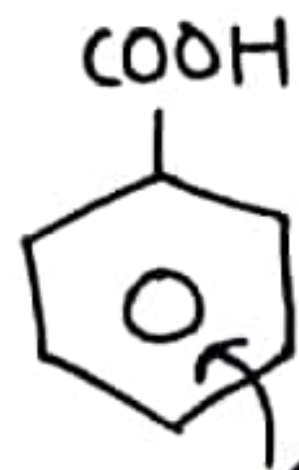


DEPTH OF BIOLOGY

- Effects of substituent on Acidity
- In general we can say that the nature of substituent & the position of substituent both affect the acidity of Aromatic Acids.
- The e^- releasing group like $-CH_3$, $-OH$, $-NH_2$ decreases the acidity because they tend to destabilize the Benzoate Ion.
- But this effect work in some case at only p-position ($-OH$, $-OCH_3$)

DEPTH OF BIOLOGY

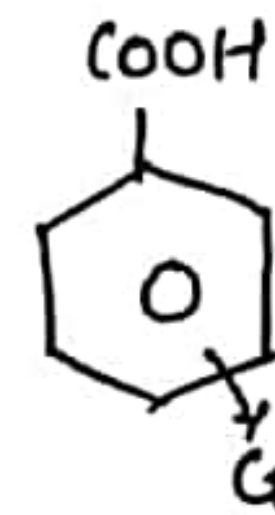


e^- releasing group destabilize an anion so acidic strength decreases.

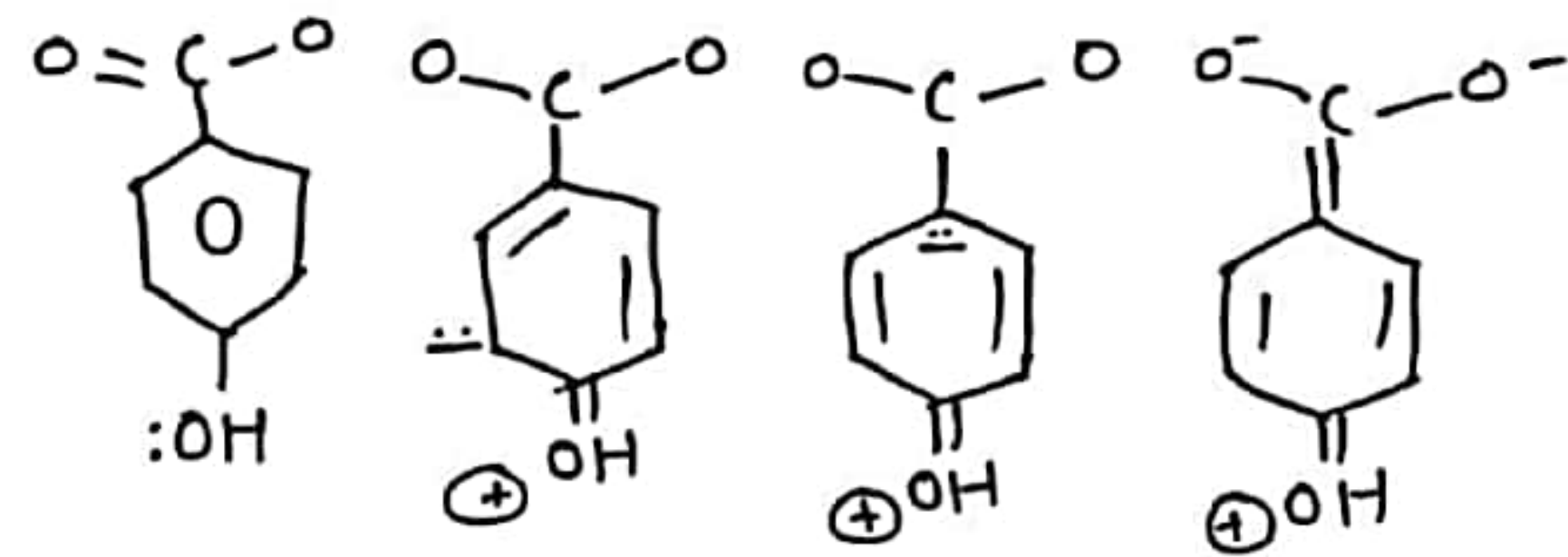
- The e^- withdrawing group like, $-CN$, $-NO_2$, $-CHO$, etc. increase the ability because they tend to stabilize the benzoate ion.

DEPTH OF BIOLOGY

DEPTH OF BIOLOGY



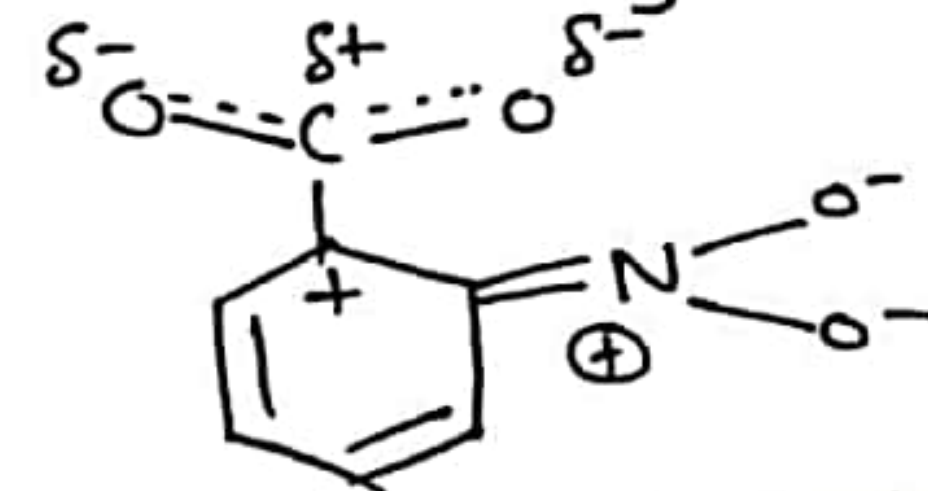
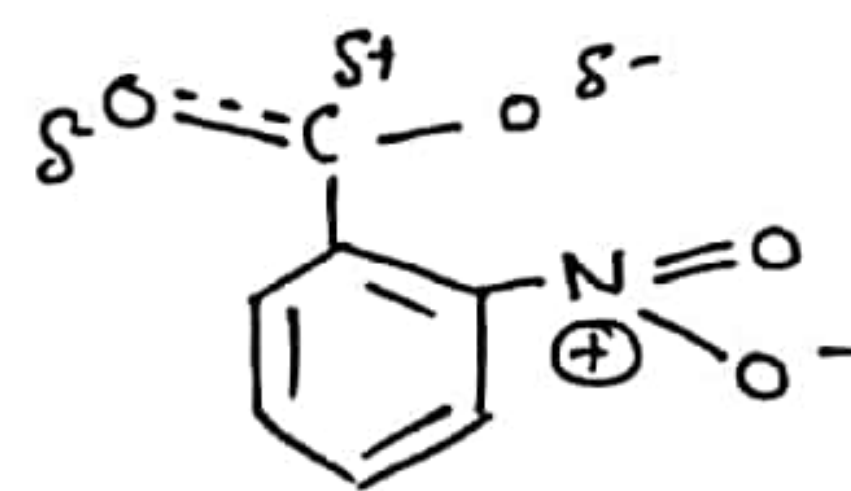
e^- withdrawing group stabilizes anion, so acidity increases.



(Resonance of carboxylate ion disturbed)
• Destabilisation of ion occurs.

e^- density $\uparrow\uparrow$ on carboxylate carbon
 $\downarrow\downarrow$ the polarity. [DEPTH OF BIOLOGY]

The case of e^- releasing Group:



Resonance at carboxylate ion maintained it! stabilize the ion.

DEPTH OF BIOLOGY

[DEPTH OF BIOLOGY]

e^- density $\downarrow\downarrow$, carboxylate carbon $\uparrow\uparrow$ the polarity.

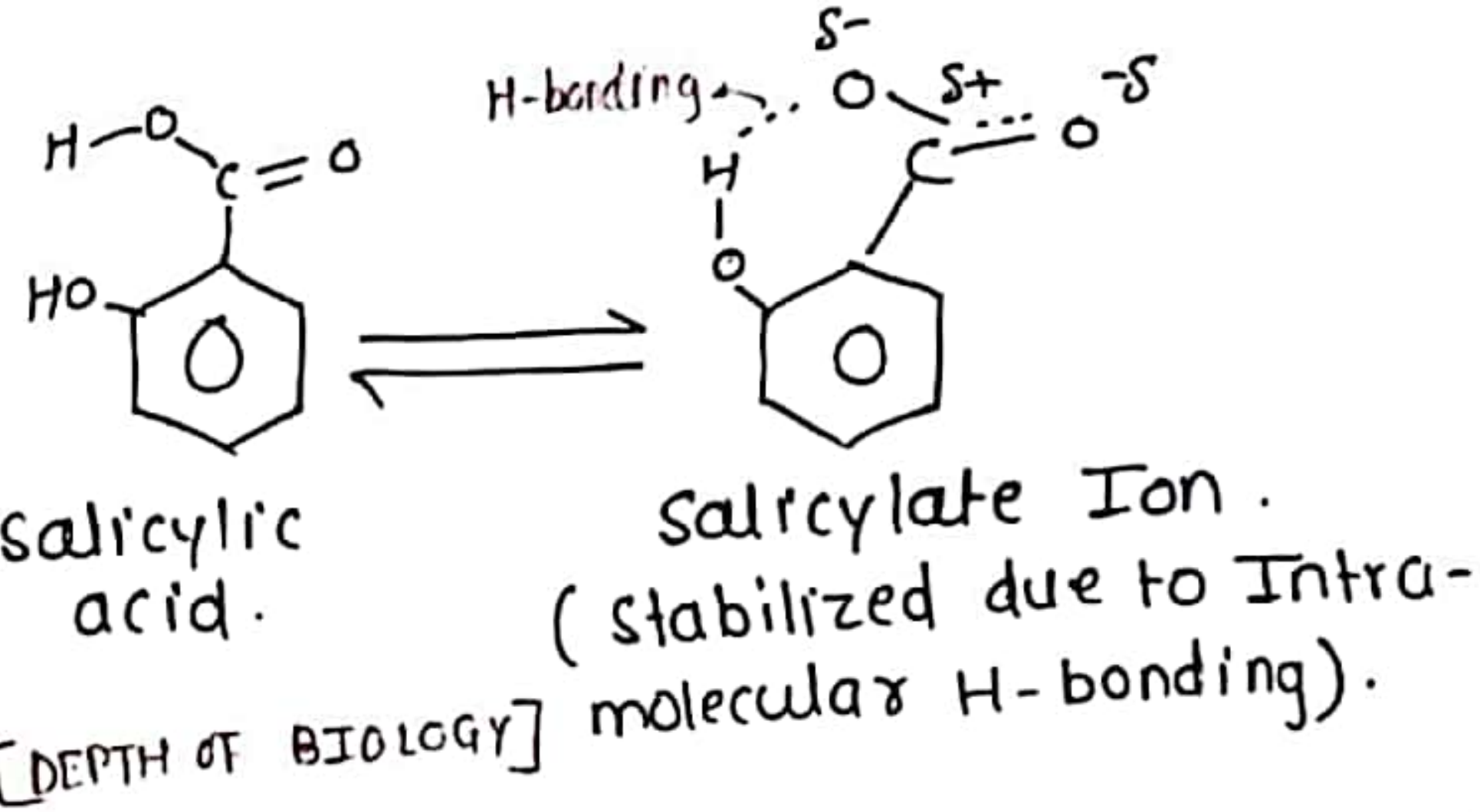
Group with Resonance & I effect at diff. positions.

- Groups like $-OH$, $-OCH_3$ at para (p-substituted) positions e^- releasing mesomeric effect dominates Inductive effect so decreases the activity.

[DEPTH OF BIOLOGY]

- But at meta position these groups shows e^- withdrawing (or) I effect only (domination of $-I$ effect) they stabilize the carboxylate Ion & $\uparrow\uparrow$ the acidity.
- These groups at ortho-position $\uparrow\uparrow$ the acidity strengths due to stabilization of carboxylate ion (due to intra-molecular Hydrogen bond).

[DEPTH OF BIOLOGY]



★ Effect of Halogen:

- Halogens ($-Cl$, $-Br$, $-I$, $-F$) have both e^- releasing & Inductive effects. but the Inductive effect ($-I$) is Stronger than the resonance effect (or) e^- releasing effect.

$\Rightarrow$ Thus Halogen groups always $\uparrow\uparrow$ the acidity of Aromatic acids.

[DEPTH OF BIOLOGY]

★ Ortho-effect:

all ortho substituent exert an acid strengthening effect, whether they are e^- releasing (or) e^- withdrawing in nature.

[DEPTH OF BIOLOGY]

(14) [DEPTH OF BIOLOGY]

★ Comparison of Acidity constants of diff. acids for better understanding of effects :

- K_a of Benzoic acids is 6.3×10^{-5} .

Substituent Name	K_a of p-subst acid.	K_a of m-subst. acid.	K_a of o-subst acid.
-NO ₂ (nitro)	p-NO ₂ 30×10^{-5}	m-NO ₂ 32×10^{-5}	O-NO ₂ 670×10^{-5}
Chloro(-Cl)	p-Cl 10.3×10^{-5}	m-Cl 15.1×10^{-5}	O-Cl 120×10^{-5}
Methyl (-CH ₃)	p-CH ₃ 4.2×10^{-5}	m-CH ₃ 5.4×10^{-5}	O-CH ₃ 12.4×10^{-5}
Hydroxy (-OH)	p-OH 2.6×10^{-5}	m-OH 8.3×10^{-5}	O-OH 105×10^{-5}
Amino (-NH ₂)	p-NH ₂ 1.4×10^{-5}	m-NH ₂ 1.9×10^{-5}	O-NH ₂ 1.6×10^{-5}