theory and practice of modern voltammetry in depth.95-97 Many authors have reported the substituent effects on peak potential measured by cyclic voltammetry.98-103