## ❖ Taft Equation

The Taft equation, just like the Hammett equation, is also a linear free energy relationship (LFER) that is employed in physical organic chemistry in the analysis of reaction mechanisms and to develop the quantitative relationships between structure and activity for organic species. Robert W. Taft developed this equation in 1952 as an amendment to the Hammett equation. Nevertheless, unlike the Hammett equation (accounts only for inductive, field, and resonance effects on rate of reaction), the Taft equation also explains the steric effects of a substituent. The mathematical form of the Taft equation is given below.

$$\log \frac{k}{k_0} = \sigma^* \rho^* + \delta E_s \tag{56}$$

where k and k_0 are the constant for the group $X \neq H$ and $X = H$, respectively; ρ^* and σ^* are the modified reaction constants (sensitivity factor for the reaction to polar effects) and substituent X (describes the field and inductive effects), respectively. The symbol δ is the sensitivity factor for the reaction to steric effects, and E_s is the steric substituent constant.

➢ Polar Substituent Constants (σ*)

The polar substituent constants explain the way a substituent affects a reaction pathway via polar (field, inductive, and mesomeric effect) influences. Taft examined the hydrolysis of methyl esters to get σ* values. The idea of using rates of ester hydrolysis to study polar effects was initially proposed by Ingold in early 1930. Esters hydrolysis can proceed via either acid- or base-catalyzed pathway, and both routes involve a tetrahedral intermediate species. During the base-catalyzed pathway, the reactant transforms from a neutral entity to a negatively charged intermediate in the rate-limiting step; whereas in the acid-catalyzed pathway, a positively charged reactant transforms to an intermediate species with a positive charge.

Base Catalyzed Ester Hydrolysis

Acid Catalyzed Ester Hydrolysis
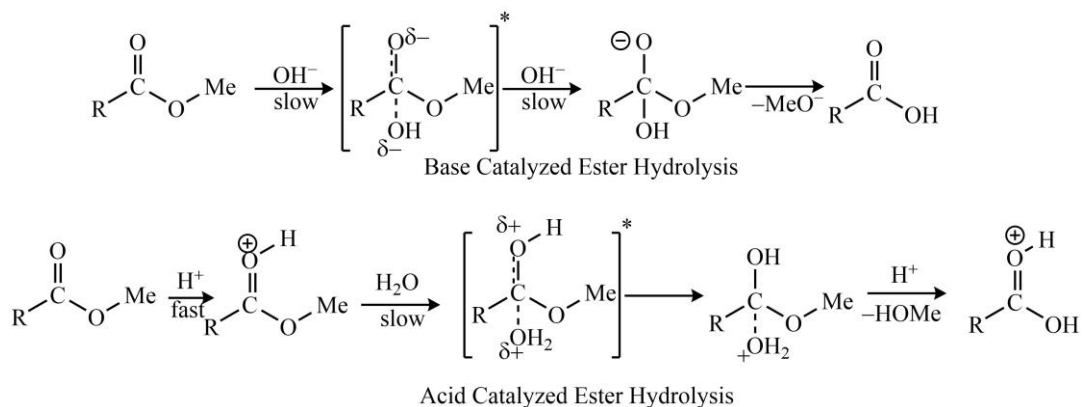
Owing to the same nature of intermediates (tetrahedral), Taft suggested that any steric factors under identical conditions should be approximately the same for the two pathways; and so would not affect the rates' ratio. Nevertheless, since a charge difference is built up in the rate-limiting steps it was suggested that polar effects would only affect the rate of reaction for base-catalyzed transformation because a new charge was created. The mathematical formulation of polar substituent constant (σ*) can be written as given below.:

$$\sigma^* = \frac{1}{2.48\rho^*}\left[\left(\log\frac{k}{k_0}\right)_B - \left(\log\frac{k}{k_0}\right)_A\right] + \delta E_s \tag{57}$$

Where $(\log k/k_0)_B$ represents the ratio of the base-catalyzed reaction rate compared to the reference transformation; whilst $(\log k/k_0)_A$ represents the ratio of the acid-catalyzed reaction rate relative to the reference transformation. The symbol ρ^* shows the reaction constant which explains the sensitivity of the series of reactions. For the base reaction series, we use $\rho^* = 1$ and R = CH$_3$ is set as the reference transformation with $\sigma^* = 0$. The incorporation of 1/2.48 is to make the magnitude σ^* equal σ values given by Hammett.

➢ *Steric Substituent Constants (Es)*

Though the base- and acid-catalyzed esters' hydrolysis yield transition states for the rate-limiting steps which have different densities of charge, their molecular structures differ by 2 H atoms only. Therefore, Taft thought that the steric effects should affect both pathways by equal extent. Owing to this fact, the magnitude of E_s (steric substituent constant) can be obtained from purely the acid-catalyzed pathway since polar effects would be excluded this way. E_s was defined as:

$$E_s = \frac{1}{\delta}\log\frac{k}{k_0} \tag{58}$$

Where symbol δ represents the reaction constant which explains the reaction's susceptibility to steric factor. The values $\delta = 1$ and $E_s = 0$ were used for the definition reaction series. The equation (49) can be combined with equation (48) to write the complete form of the Taft equation. Comparing E_s values for CH$_3$, C$_2$H$_5$, isopropyl, and tert-butyl; it is obvious that it increases with growing steric bulk. Nevertheless, E_s values can deviate from expectation due to steric interactions. For instance, the phenyl's E_s is larger than tert-butyl; however, if we compare these groups using another measure, the tert-butyl will come out to be dominant.

Table 5. Constants used in the Taft equation.

Group	E_s	σ^*
–H	1.24	0.49
–CH$_3$	0	0
–CH$_2$CH$_3$	–0.07	–0.1
–CH(CH$_3$)$_2$	–0.47	–0.19
–C(CH$_3$)$_3$	–1.54	–0.3
–CH$_2$Ph	–0.38	0.22
–Ph	–2.55	0.6

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> ➢ *Sensitivity Factors*

A brief discussion on the nature and significance of all the sensitivity factors used in the Taft equation is given below.

1. Polar sensitivity factor (ρ^*): Just like Hammett's ρ-values, Taft's ρ^*-values describe the reaction's susceptibility to polar effects. If the steric effects of substituents do not influence the rate of reaction significantly, the Taft equation will reduce to Hammett equation as given below.

$$\log\frac{k}{k_0} = \sigma^*\rho^* \tag{59}$$

The ρ^* value can be found by plotting the log of the ratio of the experimental rates (k) to the reference reaction (k_0) vs the σ^* values of different substituents. The slope of such plot will be equal to ρ^*. Just like Hammett's ρ-value:

i) If $\rho^* > 1$, a negative charge will accumulate in the transition state during the reaction, and the reaction will be accelerated by electron-withdrawing substituents.

ii) If $1 > \rho^* > 0$, a negative charge will accumulate in the transition state during the reaction, and the reaction will show mild sensitivity to polar effects.

iii) If $\rho^* = 0$, the reaction will simply not get influenced by polar effects.

iv) If $0 > \rho^* > -1$, a positive charge will accumulate in the transition state during the reaction, and the reaction will show mild sensitivity to polar effects.

v) If $-1 > \rho^*$, a positive charge will accumulate in the transition state during the reaction, and the reaction will be accelerated by electron-donating substituents.

2. Steric sensitivity factor (δ): Just like the polar sensitivity factor, δ or the steric sensitivity factor of reaction explains to what extent the rate of reaction is affected by steric effects. If the polar effects of substituents do not influence the rate of reaction significantly, the Taft equation will reduce to the equation as given below.

$$\log\frac{k}{k_0} = \delta E_s \tag{60}$$

By plotting the log of the ratio rates vs the E_s value of different substituents, we get a straight line with a slope equal to δ. Similarly to Hammett's ρ-value, the magnitude of δ gives the extent of steric effects:

i) If the δ-value is very high, the reaction will be extremely sensitive to steric effects, whereas a smaller δ-value implies that the reaction has little to no sensitivity to steric influence.

Also, owing to larger and negative E_s-values for bulkier substituents, we may conclude that the flowing point about the reaction profile.

i) If $\delta > 1$, the raise in steric bulk cuts the rate of reaction and steric effects will be higher in the transition state.

ii) If $\delta < 1$, the raise in steric bulk will raise the rate and steric effects will be reduced in the transition state.

3. Reactions influenced by polar and steric effects: If the steric, as well as polar effects, influence the rate of chemical reaction, the Taft equation can be employed to evaluate ρ^*- and δ-values via the use of standard least-squares fitting for getting a bivariant regression plane. The application of this technique was outlined by Taft in 1957 as a demonstration of accuracy.

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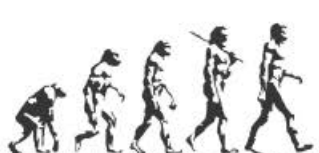
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

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