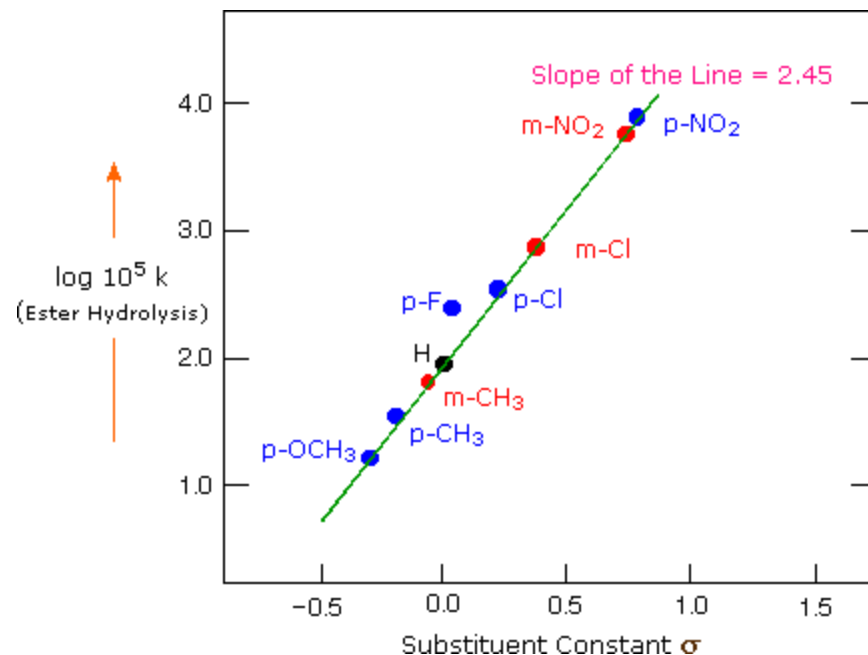


Hammett equation



Louis Plack Hammett

CHEM F212 Lecture 16



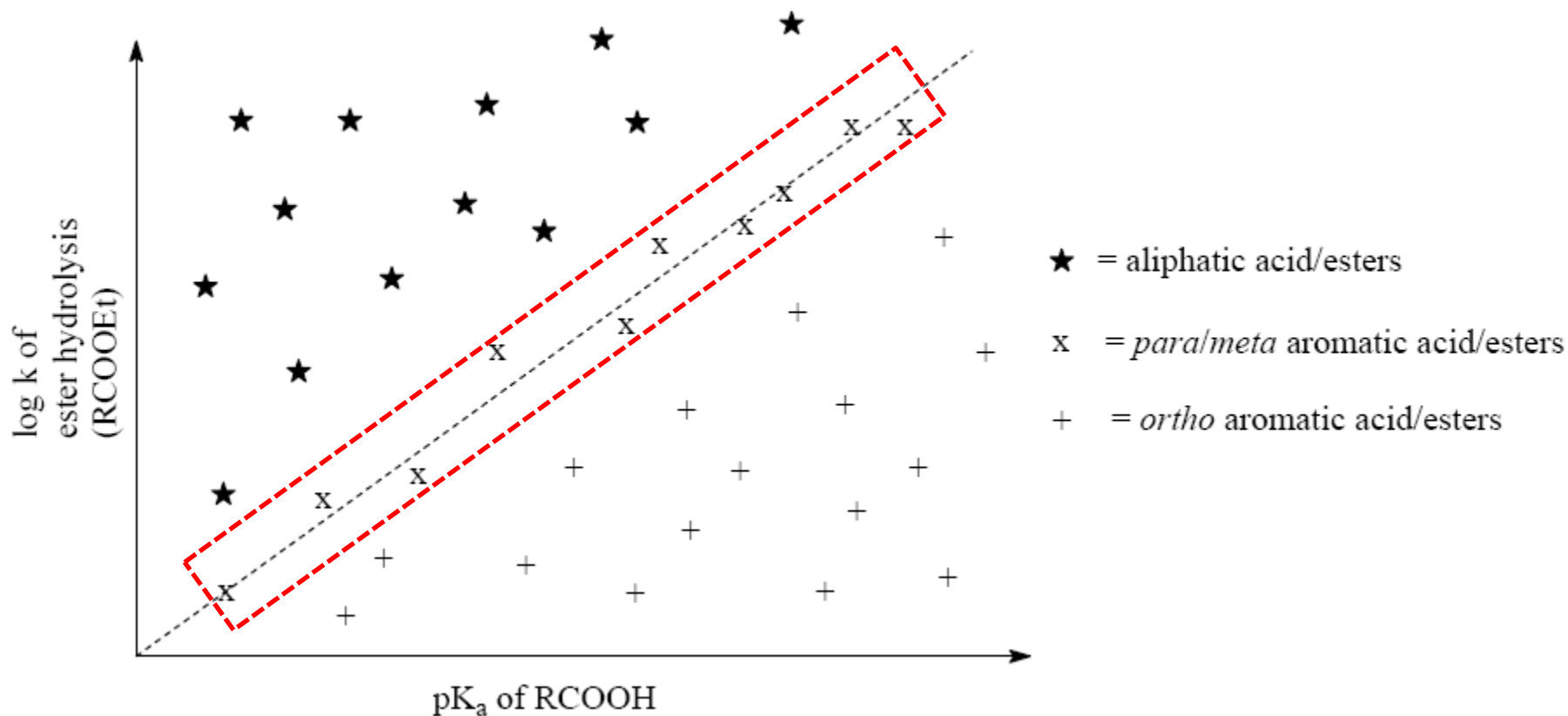
Hammett equation

Quantitative Measurement of Substituent Effects on Chemical Reactivity

Objective: Find a way to quantify the effects that electron-donating or –withdrawing groups have on the transition state or intermediate during the course of a reaction. This will then give us an idea of what the transition state is really like.

How efficient is a given group at donating & withdrawing electron?

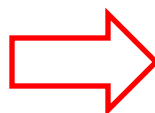
Hammett used the pK_a of an acid as a guide and tried to correlate the rate of hydrolysis of esters with the pK_a of the corresponding acid.



Substituent constant σ

$$\sigma_X = \log \left(\frac{K_a(X-C_6H_4COOH)}{K_a(C_6H_5COOH)} \right)$$

Substituent, X	pK _a of <i>p</i> -XC ₆ H ₄ COOH	pK _a of <i>m</i> -XC ₆ H ₄ COOH
NH ₂	4.82	4.20
OCH ₃	4.49	4.09
CH ₃	4.37	4.26
H	4.20	4.20
F	4.15	3.86
I	3.97	3.85
Cl	3.98	3.83
Br	3.97	3.80
CO ₂ CH ₃	3.75	3.87
COCH ₃	3.71	3.83
CN	3.53	3.58
NO ₂	3.43	3.47



Substituent, X	σ_p	σ_m	Comments
NH ₂	-0.62	0.00	groups that donate electrons have negative σ
OCH ₃	-0.29	0.11	
CH ₃	-0.17	-0.06	
H	0.00	0.00	there are no values for <i>ortho</i> substituents
F	0.05	0.34	$\sigma_p < \sigma_m$ for inductive withdrawal
I	0.23	0.35	
Cl	0.22	0.37	
Br	0.23	0.40	$\sigma_p > \sigma_m$ for conjugating substituents
CO ₂ CH ₃	0.45	0.33	
COCH ₃	0.49	0.37	
CN	0.67	0.62	groups that withdraw electrons have positive σ
NO ₂	0.77	0.73	

The more positive the charge induced on the ring by a substituent, the larger its σ value.

Negative σ means weaker acid and electron donation.

The absolute magnitude of the σ value provides a quantitative measure of the relative electron-donating and electron-withdrawing ability.

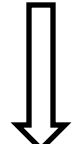
Thus,

m-CF₃ group ($\sigma = 0.46$) is a stronger ewg than m-Cl ($\sigma = 0.37$) but is a less strong ewg than m-CN ($\sigma = 0.62$).

While, a p-methyl group ($\sigma = -0.14$) is a weaker electron donor than p-OCH₃ ($\sigma = -0.28$) but a better electron donor than p-Si(CH₃)₃ ($\sigma = -0.07$).

Once σ -values for a set of substituents are known, information can be derived regarding the sensitivity of other reactions to substituent effects relative to the standard reaction (i.e. benzoic acid ionization).

$$\log\left(\frac{K_x}{K_H}\right)_{any\ rxn} \text{ or } \log\left(\frac{k_x}{k_H}\right)_{any\ rxn} = \rho\sigma_x$$


 Reaction constant

$\rho = 1$ for benzoic acid ionization

Hammett equation is a Linear free energy relationship

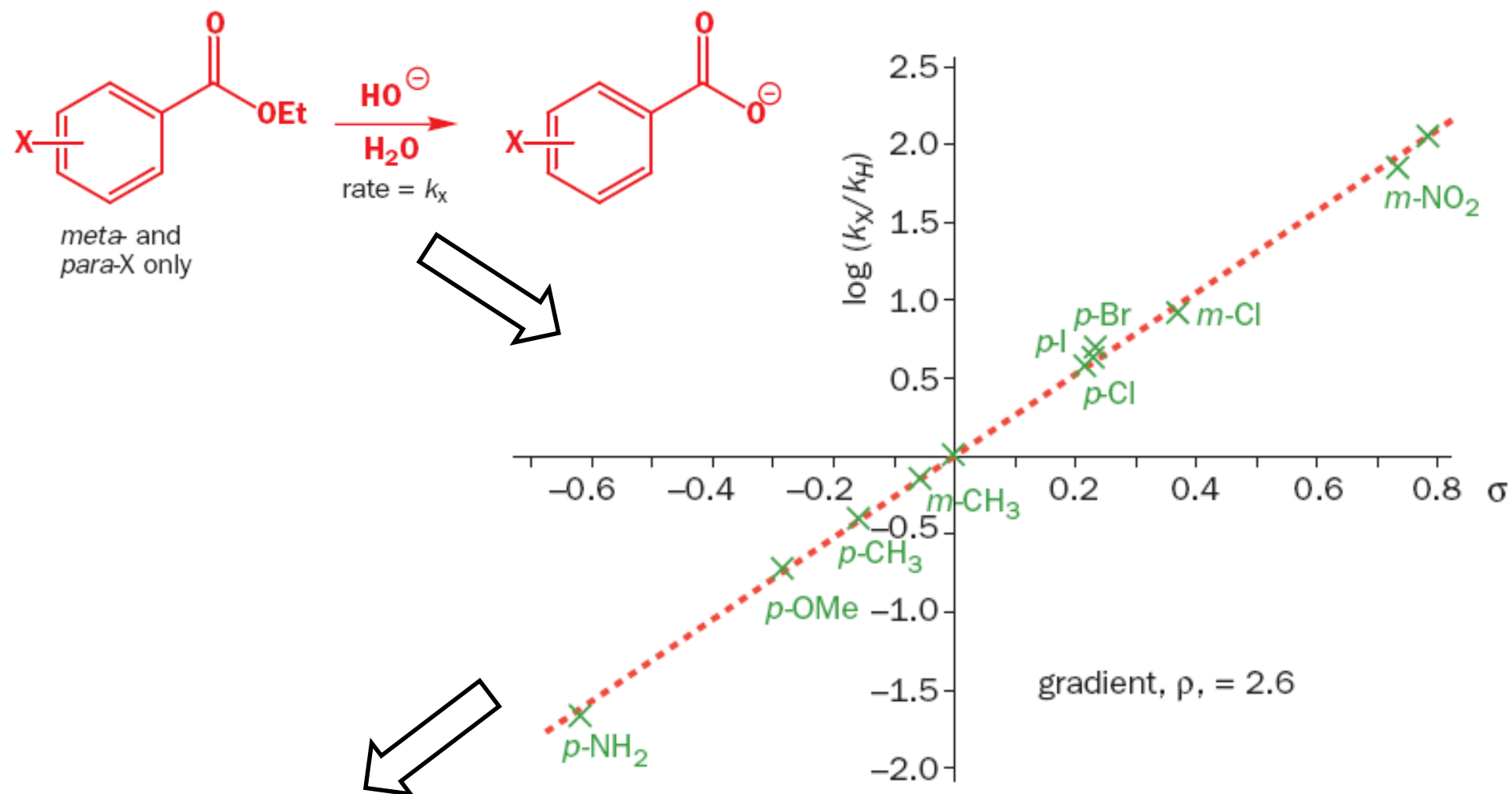
$$\begin{aligned}\Delta G_o &= -RT \ln K_o \\ \Delta G_x &= -RT \ln K_x \\ \Delta G_o - \Delta G_x &= RT \ln K_x/K_o = 2.3 RT \sigma\rho \\ \Delta G_x &= \Delta G_o - 2.3 RT \sigma\rho\end{aligned}$$

ΔG_0 and $2.3 RT = \text{constant}$ (at a specific temperature)

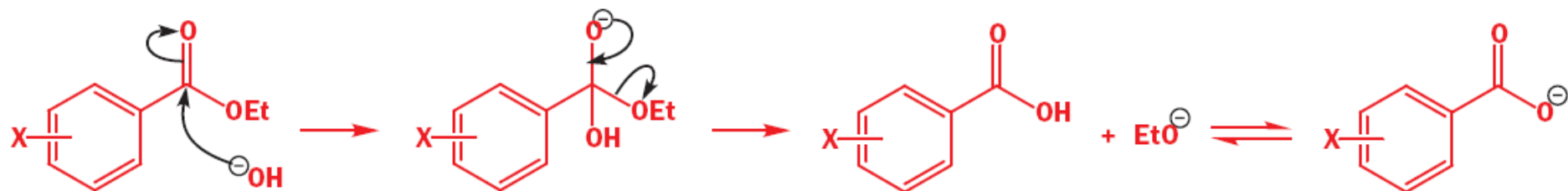
ρ = constant (if changing of the substituent on the substrate does not change the reaction mechanism)

ΔG_x has linear relationship with σ .

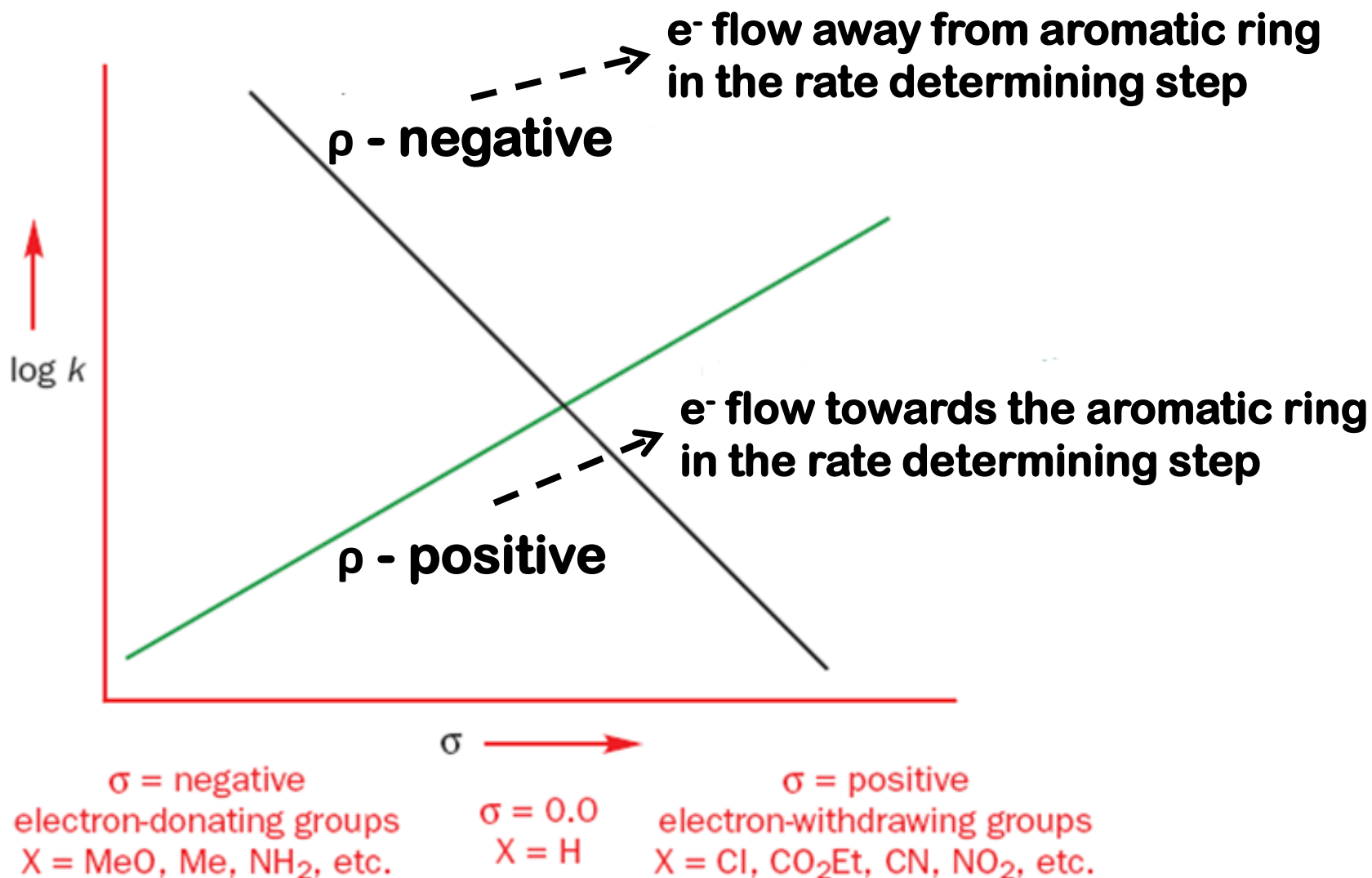
➤ We can use both K and $k \longrightarrow$ rate constant
equilibrium constant



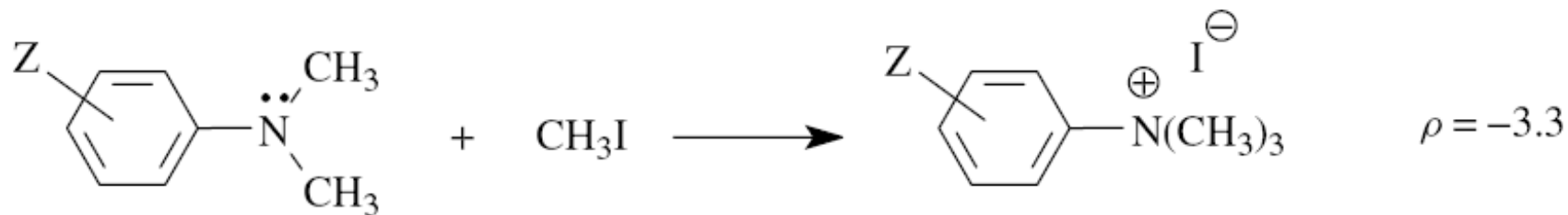
Actual mechanism:



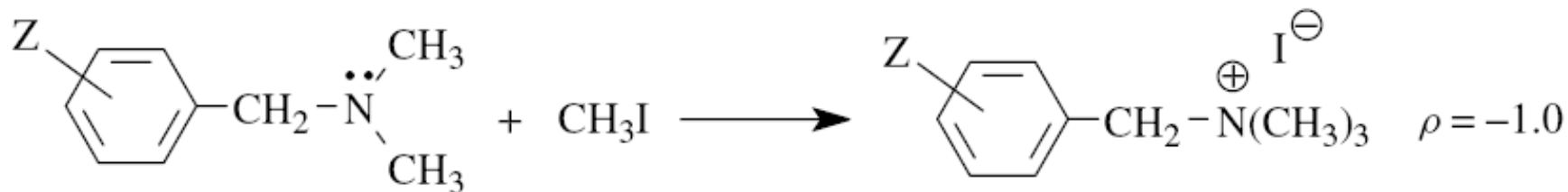
Mechanistic implication of Hammett equation



- The linear line obtained from the plot indicates that the reaction mechanism and the coordination of the transition states do not change upon the variation of the substituent.
- The sign and absolute magnitude of the ρ value determined from a Hammett plot give information about charge development at the transition state.
- The sign of ρ tells whether a positive or negative charge is being developed in the activated complex relative to the reactants.
- A positive ρ value means that electron density is increased (negative charge is being produced) in the activated complex.
- A negative ρ value means that electron deficiency is being produced (often a positive charge) in the activated complex.

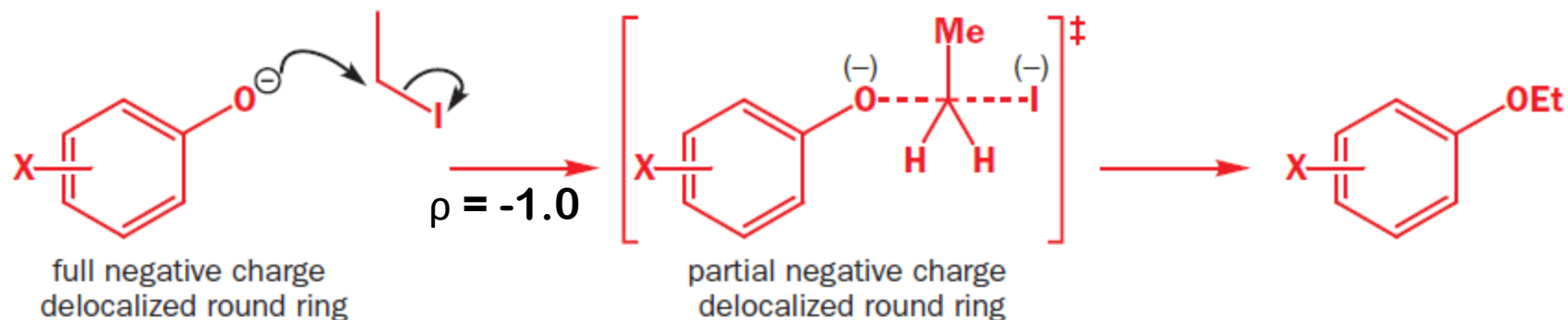


In the above reaction $\rho = -3.3$ because the nitrogen atom, on which positive charge is developed in the transition state, is directly attached to the phenyl ring and the substituents have a greater influence on the stability of the charge being developed. Hence the magnitude of ρ is much larger.

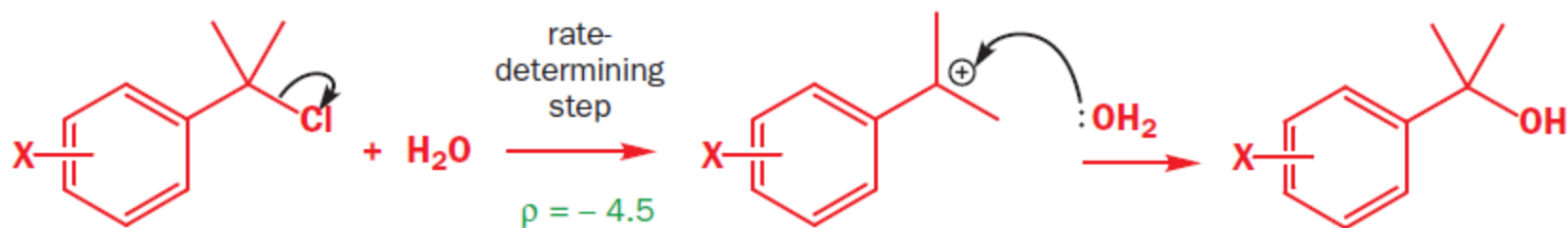


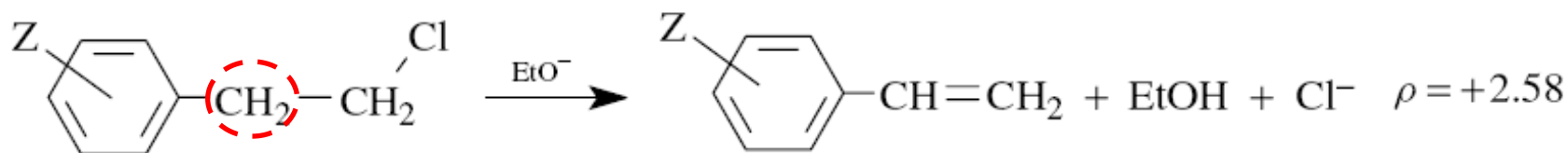
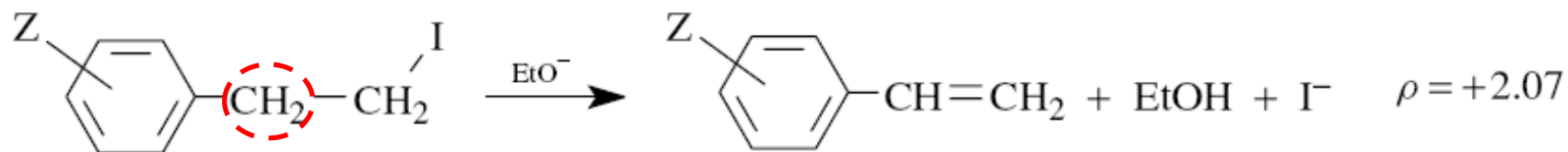
Positive charge is developed in the transition state, reaction center not is directly attached to the phenyl ring so the substituents have lesser influence on the stability of the charge being developed. Hence the magnitude of ρ is much smaller.

Some more examples

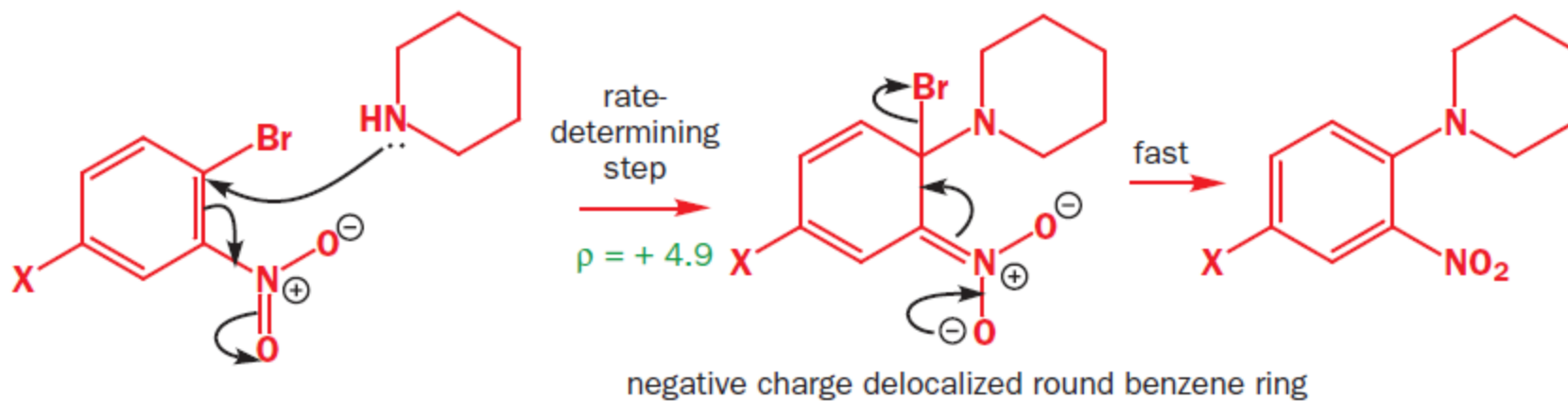


Negative ρ value means electrons flowing away from the ring.





Negative charge is developed in the transition state, reaction center is directly attached to the phenyl ring & the substituents have a greater influence on the stability of the charge being developed.



Generally ρ values have absolute magnitudes between 0 and 3, but values as high as 10 or 12 are known.

A value of $\rho = 0$ means that substituents have no electronic effect on the reaction rate, and thus no charge is being developed at the transition state.

Large absolute values of ρ mean that substituents influence the rate greatly, and thus the amount of charge developed in the activated complex is large and influenced significantly by the electronic properties of the substituents.

The meaning of Hammett ρ values

-6 -5

←-----

large negative ρ -values
positive charge on ring
or delocalized round
benzene ring

-4 -3 -2

←-----→
moderate negative ρ -values
electrons flow out of TS
positive charge near ring
loss of conjugation

-1 0 +1

←-----→

small ρ -values

1. Ar too far away
2. No electron change
3. Two ρ -values cancel each other out

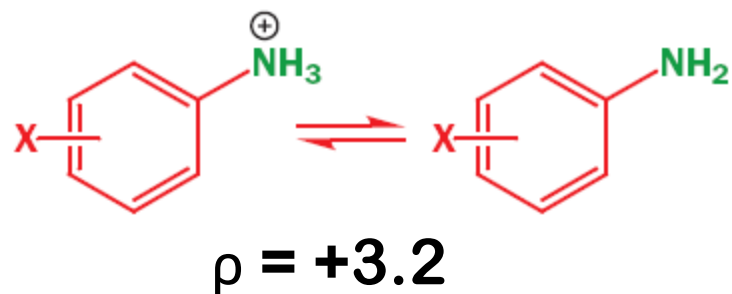
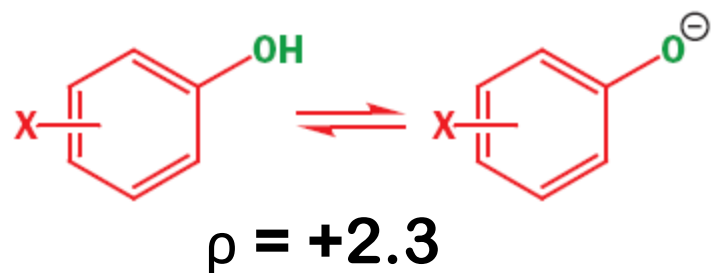
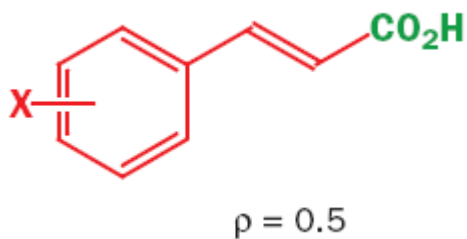
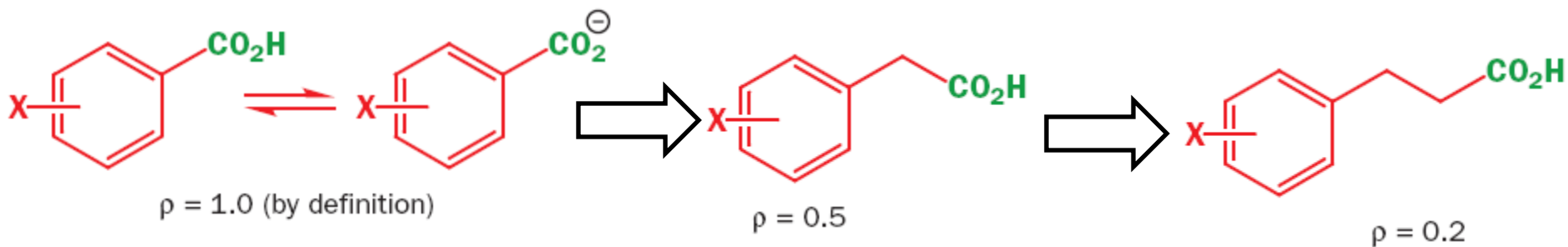
+2 +3 +4

←-----→
moderate positive ρ -values
electrons flow into TS
negative charge near ring
loss of conjugation

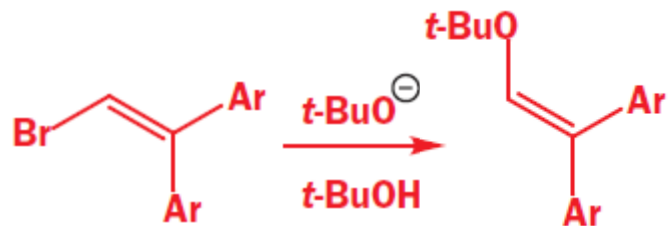
+5 +6

-----→

large positive ρ -values
negative charge on ring
or delocalized round
benzene ring

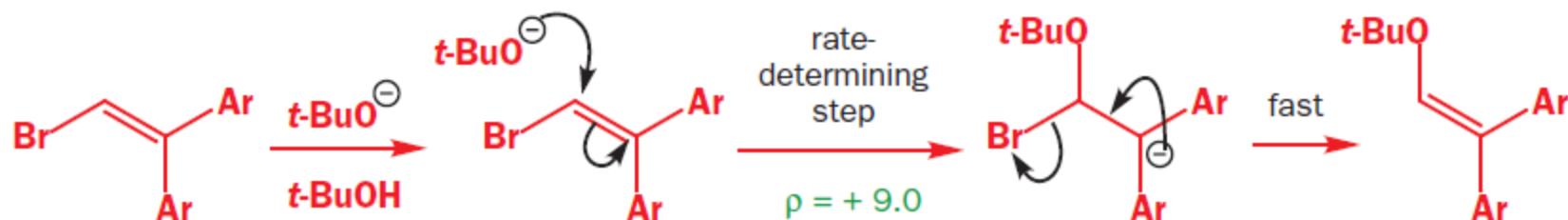


What is the sign of ρ value?

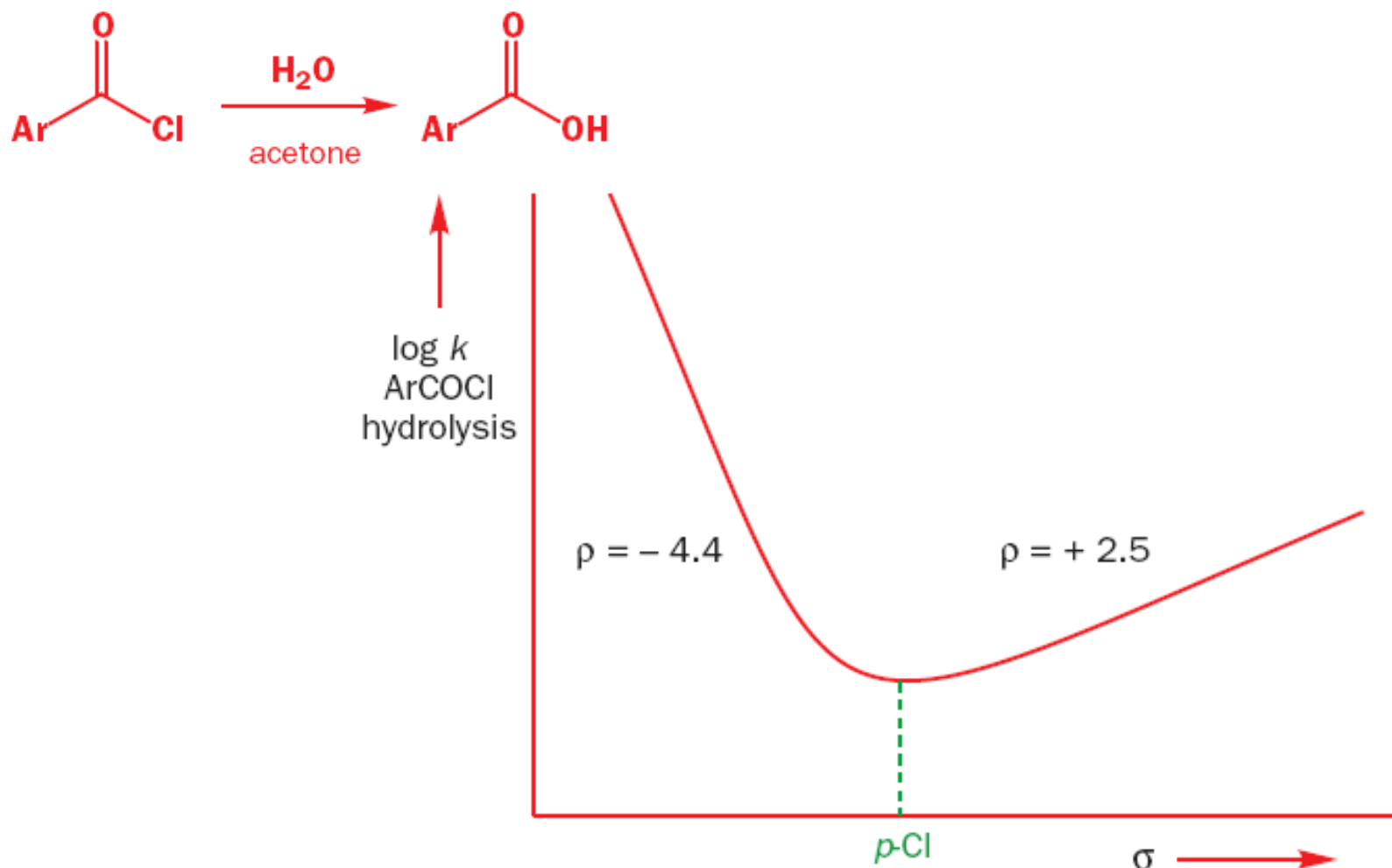


For this reaction $\rho = +9.0$?

Mechanism:



Nonlinear Hammett plots



Indicates change in the mechanism as substituents are changed