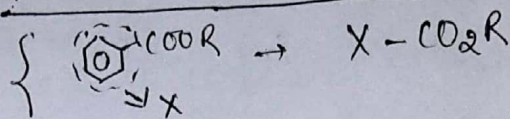


in mech^m as the electronic effects of the substituents changed.

The observed curve results from the intersection of two straight line Hammett plots.

The Hammett eqⁿ has been used to interpret biological effect of organic molecules and find correlations b/w LFERs and the effectiveness of synthetic drugs.

Separation of polar, Resonance and steric effects :-



Taft equations :- Taft analyzed the effects of substituents on the rates of rxns of a series of esters XCO_2R . If R is held constant, the rates of rxns of the esters would depend on the inductive, resonance and steric effects of group X .

Also, if a saturated carbon in 'x' were bonded to the carbonyl group, there could be no direct resonance interaction b/w 'x' and the carbonyl group.

Thus for the rates of basic hydrolysis of esters

$$\log \left(\frac{k}{k_0} \right) = \sigma^* \rho^* + E_s$$

where σ^* and E_s are constants, reflecting the inductive and steric effect respectively, of 'x'

A value of 2.48 was assigned to ρ^* to bring values of σ^* on to a scale comparable to those of Hammett ' σ ' values.

To obtain value of E_s , Taft found that the rates of acid hydrolysis of aromatic esters are not strongly affected by polar effects of substituents.

Hence if changes in 'X' strongly affects the rates of acid catalyzed hydrolysis of esters, the changes are presumably due largely to steric effects.

Hence, In acid $\log \left(\frac{k}{k_0} \right) = E_s$

The σ^+ & E_s are useful measures of inductive & steric effects respectively.