

❖ Quantitative Treatment of Reactivity in Substrates and Electrophiles

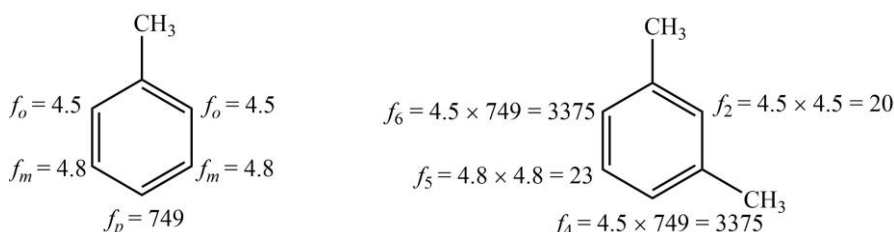
The quantitative treatment of reaction rate in case of electrophilic substitution with reference to substrate structure and attacking electrophile is given below.

➤ *Quantitative Treatments of Reactivity in the Substrate*

Unlike nucleophilic substitution where there is only one leaving group, there are many hydrogens that can leave in electrophilic substitution reactions; and therefore, the quantification of rate-ratios isn't that simple in the later category. For instance, we know the ratio of the total rate of acetylation of toluene to the total rate of acetylation of benzene, but have little to no idea about the rate ratios at individual positions. To do so, we need to carefully analyze the proportion of isomers obtained (for kinetically controlled reactions).

The partial rate factor (for a particular group and a certain reaction) may simply be defined as the rate of substitution at a single site relative to a single site in benzene.

To understand the definition more clearly, consider the case mentioned earlier i.e., acetylation of toluene. The magnitudes of partial rate factors for *o*-, *m*- and *p*-sites are 4.5, 4.8, and 749, respectively; which implies that the overall rate of acetylation of toluene at *p*-site is 749 times faster than what it is at a single site in benzene molecule. However, since there are six positions available in benzene, it will only be 125 (749/6) times faster than the total rate of benzene's acetylation. Furthermore, it is also very important to note that the group is considered as a position-activator if the partial rate factor comes out to be greater than unity, and vice-versa is also true. Hence, we can conclude that the methyl group is definitely a *p*-position activator since the partial rate factor for the same is $749 > 1$. Also, the magnitudes of partial rate factors may vary from reaction to reaction, or in the same reaction at different experimental conditions.



Now, after obtaining the partial rate factors, the ratio of possible isomers (when two or more substituents are attached on the cycle which have presumably independent effects) can be forecasted. For instance, if we consider the case of *m*-xylene, the theoretical values of partial rate factors at each site can be obtained by multiplying those from methylbenzene as shown below. Now we can easily calculate the ratio of different isomeric products arising from the acetylation of *m*-Xylene using the following expression.

$$x_i = f_i / \sum_{i=1}^{i=n} f_i$$

Where x_i and f_i are the mole fraction of isomer arising from the i th type position and 'partial rate factor' for the i th site, respectively.

For instance, the mole fraction of 1-(2,6-dimethylphenyl) ethan-1-one (i.e., 2-isomer) will be obtained by dividing the partial rate factor of the same by the sum of partial rate factors of all positions i.e.

$$x_2 = \frac{20}{20 + 3375 + 23 + 3375} = 0.002944$$

To get the isomeric proportion on the percentage scale, it will be 100 i.e., $0.002944 \times 100 = 0.2944$. Similarly, we can also obtain the percentage of mole fraction for other isomers.

Table 1. Experimental and calculated isomeric mole fractions (%) in the Acetylation of *m*-Xylene.

Site	Experimental	Theoretical
2 nd	0	0.29
4 th and 6 th (same)	97.5	99.36
5 th	2.5	0.34

Finally, the total rate-ratio for the acetylation of *m*-xylene to benzene can also be obtained theoretically sum of all 'partial rate factors' by six i.e.,

$$\text{Rate ratio} = \frac{20 + 3375 + 23 + 3375}{6} = 1132$$

It is pretty much obvious that though the isomeric mole fractions are quite reasonable, the theoretical ratio (1132) is quite different from the actual one 347. This is because the real situation isn't that simple and many other factors like steric hindrance also play an important role.

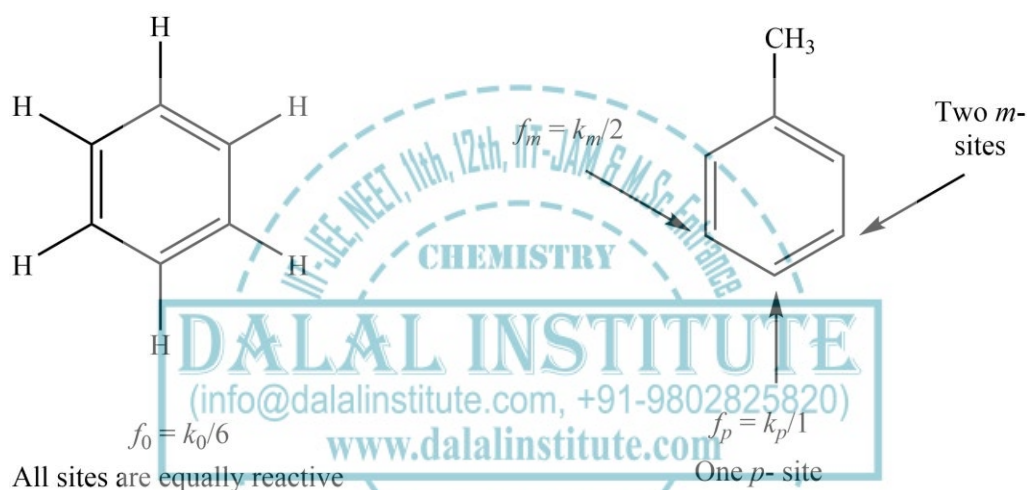
➤ Quantitative Treatment of Reactivity of the Electrophile

Different electrophiles have different magnitudes of reactivity; for instance, the NO_2^+ ion can react with benzene and also with aromatic rings having deactivating substituents, but the diazonium ions react only with aromatic rings having strongly activating substituents. The Hammett equation can be used to analyze this preferred behavior of attacking electrophiles. To do so, recall the general form of Hammett equation for the cases of *m*- and *p*- $\text{XC}_6\text{H}_4\text{Y}$ (X a variable substituent, and Y is the 'reaction spot' not group) i.e.

$$\log \frac{k}{k_0} = \sigma \rho = \log \frac{K}{K_0} \quad (1)$$

where k and k_0 are the rate constants for the substituent X and X = H; ρ and σ are the constants for reaction conditions and substituent X, respectively. The symbol K and K_0 are the equilibrium constant for the group X and X = H. Furthermore, it should also be noted that since the Hammett equation is for monosubstituted benzene rings, the substrate becomes a simple benzene ring if X = H because 'Y' the reaction spot and not any ring-attached group.

However, the equation given above is for overall rate constants (I mean, for all the available sites); and therefore, if we want to use this equation for single-site comparison, we will need to convert overall rates into partial rate factors first. This can be done by dividing k_0 by 6 (benzene has six equivalents 'reaction spots' i. e. Y), and by dividing k by 2 and 1 for *m*- and *p*- electrophile-attack, respectively (C_6H_5X have two meta and one para site). Now one might ask why we would need to convert overall rate constants into 'partial rate factors, then the answer is the same as we have discussed in the previous section; to find isomeric proportions. Now the isomeric proportions proposed by this equation were quite accurate if X is an electron withdrawing in nature. Nevertheless, large deviations were observed X is electron-donating in nature. In other words, partial rate factors derived from k values given by equation (3) weren't very reliable if group X are electron-donating in nature; and therefore, a modification was needed.



An American chemist, H.C. Brown, solved the problem by introducing modified σ -values labeled as σ^+ , where the plus symbol represents a positive charge appearing in the transition state. Substituents with negative and positive σ^+ -values position activating and deactivating, respectively. In other words, the modified equation can be used to rationalize the aromatic substitution at rings with electron-donating, as well as, electron-withdrawing groups.

Now the question arises, what does the parameter ρ correlates because σ (or σ^+) values are almost exclusively correlated with the reactivity of substrate structure in electrophilic substitution. The answer is, it is connected with the reactivity of attacking electrophile and how it affects the overall reaction-stability. Nevertheless, besides the electrophile, ρ -values may also change with the reaction's experimental conditions. A smaller negative ρ -value implies a less reactive electrophile and vice-versa. Furthermore, it should also be kept in mind that this is true only for meta- and para-sites because the Hammett equation isn't applicable to ortho sites.

Brown developed his idea on the basis of the fact that the reactivity of a particular species shows an inverse variation with selectivity. He observed that all the electrophiles can be classified on the basis of their choice of the attack on benzene vs toluene and ortho- vs para positions (in toluene).

Table 2. Comparative reaction rates and products' ratio in some typical electrophilic substitutions on benzene and toluene.

Reaction-type	<i>m</i> -isomer	<i>p</i> -isomer	$k_{\text{toluene}}/k_{\text{benzene}}$
Bromination	0.3	66.8	605
Chlorination	0.5	39.7	350
Benzoylation	1.5	89.3	110
Nitration	2.8	33.9	23
Mercuration	9.5	69.5	7.9
Isopropylation	25.9	46.2	1.8

It is obvious from the above data that if an electrophile prefers to attack toluene over benzene, it will also prefer to attack *p*-site to give major product, and vice-versa. Brown formulated this observation into the following formula.

$$S_f = \log \frac{f_p}{f_m} \quad (2)$$

Where S_f is the selectivity and $f_{p,m}$ are the partial rate factors. The conclusion from equation (2) is that more reactive species tend to attack meta-position rather than para, and vice-versa is also true. Furthermore, it is also possible to modify the Hammett-brown equation using the above result to prove the following.

$$\log f_p = \left(\frac{\sigma_p^+}{\sigma_p^+ - \sigma_m^+} \right) S_f \quad (3)$$

and

$$\log f_m = \left(\frac{\sigma_m^+}{\sigma_p^+ - \sigma_m^+} \right) S_f \quad (4)$$

and

$$S_f = (\sigma_p^+ - \sigma_m^+) \rho \quad (5)$$

Partial rate factors and ρ -values obtained by employing equation (3–4) were quite comparable with experimental data.

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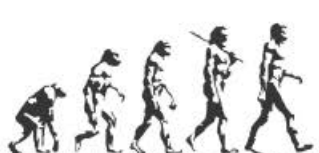
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Volume I

MANDEEP DALAL



First Edition

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