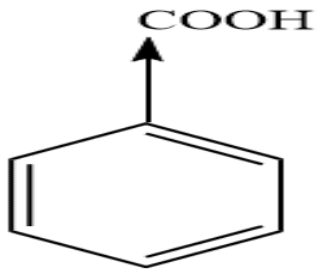


Lec.3

Dr. Mohammed Abdulameer

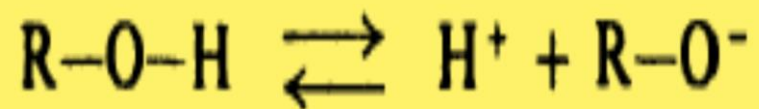


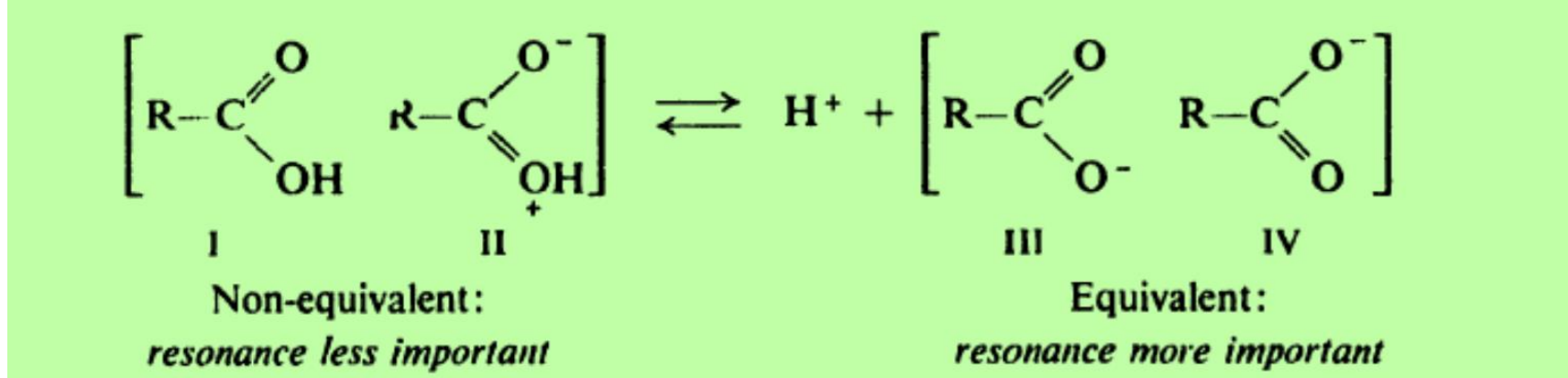
-COOH withdraws electrons, deactivates, directs to *meta* in electrophilic substitution.

Acidity of carboxylic acids:

The acidity of carboxylic acids is related to structure (**chiefly by the difference in stability between the acid and its anion**). First, and most important, there is the fact that carboxylic acids are acids at all. **How can we account for the fact that the OH of a carboxylic acid tends to release a hydrogen ion so much more readily than the OH of an alcohol?**

By examining the structures of the reactants and products in these two cases. We see that the alcohol and alkoxide ion are each represented satisfactorily by a **single structure**



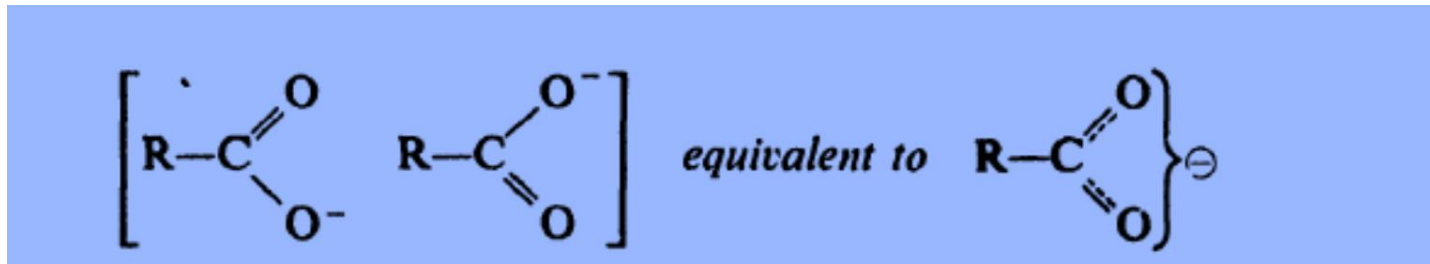


The resonance is less important for the acid because the contributing structures are of different stability, whereas the equivalent structures for the ion must necessarily be of equal stability. In structure II two atoms of similar electronegativity carry opposite charges; since energy must be supplied to separate opposite charges, II should contain more energy and hence be less stable than I. Consideration of separation of charge is one of the rules that can be used to estimate relative stability and hence relative importance of a contributing structure.

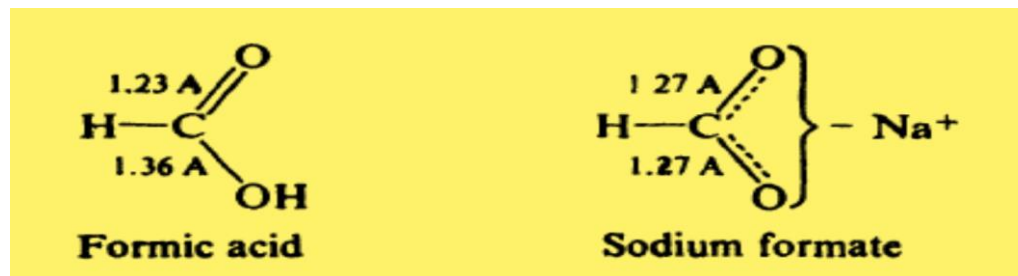
The acidity of a carboxylic acid is thus due to the powerful resonance stabilization of its anion. This stabilization and the resulting acidity are possible only because of the presence of the carbonyl group.

Structure of carboxylate ions:

According to the resonance theory, a carboxylate ion is a hybrid of two structures which, being of equal stability, contribute equally. Carbon is joined to each oxygen by a “**one-and-one-half**” bond. The negative charge is evenly distributed over both oxygen atoms

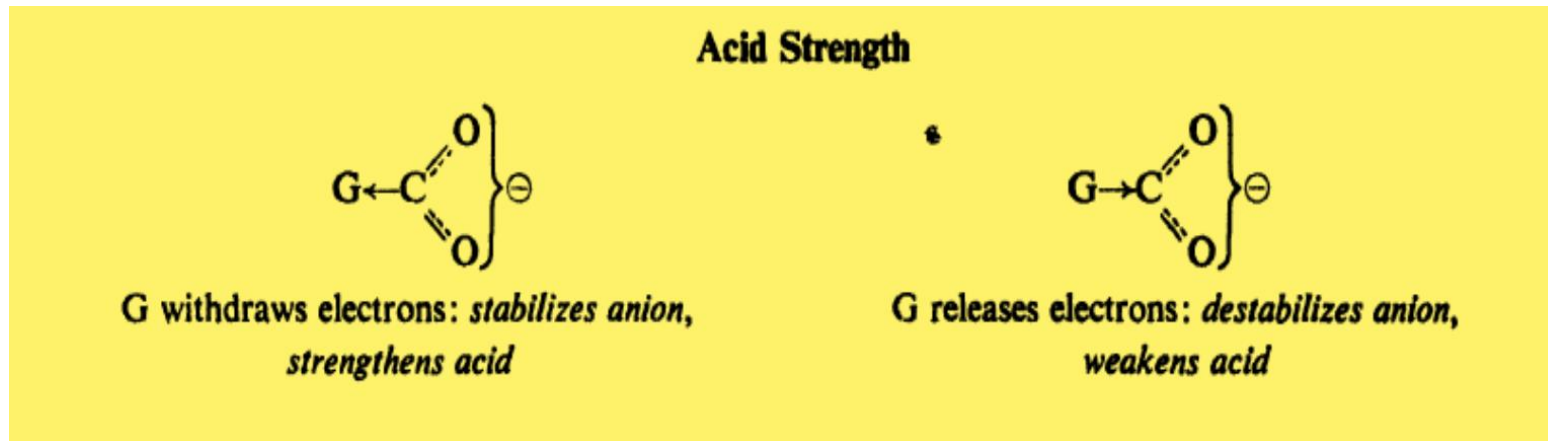


The fact that the anion is indeed a resonance hybrid is supported by the evidence of bond length. **Formic acid**, for example, contains a carbon-oxygen double bond and a carbon-oxygen single bond; we would expect these bonds to have different lengths. **Sodium formate**, on the other hand, if it is a resonance hybrid, ought to contain two equivalent carbon-oxygen bonds; we would expect these to have the same length, intermediate between double and single bonds. X-ray and electron diffraction show that these expectations are correct. **Formic acid contains one carbon-oxygen bond of 1.36 Å (single bond) and another of 1.23 Å (double bond); sodium formate contains two equal carbon-oxygen bonds, each 1.27 Å long.**



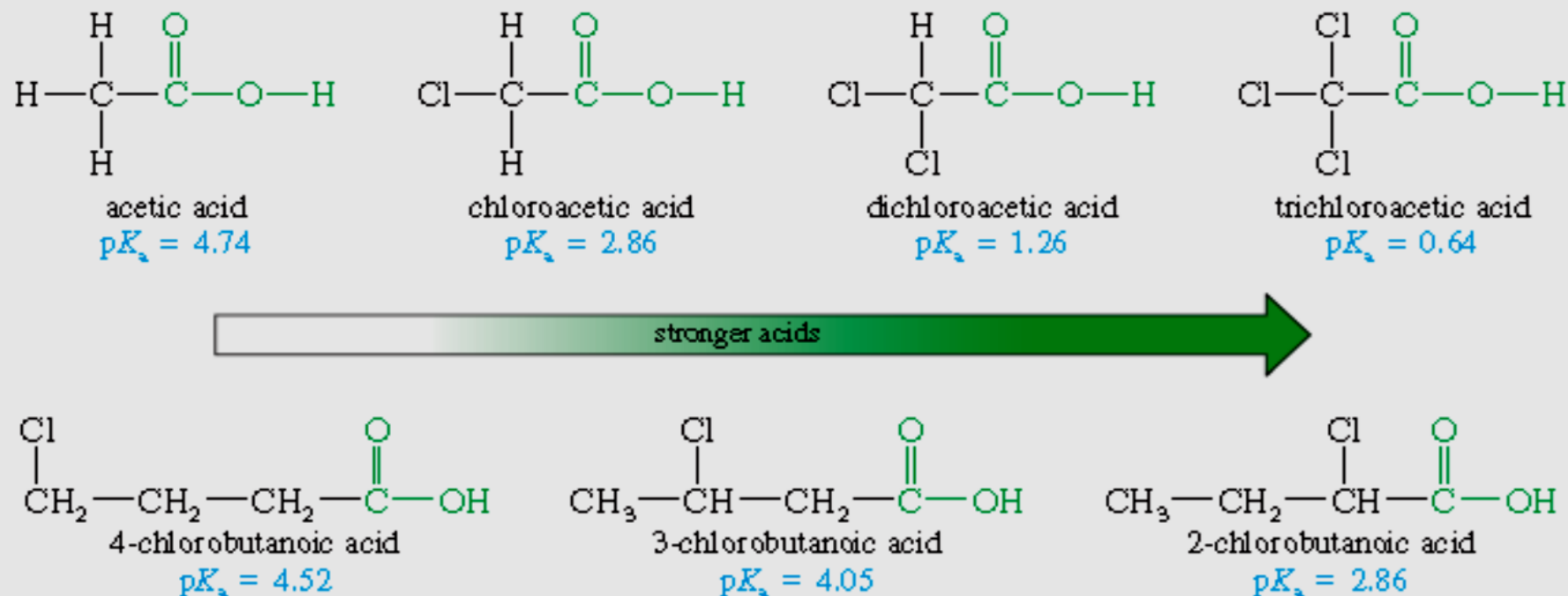
Effect of substituents on acidity:

The listing of pK_a values of carboxylic acids shown in the previous table indicates that there are substantial differences in acidity from one carboxylic acid to another. Because the dissociation of carboxylic acid is an equilibrium process, any factor that stabilizes the carboxylate anion relative to undissociated carboxylic acid will drive the equilibrium toward increased dissociation and result in increased acidity, any factor that makes the anion less stable should decrease acidity. we might reasonably expect; (*Electron-withdrawing substituents should disperse the negative charge, stabilize the anion, and thus increase acidity*) *Electron-releasing substituents should intensify the negative charge, destabilize the anion, and thus decrease acidity*).



a. Effect of substituent on aliphatic acids:

The electron-withdrawing halogens strengthen acids: chloroacetic acid is 100 times as strong as acetic acid, dichloroacetic acid is still stronger, and trichloroacetic acid is more than 10,000 times as strong as the unsubstituted acid. The magnitude of a substituent effect depends on its distance from the carboxyl group. Substituents on the carbon atom are most effective in increasing acid strength. More distant substituents have smaller effects on acidity, showing that inductive effects decrease rapidly with distance. α -Chlorobutyric acid is about as strong as chloroacetic acid. β -chlorobutyric acid is only six times as strong as butyric acid, and γ -chlorobutyric acid is only twice as strong. **(It is typical of inductive effects that they decrease rapidly with distance, and are seldom -important when acting through more than four atoms).**



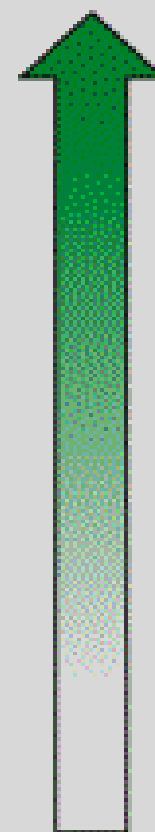
Electron withdrawing groups enhance acidity because they help to stabilize the negative charge of the conjugate base (the carboxylate ion).

Acid

pKa

F_3CCOOH
 Cl_3CCOOH
 Cl_2CHCOOH
 $\text{O}_2\text{N}-\text{CH}_2\text{COOH}$
 NCCH_2COOH
 FCH_2COOH
 ClCH_2COOH
 $\text{CH}_3\text{CH}_2\text{CHClCOOH}$
 BrCH_2COOH
 ICH_2COOH
 $\text{CH}_3\text{OCH}_2\text{COOH}$
 HOCH_2COOH
 $\text{CH}_3\text{CHClCH}_2\text{COOH}$
 PhCOOH
 PhCH_2COOH
 $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$
 CH_3COOH
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$

0.23
 0.64 stronger acids
 1.26
 1.68
 2.46
 2.59
 2.86
 2.86
 2.90
 3.18
 3.54
 3.83
 4.05
 4.19
 4.31
 4.52
 4.74
 4.82

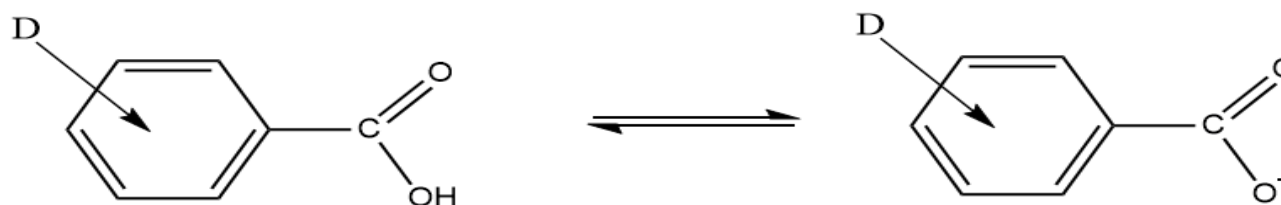
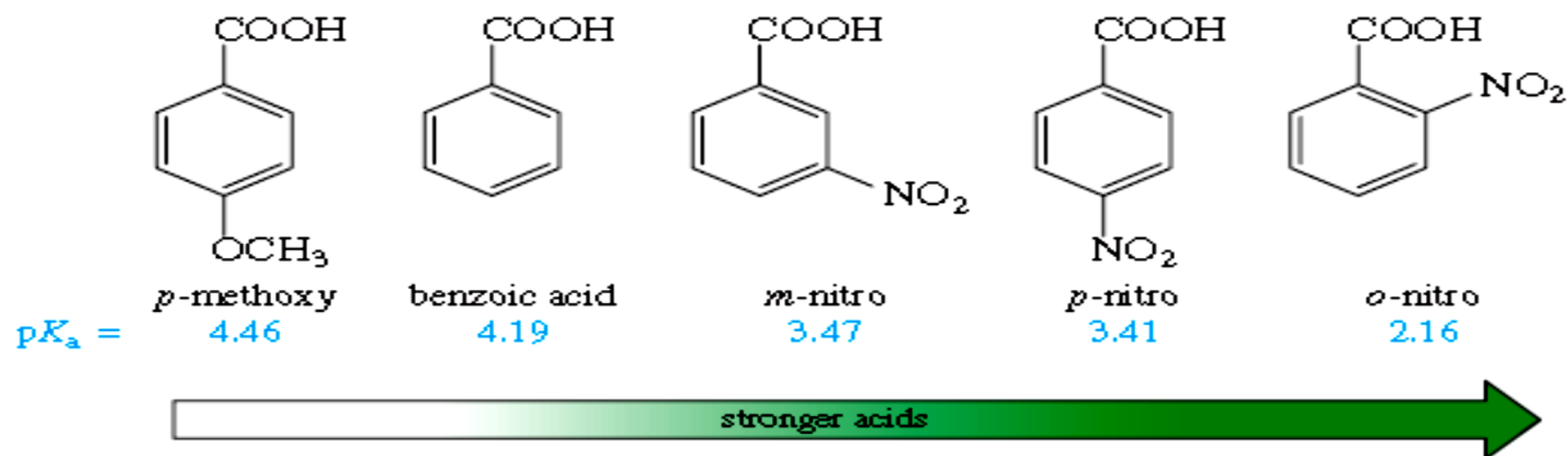


The amount of stabilization depends on:

1. The number of electron-withdrawing groups.
2. The strength of the electron-withdrawing groups.
3. The distance of the electron-withdrawing groups from the COOH group.

a. Effect of substituent on aromatic acids:

The aromatic acids are similarly affected by substituents: **CH₃**, **OH**, and **NH₂** make benzoic acid weaker, while **Cl** and **NO₂** make benzoic acid stronger. The acid-weakening groups are the ones that activate the ring toward electrophilic substitution (**and deactivate toward nucleophilic substitution**). The acid-strengthening groups are the ones that deactivate toward electrophilic substitution (**and activate toward nucleophilic substitution**). Furthermore, the groups that have the largest effects on reactivity whether activating or deactivating have the largest effects on acidity. In the examples shown below, notice that a nitro substituent (**electron-withdrawing**) increases the strength of the acid, while a methoxy substituent (**electron-donating**) decreases the acid strength. The nitro group has a larger effect in the **ortho** and **para** positions than in the **meta** position.



D: Electron -donating group

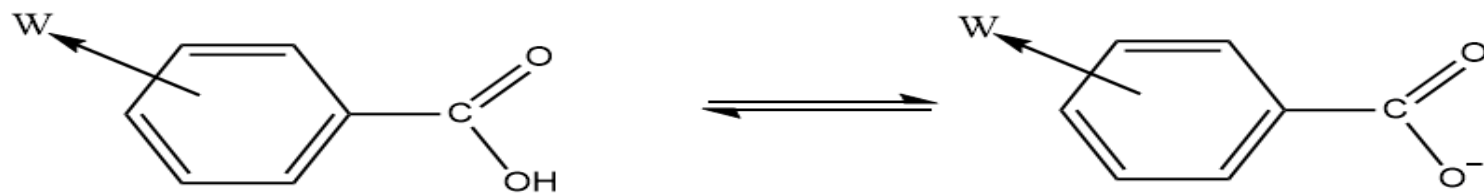
(The acid is less acidic than benzoic acid)

(D: destabilizes the carboxylate anion)

Electron donating groups increase the activity of benzene ring towards the electrophilic attacks and decrease the acidity of benzoic acid.

Common electron donating groups include (R) group and groups that contains lone pair of electrons like **N** or **O** atoms bonded to benzene ring.

substituent	Effect on electrophilic substitution	Effect on the acidity of substituted benzoic acid
:NH ₂ ,:NHR,:NR ₂	Activating groups	These groups make benzoic acid less acidic
:OH		
:OR		
:NHCOR		
R		



W: Electron -withdrawing group

(The acid is more acidic than benzoic acid)

(W: stabilizes the carboxylate anion)

Electron withdrawing groups decrease the activity of benzene ring towards the electrophilic attacks and increase the acidity of benzoic acid. Common electron withdrawing groups include **halogens** and groups that contains **full or partial positive charge** bonded to benzene ring.

substituent	Effect on electrophilic substitution	Effect on the acidity of substituted benzoic acid
-X (F, Cl, Br, I)	Deactivating groups	These groups make benzoic acid more acidic
-CHO		
-CO-R		
-COOR		
-COOH		
-CN		
-SO ₃ H		
-NO ₂		
-N ⁺ R ₃		