❖ The Hammett Equation and Linear Free Energy Relationship

In this section, we will discuss the quantitative treatments of the effect of structure on reactivity i.e. how the resonance effect, field-effect, and steric effect impact the reaction rate in measurable numbers.

➢ *The Hammett Equation*

Consider an organic reaction is carried out on a substrate which can be denoted as XRY, X a variable substituent and Y is the reaction spot, and R represents the basic substrate structure. In this type of case, replacing X = H with X = CH_3 results in an increment in the rate of reaction up ten times. However, it is still a mystery what part of the rate enhancement comes from resonance effect, field-effect, or steric effect. To do so, it is reasonable to use compounds where one or two effects are so small that they simply can be neglected. Although it is the oversimplification of the problem, quantitative results can still be obtained. The Hammett equation is the first attempt to give numerical values for the quantitative treatment of structure on reactivity. Hammett proposed the equation for the cases of *m*- and *p*-XC_6H_4Y as given below.

$$\log\frac{k}{k_0} = \sigma\rho \tag{23}$$

where k and k_0 are the constant for the group X ≠ H and X = H; ρ and σ are the constants for reaction conditions and substituent X, respectively.

➢ *Derivation of Hammett Equation*

To derive the Hammett equation, we need to recall the quantitative relationship between the structure and reactivity first. To do so, we need to find some mathematical parameter that can be used to represent the combined magnitude of inductive and resonance effects of different substituents. This can be achieved by considering the hydrolysis of a series of different benzoic acids as given below.

$$XC_6H_4COOH + H_2O \overset{K_a}{\rightleftharpoons} XC_6H_4COO^- + H_3O^+ \tag{24}$$

Where X is a substituent at the *m*- or *p*-position and K_a is the dissociation constant. As expected, the dissociation constant was found to be different for differently substituted substrates.

Since an electron-withdrawing group will better stabilize the conjugate base (i.e., $XC_6H_4COO^-$), resulting in a larger magnitude of K_a (lower pK_a). On the other hand, an electron-donating group will destabilize the conjugate base (i.e., $XC_6H_4COO^-$), resulting in a smaller magnitude of K_a (higher pK_a). Therefore, we can say that the electronic effect (inductive plus mesomeric effect) of a substituent can be represented as the difference between the pK_a value of its benzoic acid derivative and the pK_a value of benzoic acid itself; mathematically, we can say

$$\sigma_X = \log(K_a) - \log(K_a)_0 = -p(K_a) + p(K_a)_0 \tag{25}$$

Where the parameter σ_X (or simply σ) is called as substituent constant; and was found for several different groups just subtracting its benzoic acid derivative's pK_a value from pK_a value of benzoic acid.

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Table 1. pK_a values and substituent constants for XC_6H_6COOH using benzoic acids $p(K_a)_0 = 4.21$.

Substituent	$p_m(K_a)$	$p_p(K_a)$	$\sigma_m = p(K_a)_0 - p_m(K_a)$	$\sigma_p = p(K_a)_0 - p_p(K_a)$
NO_2	3.50	3.43	0.71	0.78
CH_3	4.28	4.38	−0.07	−0.17
OCH_3	4.09	4.48	0.12	−0.27
$CH(CH_3)_2$	4.28	4.36	−0.07	−0.15
F	3.87	4.15	0.34	0.06
Br	3.82	3.98	0.39	0.23
Cl	3.84	3.98	0.37	0.23
I	3.86	3.93	0.35	0.28
$COCH_3$	3.83	3.71	0.38	0.50

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Using $\log m - \log n = \log m/n$, equation (36) can also be written as

$$\log \frac{(K_a)}{(K_a)_0} = \sigma \tag{26}$$

Now if we plot a curve between $\log(K_a)/(K_a)_0$ vs σ, we will definitely get a straight line with a slope = 1.

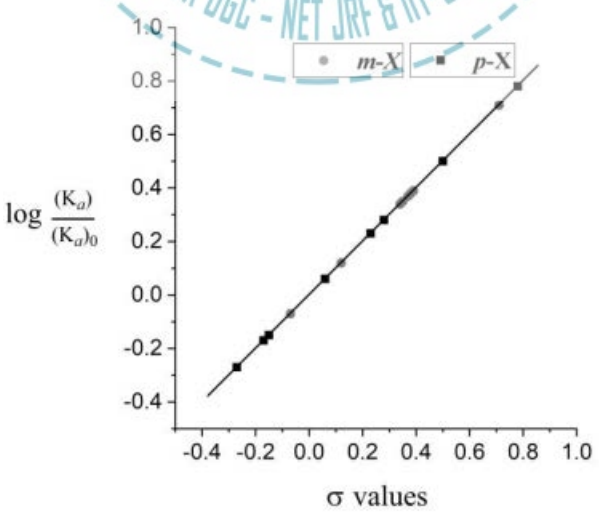

Figure 17. Variation of $\log(K_a)/(K_a)_0$ vs σ for substituted benzoic acids.

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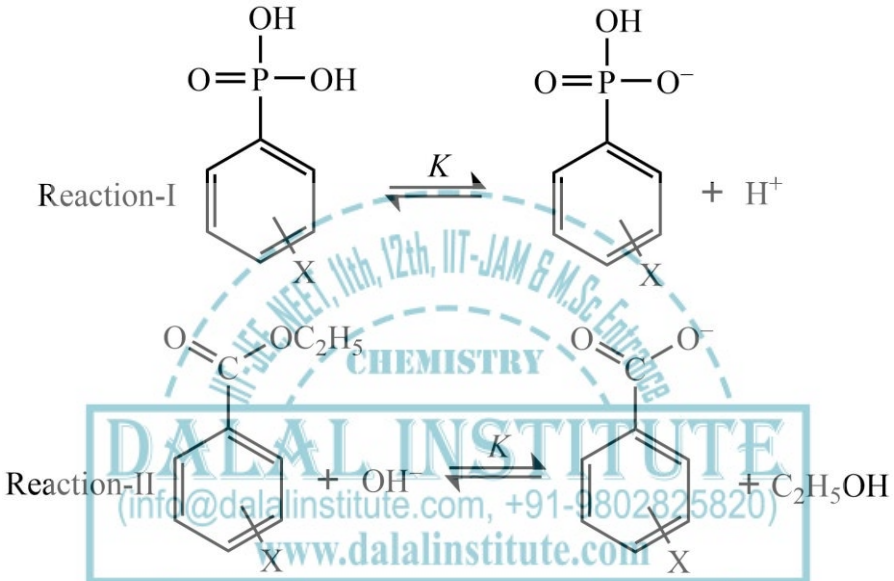
Now we need to check if these σ values (i.e., of substituted benzoic acids) can also be used for other meta- or para-substituted benzene derivatives. To do so, consider two series of reactions; the first one is the acid dissociation of phenyl phosphonic acid, and the second one is the base hydrolysis of substituted ethyl benzoate. Here we will find if different substituents affect their dissociation constants or rates in the same manner as affected in the case of substituted benzoic acid. Also, we did not use ortho-substituents or substituents in the aliphatic system because they also contain steric factors and don't not linear variation.



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The experimental $\log(K_a)/(K_a)_0$ for the reaction-I and experimental $\log k/k_0$ for reaction-II are given below.

Table 2. Experimental values of $\log(K_a)/(K_a)_0$ and $\log k/k_0$ for the acid dissociation of phenyl phosphonic acid and base hydrolysis of substituted ethyl benzoates, respectively.

Substituent	*meta*-$\log(K_a)/(K_a)_0$	*para*-$\log(K_a)/(K_a)_0$	*meta*-$\log k/k_0$	*para*-$\log k/k_0$
NO_2	0.53	0.59	1.83935	2.06423
Br	0.29	0.23	–	–
Cl	0.28	0.17	0.88536	0.63347
CH_3	–	−0.15	−0.16115	−0.34679
OCH_3	–	–	–	−0.67923

When plotted the experimental $\log(K_a)/(K_a)_0$ for the reaction-I and experimental $\log k/k_0$ for reaction-II vs the substituent constants obtained for the substituted benzoic acids, we get the following curves.

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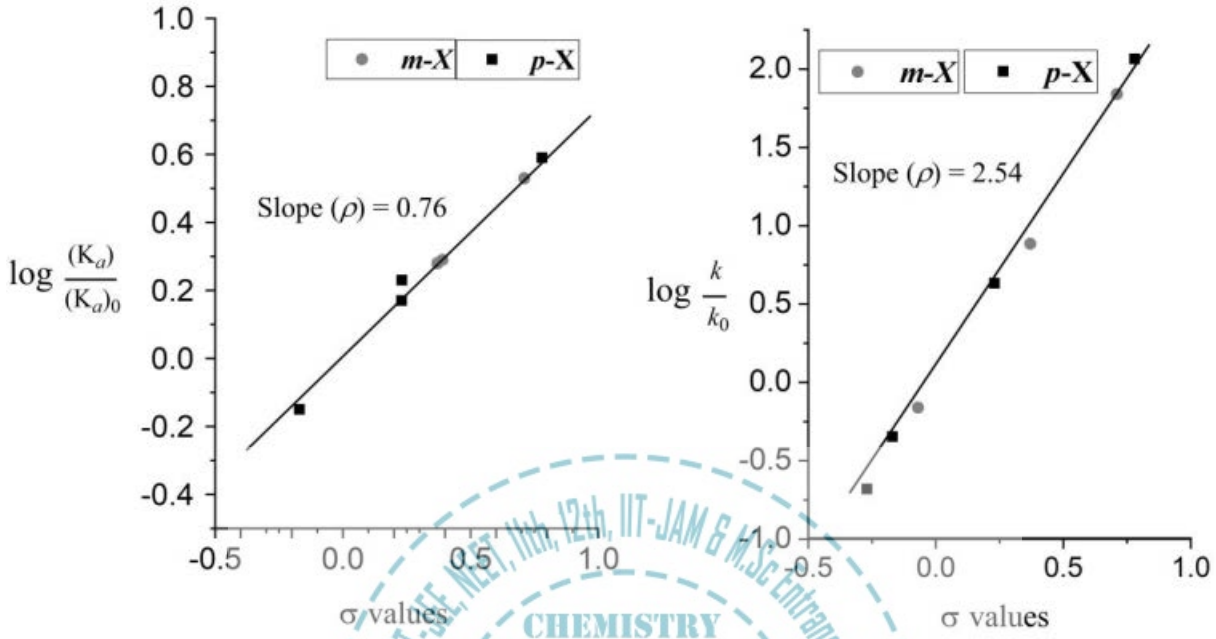

Figure 18. $\log(K_a)/(K_a)_0$ and $\log k/k_0$ vs σ for reaction-I and reaction-II.

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It is obvious that the plots are still linear like in Figure 3 but the slope has changed. This implies that the order and relative effects for different substituents on both reactions remain the same though the magnitude has been changed which can be attributed to the different nature reaction considers from 'base reaction'.

Therefore, our aim, in this case, should be the determination of the slope (let us say ρ). Since on the vertical side we have '$[\log(K_a)/(K_a)_0]_{sppa}$' for reaction-I (acid dissociation of phenyl phosphonic acid) and on the horizontal side we have 'σ *or* $[\log(K_a)/(K_a)_0]_{sba}$' for base reaction (hydrolysis of substituted benzoic acid), the slope should be

$$\rho = \frac{[\log(K_a)/(K_a)_0]_{seb}}{[\log(K_a)/(K_a)_0]_{sba}} \tag{27}$$

or

$$\rho[\log(K_a)/(K_a)_0]_{sba} = [\log(K_a)/(K_a)_0]_{seb} \tag{28}$$

But from equation (26), we know that $[\log(K_a)/\log(K_a)_0]_{sba} = \sigma$; and therefore, equation (40) takes the form

$$\left[\log\frac{(K_a)}{(K_a)_0}\right]_{seb} = \rho\sigma \tag{29}$$

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$$\log K_a = \rho\sigma - \log (K_a)_0 \tag{30}$$

Similarly, on the vertical side we have '$\log k/k_0$' for reaction-II (base hydrolysis of substituted ethyl benzoate) and on the horizontal side we have '$\sigma\ or\ [\log(K_a)/(K_a)_0]_{sba}$' for base reaction (hydrolysis of substituted benzoic acid), the slope should be

$$\rho = \frac{[\log k/k_0]_{seb}}{[\log(K_a)/(K_a)_0]_{sba}} \tag{31}$$

or

$$\rho[\log(K_a)/(K_a)_0]_{sba} = [\log k/k_0]_{seb} \tag{32}$$

But from equation (26), we know that $[\log(K_a)/\log(K_a)_0]_{sba} = \sigma$; and therefore, equation (32) takes the form

$$\left[\log\frac{k}{k_0}\right]_{sppa} = \rho\sigma \tag{33}$$

For any reactions,

$$\log k = \rho\sigma - \log k_0 \tag{34}$$

The results given by equation (29, 30, 33, 34) are called as Hammett's equations; which shows that the rates of ortho and para-substituted benzene derivatives can be obtained if the substituent contents for substituted benzoic acid are known. Now we will discuss the substituent and reaction constants in more detail

- ***Linear Free Energy Relationship (LFER)***

The Hammett equation is a linear free energy relationship that can be proved for any group X by recalling the kinetics of organic reactions is in the framework of "Activated complex Theory", which states that the rate constant (k) for a typical reaction is

$$k = \frac{RT}{Nh}e^{-\frac{\Delta G^*}{RT}} \tag{35}$$

Where ΔG^* is the free energy change of the activation step at temperature T. The symbols R, N, and h are the gas constant, Avogadro number, and Planck's constant, respectively. Similarly, for k_0 we have

$$k_0 = \frac{RT}{Nh}e^{-\frac{\Delta G_0^*}{RT}} \tag{36}$$

After putting the value of equation (35) and equation (36) in Hammett equation (23), we get

$$\log\frac{\frac{RT}{Nh}e^{-\frac{\Delta G^*}{RT}}}{\frac{RT}{Nh}e^{-\frac{\Delta G_0^*}{RT}}} = \sigma\rho \tag{37}$$

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$$\log \frac{e^{-\frac{\Delta G^*}{RT}}}{e^{-\frac{\Delta G_0^*}{RT}}} = \sigma\rho \tag{38}$$

Multiplying both sides by 2.303, we have

$$2.303 \log \frac{e^{-\frac{\Delta G^*}{RT}}}{e^{-\frac{\Delta G_0^*}{RT}}} = 2.303\ \sigma\rho \tag{39}$$

$$\ln \frac{e^{-\frac{\Delta G^*}{RT}}}{e^{-\frac{\Delta G_0^*}{RT}}} = 2.303\ \sigma\rho \tag{40}$$

$$\ln e^{-\frac{\Delta G^*}{RT}} - \ln e^{-\frac{\Delta G_0^*}{RT}} = 2.303\ \sigma\rho \tag{41}$$

or

$$\left(-\frac{\Delta G^*}{RT} \ln e\right) - \left(-\frac{\Delta G_0^*}{RT} \ln e\right) = 2.303\ \sigma\rho \tag{42}$$

or

$$-\frac{\Delta G^*}{RT} + \frac{\Delta G_0^*}{RT} = 2.303\ \sigma\rho \tag{43}$$

Which implies

$$\frac{\Delta G_0^*}{RT} - \frac{\Delta G^*}{RT} = 2.303\ \sigma\rho \tag{44}$$

or

$$\frac{\Delta G_0^* - \Delta G^*}{RT} = 2.303\ \sigma\rho \tag{45}$$

or

$$\Delta G_0^* - \Delta G^* = 2.303 RT\ \sigma\rho \tag{46}$$

or

$$-\Delta G^* = 2.303 RT\ \rho\sigma - \Delta G_0^* \tag{47}$$

Hence, the variation of negative of the free energy of activation varies linearly with slope $2.303 RT\rho$ and $-\Delta G_0^*$ as intercept.

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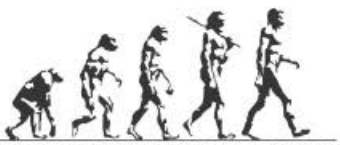

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Volume I

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