I MSc., CHEMISTRY
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UNIT – 5
QUANTITATIVE TREATMENT OF ORGANIC REACTIONS

- **Hammett and Taft equation.**

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UNIT V

HAMMETT EQUATION & its SIGNIFICANCE

① Hammett obtained a equation, connecting the rate constants of unsubstituted and meta/para substituted aromatic compound undergoing similar reaction, which is a linear free-energy relation (LFER).

$$\log \frac{k_s}{k_0} = \rho\sigma$$

ρ : Reaction constant

σ : Substituent constant

k_s : Rate constant of substituted acid

k_0 : Rate constant of unsubstituted acid

② ρ is a constant for a particular type of reaction for a series of compounds derived from the same parent compound but σ value differ from each other, regarding the nature and position of the substituent.

③ ρ changes only when the nature of the reaction is changed (i.e) hydrolysis to reduction or to saponification.

④ σ depends on the nature and the position of the substituents. For eg) σ for NH_2 group is different from that of $-OCH_3$ group. σ for $m-NO_2$ group is different from that of $p-NO_2$ group.

⑤ For electron withdrawing substituents, σ is positive and for electron donating substituents σ is negative

⑥ In an equilibrium ~~constant~~ reaction, (ionisation of weak acid), the ratio of the rate constants can be replaced by the ratio of equilibrium constants. Hammett equation takes the form

$$\log \frac{K_s}{K_0} = \rho\sigma \quad ①$$

K_S = Equilibrium constant for a substituted compound

K_0 = Equilibrium Constant for an unsubstituted compound.

⑦ From equation ①

$$\log_{10} K_s - \log_{10} K_0 = \rho\sigma$$

In terms of pK values

$$-pK_s + pK_0 = \rho\sigma$$

$$pK_0 - pK_s = \rho\sigma$$

For a system involving the dissociation of benzoic acid and its meta & para substituted compounds. $\rho = 1$

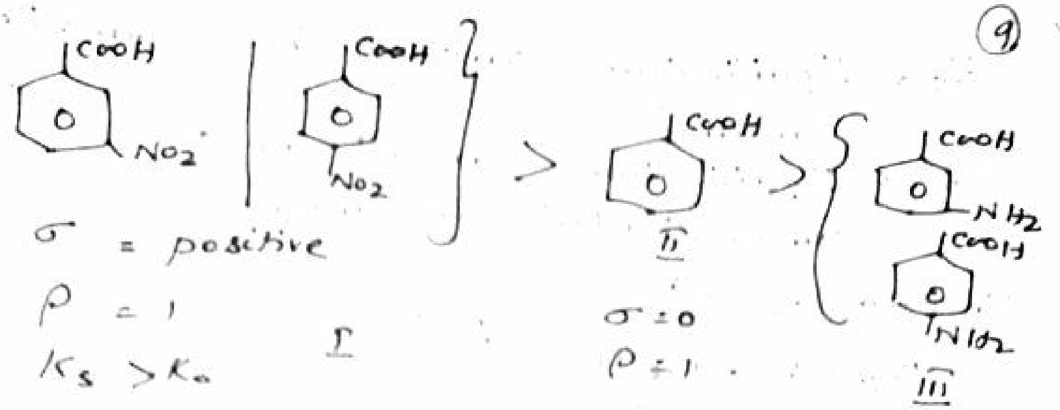
$$pK_0 - pK_s = \sigma \quad ②$$

⑧ From equation ②, if σ is positive, then $pK_s > pK_0$ and the substituted acid is stronger than unsubstituted acid. If σ is negative $pK_s < pK_0$ and the substituted acid is weaker than unsubstituted acid.

⑨ For the ionisation of benzoic acid, the reaction constant ρ is 1 and σ is positive when the substituent is electron withdrawing like NO_2, Cl etc. The electron withdrawing character of the substituent increases the stability of the anion of the substituted acid and thereby increasing the acid strength. In this case $K_s > K_0$.

⑩ If the substituent is electron donating it decreases the stability of the substituted acid and $K_s < K_0$ and σ is negative

⑪ The strengths of meta/para substituted acids decreases as follows.



σ = positive
ρ = 1
$K_s > K_o$
I

II
σ = 0
ρ = 1

III
σ = negative
ρ = 1
$K_s < K_o$

Acid I is stronger than II and III is weaker than II.

⑫ For a given group, sometimes σ changes when its substituent position changes from meta to para and vice-versa. The resonance effect of benzene ring are responsible for this change. Thus OMe group at the meta position attracts electrons and its σ value +0.12 and at the para position it donates electrons and σ value is −0.27.

⑬ The limiting value of σ is −1 and +1. When there is certain group in the meta position inductive effect is dominant and when it is in para position, resonance effect is of great importance.

⑭ σ is independent of solvent, composition and temperature, but there are few exceptions such as OH group which has a tendency to interact with solvent. So σ changes when the solvent composition is changed.

⑮ If both σ & ρ are positive, the rate of substituted acid is more than that of unsubstituted acid and the transition state develops higher electron density than the initial state, since electron withdrawing substituent is present.

Likewise ρ + σ are negative, the rate of substituted acid is greater than that of unsubstituted acid and electron density is lesser in the transition state than in the initial state

TAFT EQUATION AND ITS SIGNIFICANCE:-

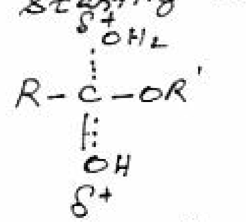
① Taft equation is a structure - reactivity equation that correlates only field effects.

② In hydrolysis of carboxylic esters, steric and resonance effects will be the same, whether the hydrolysis is catalysed by acid or base

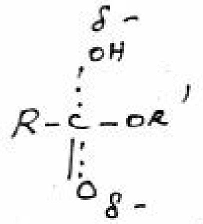
③ Rate differences are caused by the field effects of R and R' in RCOOR'.

④ Transition state for acid-catalysed hydrolysis has a positive charge than the starting ester (and hence destabilized by -I and stabilized by +I substituents).

Transition state for base-catalysed hydrolysis has a greater negative charge than the starting ester.



Transition state
(Acid-catalysed
hydrolysis)



Transition state
(Base-catalysed
hydrolysis)

5) Field effect of substituent X could therefore be determined by measuring the rates of a acid and base catalysed hydrolysis of a series XCH_2COOR' where R' is constant. From these rate constants, the value of σ_I could be determined by the following equation

$$\sigma_I = 0.181\left[\log\left(\frac{k}{k_0}\right)_B - \log\left(\frac{k}{k_0}\right)_A\right]$$

6) $$\left(\frac{k}{k_0}\right)_B = \frac{\text{Rate constant for basic hydrolysis of } XCH_2COOR'}{\text{Rate constant for basic hydrolysis of } CH_3COOR'}$$

⑦ $$\left(\frac{k}{k_0}\right)_A = \frac{\text{Rate constant for acid hydrolysis of } XCH_2COOR'}{\text{Rate constant for acid hydrolysis of } CH_2COOR'}$$

0.181 = Constant

σ_I = Substituent constant for a group X, substituted at a saturated carbon, that reflects only field effects.

$\log\frac{k}{k_0} = \rho_I\sigma_I$ holds for a number of reactions.

⑧ σ_I is a constant for a given reaction under a set of conditions. For very large groups, because of steric effects, the relationship may fail.

⑨ The equation also fails when X enters into resonance with the reaction centre to different extents in the initial and transition states.

⑩ σ_p = Sum of resonance and field effects

$\sigma_R = \sigma_p - \sigma_I$

σ_R value depends on the nature of the reaction

⑪ Special σ_R value called σ_R°, that measure the ability to delocalize π electrons into or out of an unperturbed or neutral benzene ring.

$\log\frac{k}{k_0} = \rho_I\sigma_I + \rho_R\sigma_R^\circ$ — Dual substituent parameter equation

SIGNIFICANCE:-

1) If $\log \frac{k}{k_0}$ is linear with the appropriate σ, it is likely that the mechanism operates throughout the series.

2) If not a smooth curve usually indicates a gradual change in mechanism.

3) A pair of intersecting straight lines indicates an abrupt change

4) Non-linear plots, indicate the complications arising from side reactions.

5) If a reaction series follows σ^+ or σ^-, better than σ, it generally means, that there is extensive resonance interactions in the transition state.

6) Negative ρ value indicates a large electron demand at the reaction center - a highly electron deficient center, ~~poss~~ perhaps a carbocation.

7) Positive ρ value is associated with a developing negative charge in the transition state.

8) $\sigma\rho$ relationship even applies to free radical reactions, because free radicals can have some polar character. ρ values are usually small whether positive or negative.

9) Reactions involving cyclic transition states also exhibit very small ρ values