

- Acidic character of carboxylic acid

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Chemistry Department

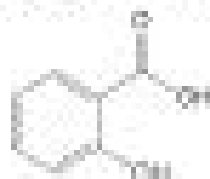
Naming Aromatic Carboxylic Acids

- The simplest aromatic carboxylic acid is benzoic acid.
- Substituted benzoic acids are named with **benzoic acid** as the parent name.
- Derivatives are named using numbers to show the location of substituents relative to the carboxyl group.
- The ring carbon attached to the carboxyl group is the #1 position.



Benzoic acid

Benzene carboxylic acid

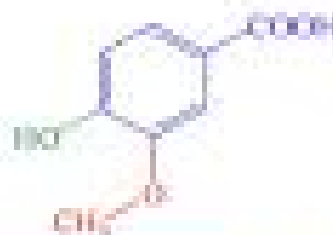


Salicylic acid

2-Hydroxybenzoic acid



2-Amino-4-chlorobenzoic acid



4-Hydroxy-3-methoxybenzoic acid

Table 30: Formulas and Nomenclature of Carboxylic Acids and Their Derivatives

class of compound	Z in $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Z}$	add to root*	
		prefix	suffix
Carboxylic acid	$-\text{OH}$		-ic acid
Salt	$-\text{OM}$ (metal)	metal	-ate
Acyl halide	$-\text{Cl}, -\text{Br}, \text{etc.}$		-yl chloride (bromide, etc.)
Anhydride	$-\text{OOCR}$		-ic anhydride
Carboxylic ester	$-\text{OR}', \text{OR}_2$	alkyl, aryl	-ate
Amide	$-\text{NH}_2$		-amide
Amide	$-\text{NHR}'$	<i>N'</i> -alkyl	-amide
Amide	$-\text{NR}'_2$	<i>N,N'</i> -dialkyl	-amide
Hydrazide	$-\text{NHNH}_2$		-hydrazide
Hydroxamic acid	$-\text{NHOH}$		-hydroxamic acid
Azide	$-\text{N}_3$		-yl azide
Peroxy acid	$-\text{OOH}$	per- or peroxy-	-ic acid
Nitrile	$\text{R}-\text{C}\equiv\text{N}$		-nitrile
Amidine	$\text{R}-\overset{\text{NH}}{\parallel}{\text{C}}-\text{NH}_2$		-amidine

*For example, acet-, propion-, etc., for common names; methyl-, ethyl-, etc., for IUPAC names.

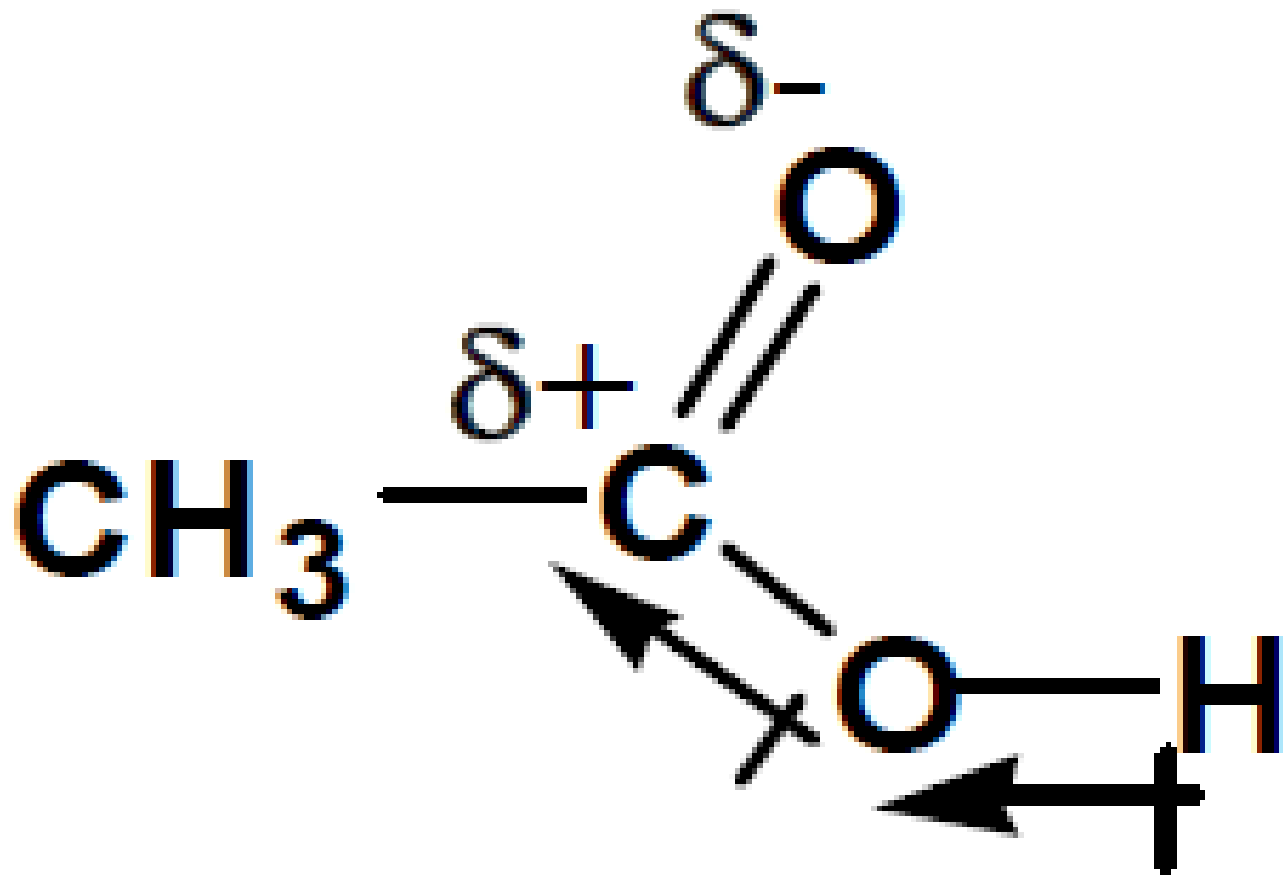
Summary: Reactions of negatively charged nucleophiles with carboxylic acid derivatives (excluding RCO^- and RCO^-)

Electrophile

Nucleophile	Acid chloride	Anhydride	Ester	Amide	Carboxylic acid
Cl^-	---	---	---	---	---
RCO^-		---	---	---	---
RO^-				---	---
NR_2^- (or MHR/NH_2)				---	---
OH^-					---

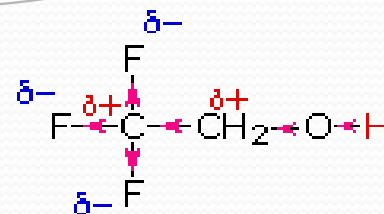
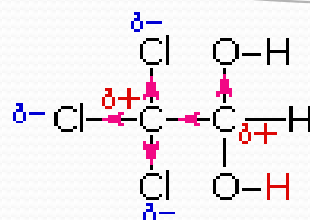
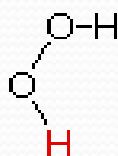
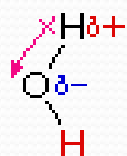
*** This reaction is called "trans-esterification". Note that this is an equilibrium reaction, since the leaving group has a near-identical basicity. The desired product can be made by using a large excess of nucleophile.

**** converting amides into carboxylic acids goes against the order of basicity; it is likely that NH_2 is protonated under these conditions, which would make it a much better leaving group. (This reaction requires high temperature)



- The resonance effect described here is undoubtedly the major contributor to the exceptional acidity of carboxylic acids. However, inductive effects also play a role. For example, alcohols have pK_a 's of 16 or greater but their acidity is increased by electron withdrawing substituents on the alkyl group.

1.



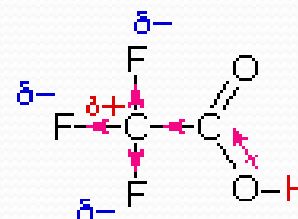
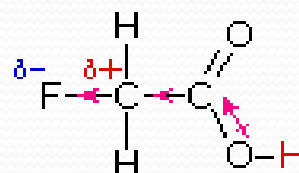
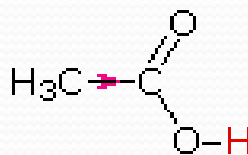
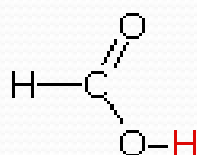
pK_a 15.7

11.6

10.0

12.2

2.



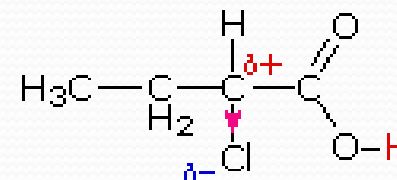
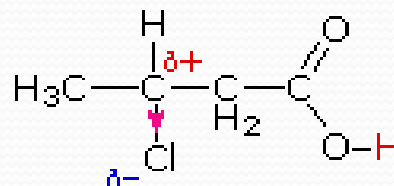
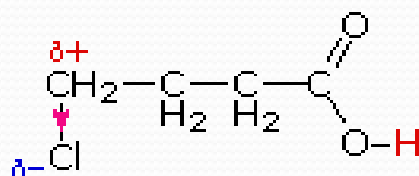
pK_a 3.75

4.74

2.65

0.0

3.



pK_a 4.53

4.05

2.89

Factors Affecting Acid Strength

	Group 17			
	F	Cl	Br	I
Period 2	HF_2 No acid or weak monoprotic	HCl Weak base	HBr ---	HI Weak acid
Period 3	H_2F_2 No acid or weak monoprotic	HClO_4 Weak base	HBrO_3 Weak acid	HIO_3 Strong acid

- The more polar the H-X bond and/or the weaker the H-X bond, the more acidic the compound.
- Acidity increases from left to right across a row and from top to bottom down a group.





3) Acid Strength

- Carboxylic acids are stronger acids compared to alcohols and phenols
- Electron withdrawing substituents near the carboxyl group increase the acidity
- Whereas electron donating substituents decrease the acidity.

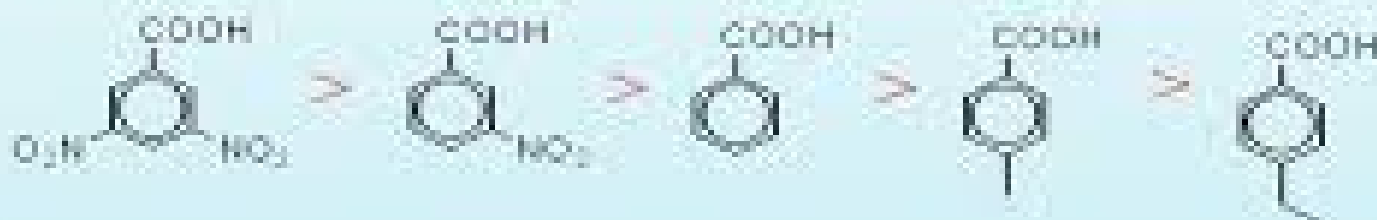
Inhibitor of Feet



$\text{HCOOH} > \text{CH}_3\text{COOH} > \text{CH}_3\text{CH}_2\text{COOH} > \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ (size of R group)

$\text{Cl}_3\text{CCOOH} > \text{Cl}_2\text{CHCOOH} > \text{ClCH}_2\text{COOH} > \text{CH}_3\text{COOH}$ (number of a.w.g.)

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{Cl})\text{COOH} > \text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_2\text{COOH} > \text{CH}_3\text{CH}(\text{Cl})\text{CH}_2\text{CH}_2\text{COOH} > \text{CH}_3(\text{Cl})\text{CH}_2\text{CH}_2\text{CH}_2\text{COOH}$ (position of a.w.g. relative to COOH group)





3-Ethyl-6-methyl
octanedioic acid
(3-甲基-6-乙基
辛二酸)



3-Bromocyclohexane-
carboxylic acid
(3-溴环己烷甲酸)

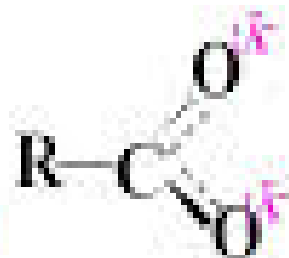
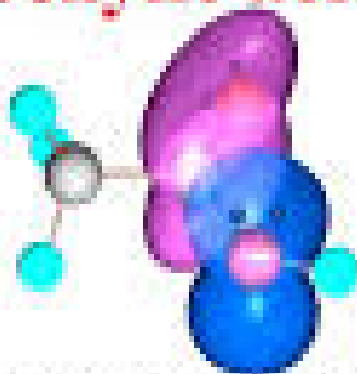


1-Cyclopentene-
carboxylic acid
(1-环戊烯甲酸)

13.2 Acidity of carboxylic acids



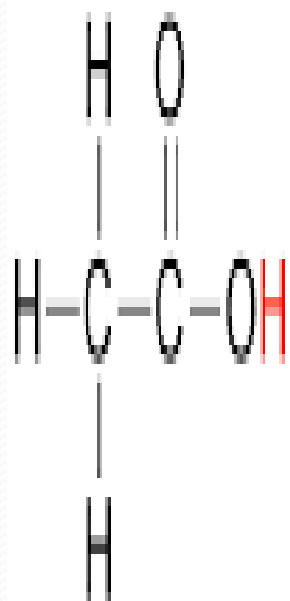
sp^2 hybridization,
 $p - \pi$ conjugation



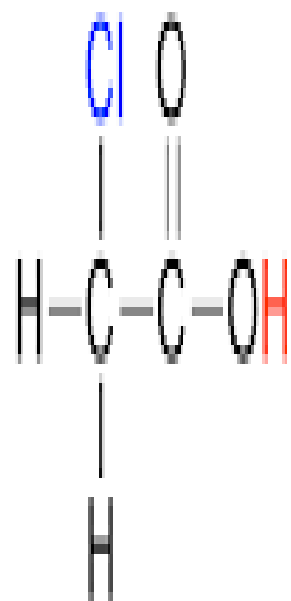
pk_a : 4 ~ 5 6.38 10 15.74 16 ~ 19



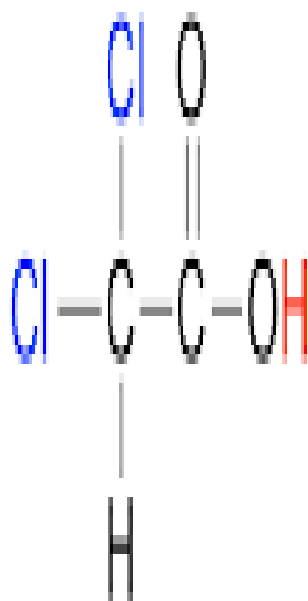
 ~ 25 ~ 34 ~ 50



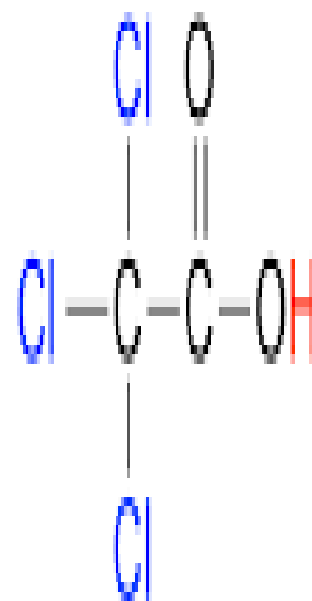
$$pK_a = 4.8$$



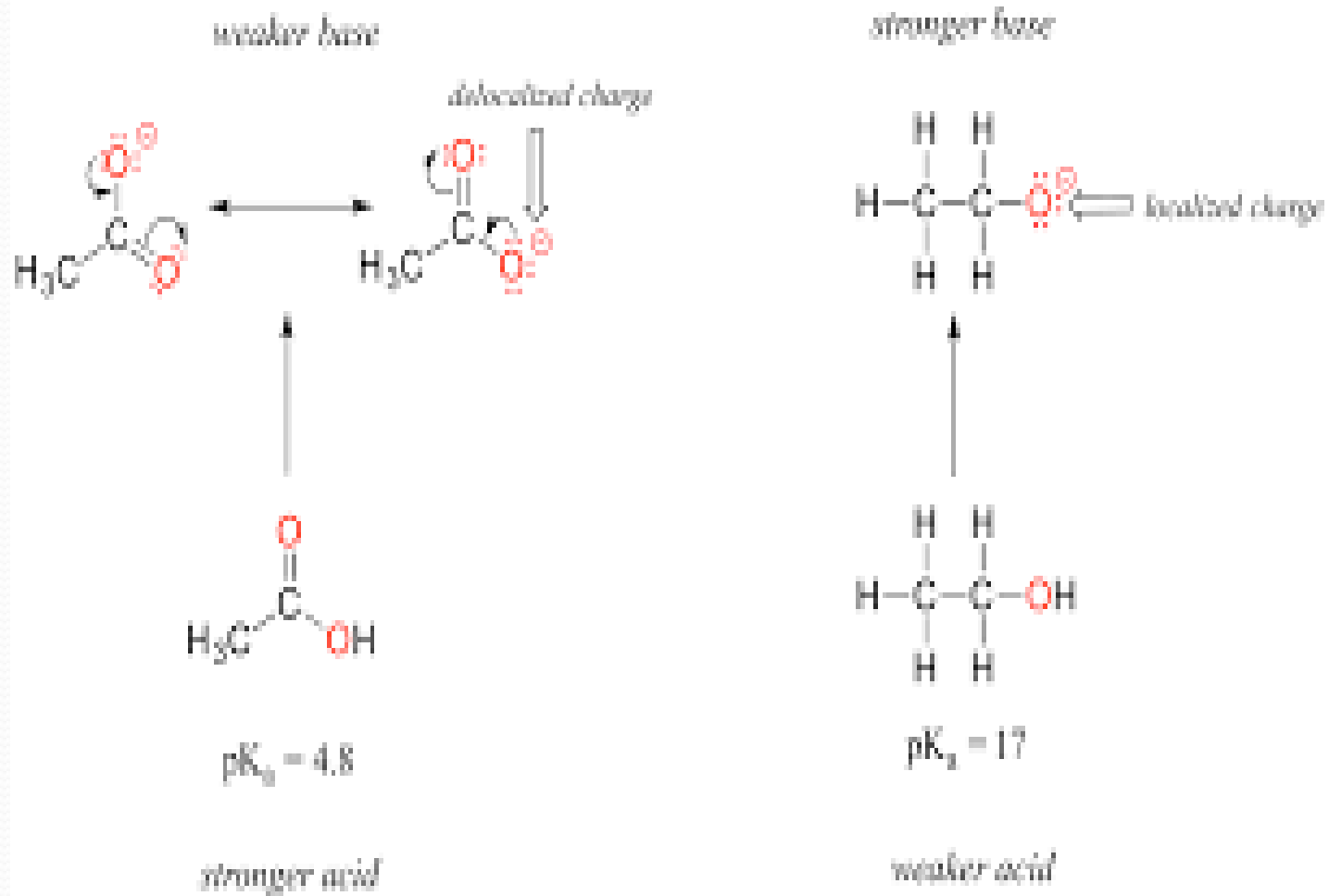
$$pK_a = 2.8$$



$$pK_a = 1.3$$



$$pK_a = 0.64$$

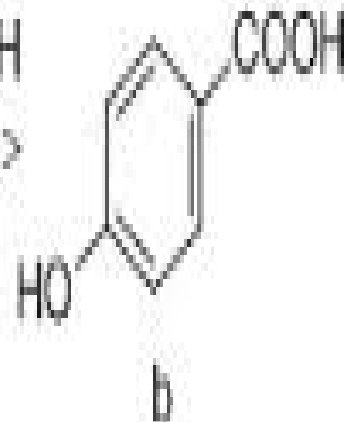
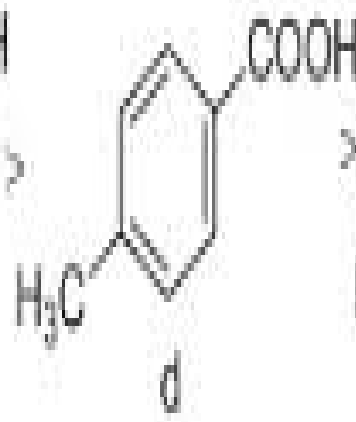
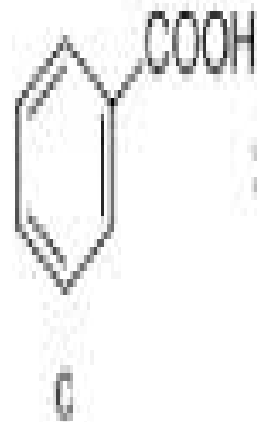
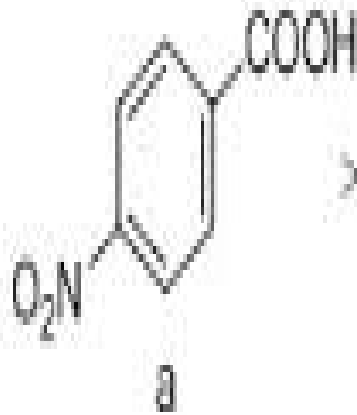


$PK_a = 3.42$

$PK_a = 4.2$

$PK_a = 4.36$

$PK_a = 4.58$



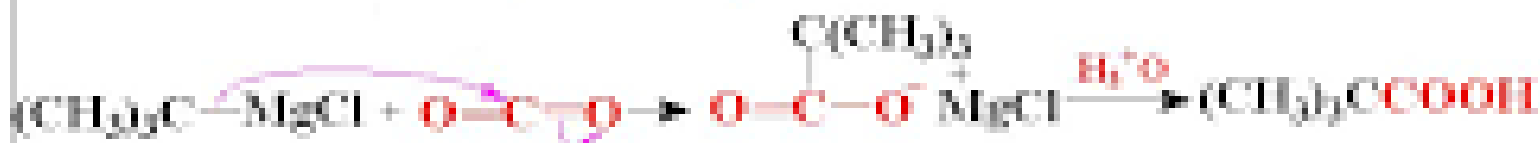
Acidity decrease



13.3 Preparation of carboxylic acids

13.3.1 Preparation of carboxylic acids by carboxylation (羧化作用) of Grignard reagent

Grignard reagents react with carbon dioxide to yield Mg salt of carboxylic acids , acidification (酸化) produces RCOOH



P316,
10.4

1) $\text{RX} \rightarrow \text{RCOOH}$

2) Extension of C skeleton
by 1 carbon atom.

3) Limitation: OH, NH, SH or C=O

2,2-Dimethyl
propanoic
acid(80%)



Carbonation = carboxylation Benzoic acid(85%)

2) Effects of substituent groups on the acidity of carboxylic acids.

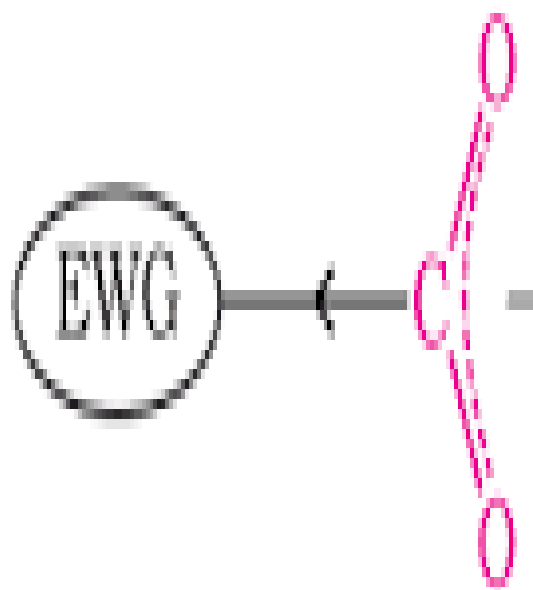
electron-withdrawing groups increase acidity

any factor that stabilises the carboxylate anion relative to undissociated carboxylic acid will shift the equilibrium to the right and result in increased acidity.

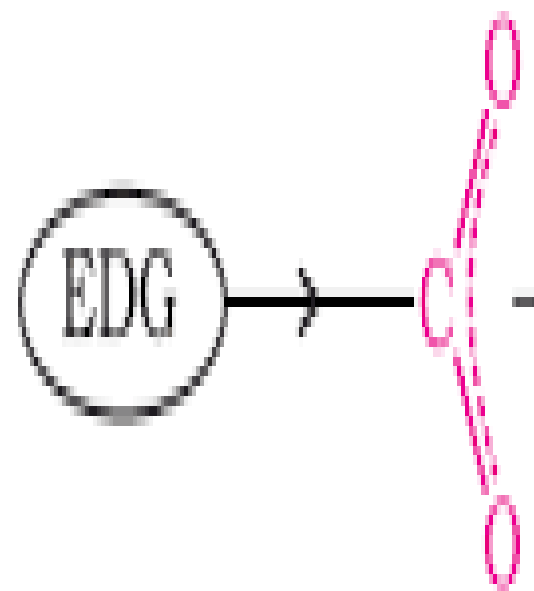
- any factor that destabilises the carboxylate anion relative to the undissociated acid will result in decreased acidity.

- for example, an electron-withdrawing atom (such as halogen atom) or an electron-withdrawing group (such as $-\text{NO}_2$) in the carboxylic acid molecule will withdraw electron density from carboxylate anion and delocalise the negative charge.

- the carboxylate anion is stabilised and acidity increases.



Electron withdrawing group (EWG)
stabilises the carboxylate anion
and strengthens the acid




Electron donating group (EDG)
destabilises the carboxylate
anion and weakens the acid

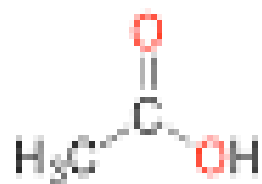
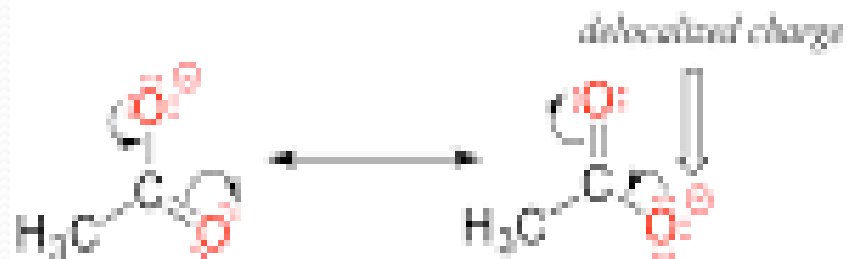
Nucleophilic substitution on carbonyl groups - Carboxylic acid derivatives

- Carboxylic acids are weak acids
 - values of pK_a for most aliphatic and aromatic carboxylic acids fall within the range 4 to 5
 - the greater acidity of carboxylic acids relative to alcohols, both of which contain an OH group, is due to resonance stabilization of the carboxylate anion
- electron-withdrawing substituents near the carboxyl group increase acidity through their inductive effect

	CH_3COOH	ClCH_2COOH	Cl_2CHCOOH	Cl_3CCOOH
	Acetic acid	Chloroacetic acid	Dichloroacetic acid	Trichloroacetic acid
pK_a :	4.76	2.86	1.48	0.70


Increasing acid strength

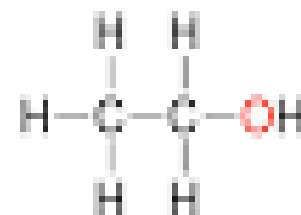
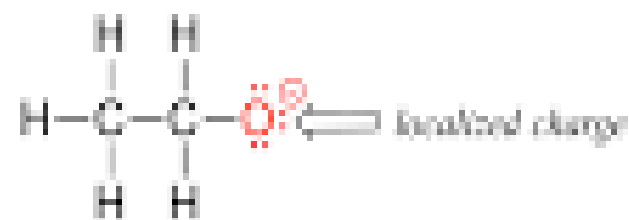
weaker base



$\text{p}K_a = 4.8$

stronger acid

stronger base



$\text{p}K_a = 17$

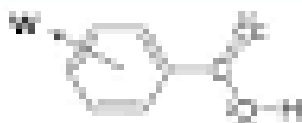
weaker acid

Substituent Effects in Aromatic Carboxylic Acids

- [2] **Electron-withdrawing groups stabilize a conjugate base, making an acid more acidic. The conjugate base is stabilized because electron density is removed from the negatively charged carboxylate anion.**

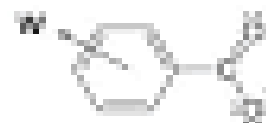
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W = Electron-withdrawing group



This acid is more acidic than benzoic acid.

$pK_a < 4.2$



W stabilizes the carboxylate anion.

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Electron-donor groups
D

- activate benzene to electrophilic attack
- make a benzoic acid less acidic

Electron-withdrawing groups
W

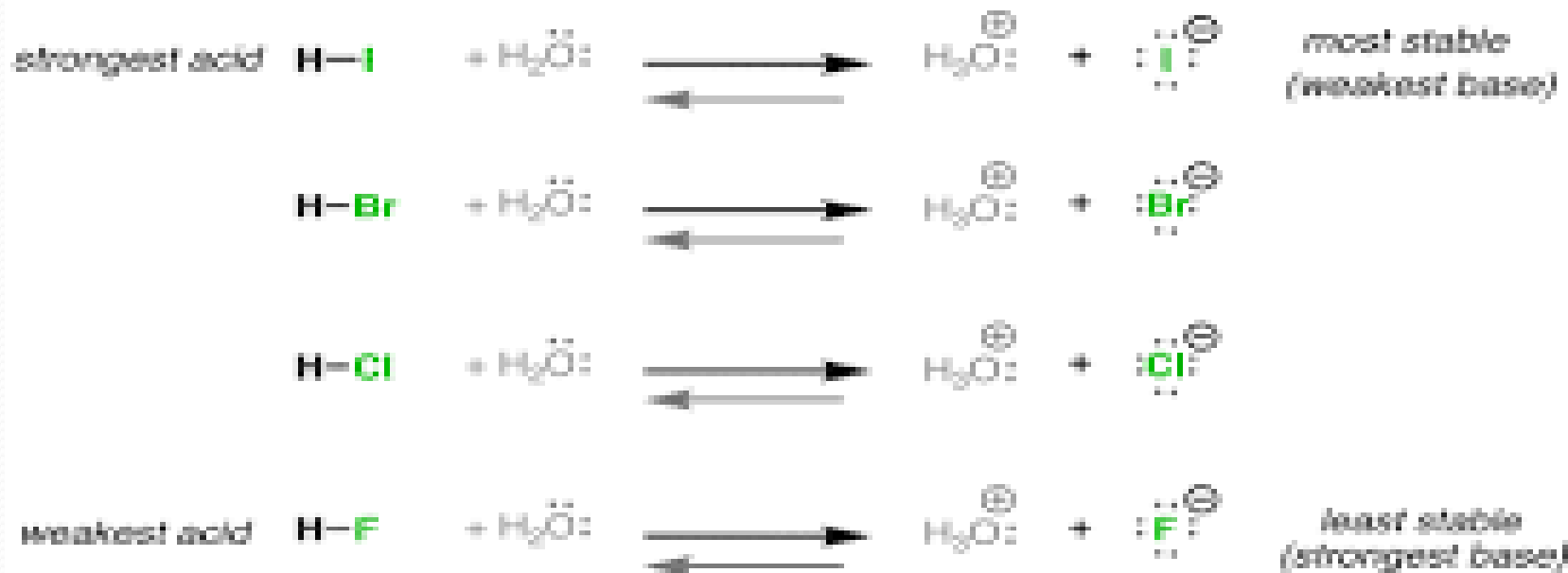
- deactivate benzene to electrophilic attack
- make a benzoic acid more acidic

2. Going **down** the periodic table, greater polarizability stabilizes negative charge.



least polarizable
(least stable)

most polarizable (most stable)



RESONANCE EFFECT OR MESOMERIC EFFECT :

The mesomeric effect is defined as the polarity produced in the molecule by the interaction of two π bonds or between a π bond and lone pair of electrons present on an adjacent atom. It is symbolized by M or R.



Inductive Effects on Acidity

The increased acidity of carboxylic acids can be attributed to electrostatic effects, such as induction. More electronegative groups will greatly change the distribution of electron density in the molecule by withdrawing electrons. This effect will make the proton more acidic.



Acidity increases as more electronegative substituents are added to the molecule and withdraw electron density from the acidic proton.

The relative distance of the electronegative group also affects the acidity of carboxylic acids. The closer the electron withdrawing substituent is to the reactive proton, the more acidic the molecule becomes.

Compound	pKa
$\text{CH}_3\text{CO}_2\text{H}$	4.74
$\text{BrCH}_2\text{CO}_2\text{H}$	2.9
$\text{ClCH}_2\text{CO}_2\text{H}$	2.85
$\text{FCH}_2\text{CO}_2\text{H}$	2.65
$\text{CH}_3\text{OCH}_2\text{CO}_2\text{H}$	2.89
$\text{CH}_3\text{OCH}_2\text{CO}_2\text{H}$	4.05
$\text{ClCH}_2\text{CH}_2\text{CO}_2\text{H}$	4.53

Reusch, W. Carboxylic Acids. <http://www2.chemistry.msu.edu/academic/reusch/VirtTxtLrnCenter/11.htm> (Accessed October 2015).

❏ Difference between inductive effect and Mesomeric effect :-

Inductive effect	Mesomeric effect
1. It is operative in saturated and unsaturated compounds.	1. It is operated in unsaturated compound, specially having conjugated system.
2. It involves electrons of sigma bonds	2. It involves electrons of π -bonds or lone pair of electrons.
3. The electron pair is displaced from its position and thus partial charges are developed	3. The electron pair is completely transferred and thus full positive and negative charges are developed.
4. It is transmitted over a quite short distance .The effect become negligible after third carbon atom in the chain .	4. It is transmitted from one end to other end of the chain provided conjugation is present