→ Taft Extended LFER to aliphatic systems which steric factors (δ) are imp.

(*) Taft Equation: structure reactivity eq. that correlates only field effects

→ developed by Robert W. Taft in 1952 as a modification to Hammett equation.

→ H. Eq. accounts for how field, inductive & R effects influence reaction rates while Taft Eq. also describes steric effect of a substituent.

$$\log\left(\frac{K_s}{K_{CH_3}}\right) = \rho^*\sigma^* + \delta E_s$$

↓ ratio of rate of sub. rx compared to ref. Rx.

σ^* → Polar sub. Constant, describing field & inductive effects of substituent.

ρ^* → sensitivity factor for Rx to polar effects

δ → " " to steric effects.

E_s → steric sub. Constant.

σ^*:-

→ Polar sub. constants describe the way a sub. will influence a rx thru polar (Ind, field & resonance) effects. To determine σ^*, Taft studied hydrolysis of methyl esters (RCOOMe). It was suggested by Ingold in 1930 using ester hydrolysis rates to study polar effects.

→ Hyd. can occur thru either acid & base catalyzed mechanism:

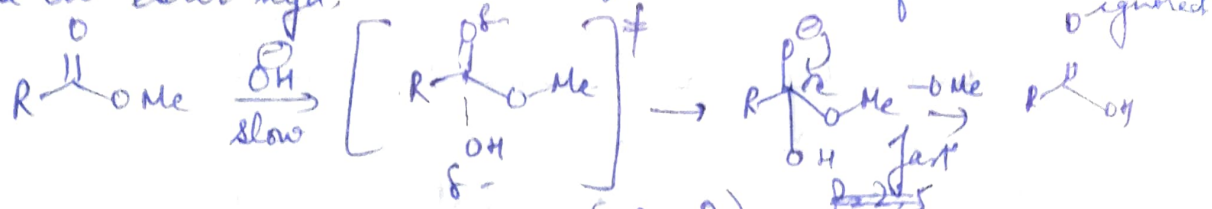
Base cat. → Rx (neutral) —slow step→ negat. charged int.

Acid cat. → +ve charged reactants → +vely charged int.

$\rho = 2-3$ in basic med.
& 0.1 in acidic med.

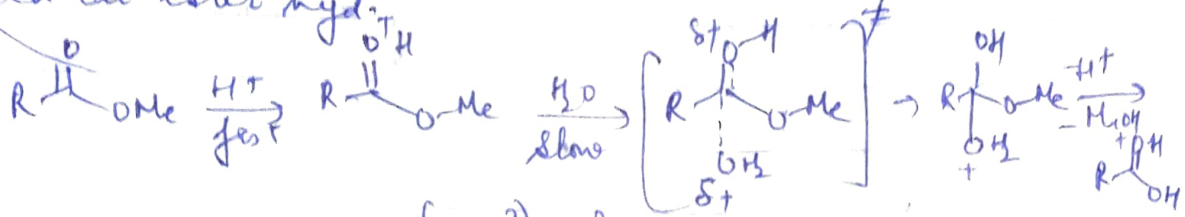
In case of Base cat., electronic inf. of sub can't be ignored

Base cat. ester hyd.



$(B_{AC}2)\ \rho = 2.51$

Acid cat. ester hyd.



$(A_{AC}2)\quad \rho = 0.03$

One of ⊥ tetrahedral int., Taft proposed that under identical cond., any steric factor should be nearly the same for 2 mech. & thus, not influence the ratio of rates.

→ Thus, due to diff. in charge buildup in rate determining step, the polar effects only influence Rx rate of base catalyzed Rx since a new charge was formed.

$$\sigma^* = \left(\frac{1}{2.48\rho^*}\right)\left[\log\left(\frac{K_S}{K_{CH_3}}\right)_B - \log\left(\frac{K_S}{K_{CH_3}}\right)_A\right]$$

- σ^* (polar sub. constant)
- $2.48\rho^*$: Rx. constant describing sensitivity of Rx series
- $\left(\frac{K_S}{K_{CH_3}}\right)_B$: rate of base catalyzed as compared to reference rx.
- $\left(\frac{K_S}{K_{CH_3}}\right)_A$: rate of acid catalyzed rx as comp. to ref rx

ρ^* was set to 1
& $R = CH_3$ ($\sigma^* = 0$)

Factor $\left(\frac{1}{2.48}\right)$ = is included to make σ^* is in magnitude to Hammett σ values.

Values = 2.48 → obt. by sub. ρ value for acid catalyzed hydrolysis of ~~ben~~ benzoate esters from ρ value for base catalyzed hydrolysis of same esters. (Ref. sub R = Me rather than $R = H$)

Steric Sub. Constants E_s :-

→ Acid cat. & base cat., have differing charge densities. their st. differ only by 2 H atoms (very small) little steric hind.

→ Thus, Taft assumed that steric effect influence both rx mech. equally.

→ Due to this, steric sub. constant E_s was determined solely from acid catalyzed Rx as this would not include polar effects.

$$E_s = \frac{1}{\delta} \log\left(\frac{k_s}{k_{CH_3}}\right)$$

k_s → rate of studied Rx

k_{CH_3} → Rate of ref. Rx

δ ↓ Rx constant that describes susceptibility of a rx series to steric effects.

δ = set to 1

E_s for ref. rx = 0

E_s $CH_3 < CH_3CH_2 < (CH_3)_2CH < (CH_3)_3C$

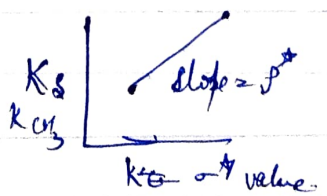
→ E_s value ↑ ves

Sensitivity factors ρ^* :-

→ ρ^* for Taft plots → describe susceptibility of a rx series to polar effects.

When steric effects of sub. do not significantly inf. Rx rate, Taft eq. simplifies to form of Hammett eq.

$$\log\left(\frac{k_s}{k_{CH_3}}\right) = \rho^* \sigma^*$$



~~$\rho^* > 0$~~ = Rx accumulates -ve charge in TS & accelerated by

$\rho^* > 1$ = e^- with gp.

$1 > \rho^* > 0$ = mildly effective to polar effects.

$\rho^* = 0$ not effected by polar effects.

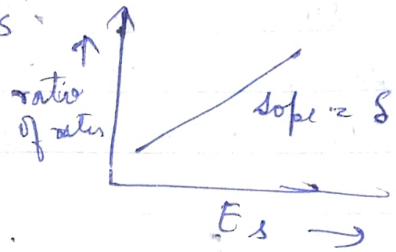
$-1 > \rho^*$ → e^- donating gp.

Steric Sensitivity factor, δ :-

→ It describe to what magnitude, rx. rate is influenced by steric effects.

When Rx not influenced by polar effects, Taft Eq. reduces to :-

$$\log\left(\frac{k_s}{k_{CH_3}}\right) = \delta E_s$$



δ = +ve (increasing steric bulk ↓ ses Rx rate & steric effects are greater in TS)

δ = −ve (Tse " " Tses Rx rate & steric effects lessened in T.S.

Steric & polar parameters for aliphatic systems

X	E_s	σ^*
H−	1.24	+0.49
$-CH_3$	0.00	0.00
CH_3-CH_2-	−0.07	−0.10
$CH_3-\underset{CH_3}{CH}-$	−1.54	−0.19
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-$	−1.74	−0.165
$Cl-CH_2-$	−0.24	+1.05