LFER (Linear Free Energy Relationship)

→ It compare the effects that substituent have on a rate or equilibrium process to the effects on a standard rate or equilibrium

→ attempts to develop quantitative relationships b/n structure & activity.

→ change in structure produces proportional change in $\Delta G^{\neq}$.

$$-\Delta G = RT \ln k = 2.303 RT \log k.$$

logarithm of k is $\propto$ to $\Delta G^{\neq}$ (free energy of activation)
rate constant

logarithm of Eq. constant (K) is $\propto$ ΔG° (change in standard free energy of activation)

$$k = \kappa' kT/h \, e^{-\Delta G/RT} \quad -(1)$$

$$K = e^{-\Delta G^{\circ}/RT} \quad -(2)$$

Hammett Equation :- LFER which describes the effects of polar factors (I and R) on reactivity in aromatic compounds.

Consider a particular rx. b'n two substrates

* We carry out a series of rxs by varying one of the reactants slightly i.e. by studying substituents with a range of electronegativities.

→ We may expect that rx. rate or position of the equilibrium b'n reactants & products will change as we change the reactant.

* If same series of changes effects a II rx in same way as it effected the first rx.
then we say that there exists a LFER b'n two sets of effects.
Such relationship will be helpful in elucidating rx mech. & predicting rates or equilibria.

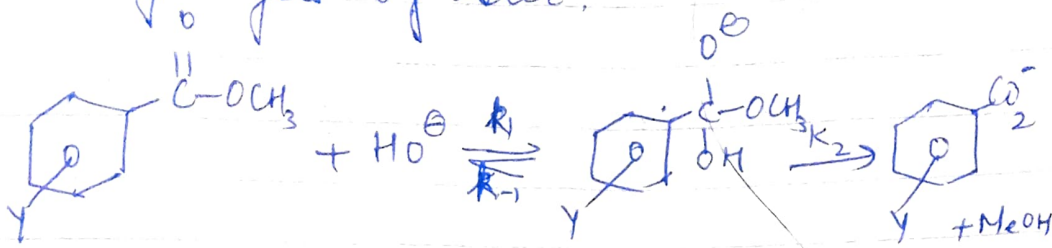
Hammett Equation

→ One of the most widely used means for the study and interpretation of organic rxs & their mechanisms.

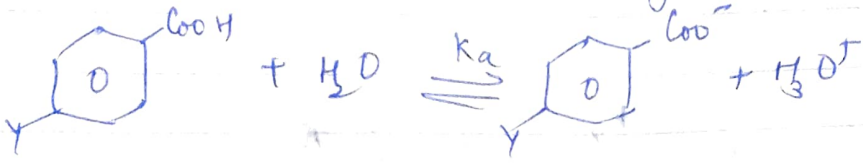
→ Hammett equation correlates rates and equilibria for many reaction of compounds containing sub. phenyl gps.

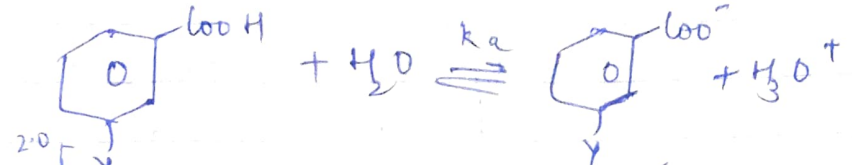
Hammett plotted log K for hydrolysis of esters against log K for ionization of the acids, a straight line was obtained.

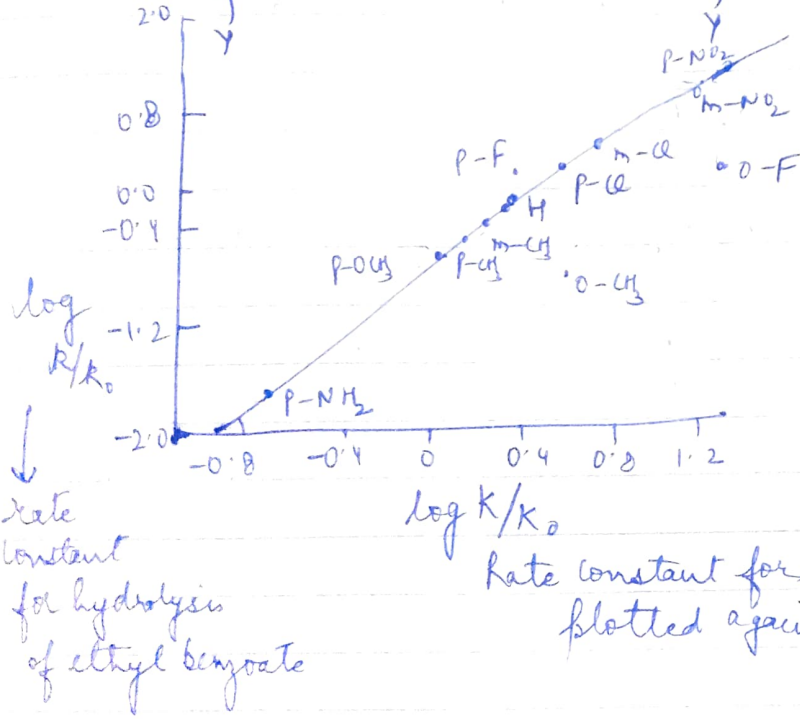
Basic hydrolysis of ester:



Ionization rx. of p- & m- Sub. benzoic acids:







Rate constant for hydrolysis of ethyl benzoate

Rate constant for sub. esters plotted against log K/K0

p- & m- benzoic acid derivatives lie in a straight line, but o- derivatives lie off the straight line.

→ Aliphatic derivatives lie to the other side.

→ m- & p- sub. compounds correlate well but o- sub. compds do not.

→ Aliphatic compounds can adopt a variety of conformations & the substituent in some of them will interfere with the rx.

In o- sub., nearby sub. might exert steric hindrance on the rx.

$\log k_x = \rho \log k_x + c$ — rate of basic hydrolysis of ethyl benzoate

diss. constant of benzoic acid

ρ = slope of straight line

x = m/p sub. unsub. $x = H$.

$\therefore \log k_H = \rho \log k_H + c$

$\log k_x - \log k_H = \rho (\log k_x - \log k_H)$

$\log \frac{k_x}{k_H} = \rho \log \frac{k_x}{k_H}$

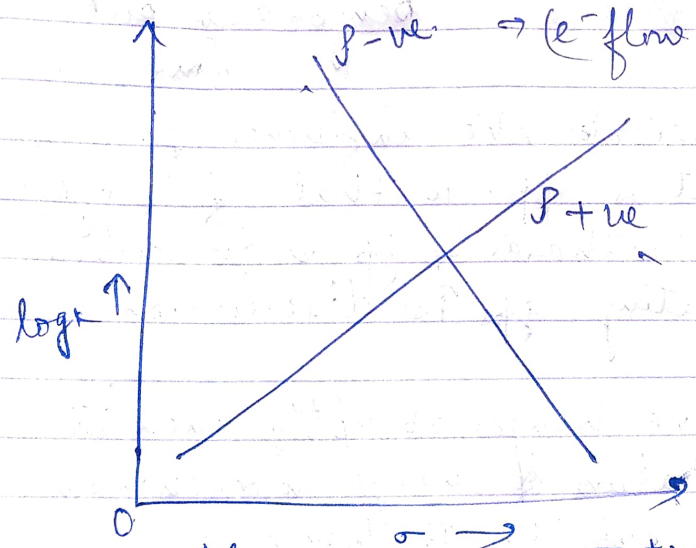
Now, $\log \frac{k_x}{k_H} = \rho \sigma_x$ → [Hammett eq.]

ρ = rx constant

σ = sub. constant

Slope of the line

Sub.	meta σ	para σ
H	0	0
F	+ 0·34	+0·06
Cl	+0·37	+0·23
Br	+0·39	+0·23
I	+0·35	+0·28
CH_3	−0·07	−0·17
C_2H_5	−0·07	−0·15
$(CH_3)_2CH$	−0·10	−0·20
Ph	+0·06	−0·01
CF_3	+0·43	+0·54
CN	+0·56	+0·66
NO_2	+0·71	+0·78
COOH	+0·36	+0·41



ρ -ve ⇒ (e⁻ flow away from Aromatic ring in rate det. step)

ρ +ve (e⁻ flow away from aromatic ring in rate det. step)

Hammett plot

Conclusions from Hammett plot:

→ A straight line obtained indicates that free energy relation of rx is valid.

→ Slope of line is ρ of rx.

→ +ve of ρ indicates that rx responds to Sub. effects as in benzoic acid i.e. e^- withdrawing gps ↑se dissociation & donating gps ↓ dissociation.

→ $\rho > 1$, rx is more sensitive to effects than in benzoic acid.

∴ $\rho = 1$ (Benzoic acid)

ρ b/w 0 & 1 → effect is as in benzoic acid but lower

→ -ve of ρ indicates the influence of substituent is opp. to that of benzoic acid i.e. e^- withdrawing gp ↓ dissociation & e^- donating gps ↑se dissociation.

* If slope of line changes abruptly then it is an indication of change in mechanism as the substituents change.

Substituent effects:-

→ Changes on a rx or property in the unchanged part of the molecule resulting from substituent variation.

→ effects of substituents on known reactions or properties of molecules tell us about the steric & electronic characteristics of substituents.

$$\sigma_x = \text{Sub. constant} = \log \frac{K_x}{K_H}$$

Its value remains constant for a specific position (m/p) irrespective of the nature of particular rx in which a benzene derivatives carrying this substituent is involved.

Importance of σ_x:-

→ It is independent of nature of rx & is a quantitative measure of the polar effects in any reaction of a given m or p Sub. relative of H i.e it represents e^- withdrawing or e^- releasing power of Sub. gp

→ More +ve σ = more e^- withdrawing (−I/−R) Sub
More −ve σ = more e^- releasing (+I/+R) Sub

σ value of H = 0

→ Sub. may exert a field effect operating thru the medium but will act in the same direction as Inductive effect.

→ Polar effects are greater in p-position than meta (Halogens are exceptions).

Reaction Constant (ρ):-

→ Measure of susceptibility to the influence of sub. groups on the rate constant or equilibrium constant of a particular org. rx.

→ Rxs with +ve ρ value are accelerated by sub. with +ve σ constants.

→ Sub. Ē a +ve σ increase the acidity of benzoic acid, such sub. are generally described as attracting e⁻ away from the aromatic ring.

If follows that rxs with a +ve ρ value are considered to involve a transition state (or rx. product) so that diff. in energy b'n this state & reactants is lowered by a reduction in e⁻ density at the reactive site of the substrate.

ρ = dependent on the nature of rx & on the conditions.

It is a measure of sensitivity of a given rx. series to the polar effects of ring substituents i.e. to changes in σ value of the substituent.

If σ is positive (EWG) $k > k_0$ (or $K > K_0$) if ρ is +ve. Thus, for rxns in which rates or equilibria are facilitated by EW gps, ρ is +ve or we can say, rxns for which ρ is +ve are aided by EWG.

If σ is negative, then $k < k_0$ (or $K < K_0$) if ρ is -ve. Thus, for rxns in which rates or equilibria are hindered by EWG, ρ is -ve, or we can say, rxns for which ρ is -ve are hindered by EWG.

→ Rxns with a +ve ρ are hindered by ER gps (σ is -ve) & those with a negative ρ are facilitated.

→ +ve ρ value means more e^- in T.S. than in starting mat. & -ve ρ value means fewer e^- in T.S. than in the starting materia

→ more +ve σ, more +ve ρ, greater is the effect of sub. on that rx or more sensitive is that rx. to polar effects. (k or $K > k_0$ or