

# Acidity of Carboxylic Acids

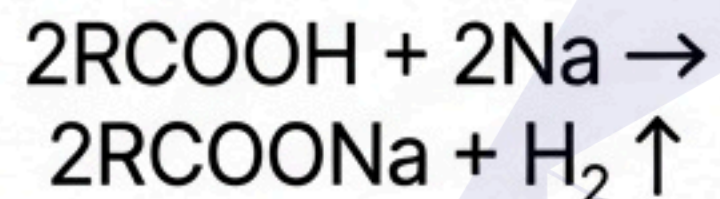
Cleavage of the O–H Bond:  
Mechanisms, pKa, and  
Substituent Effects



A **visual guide** to organic acidity,  
focusing on resonance stabilization  
and **inductive power rankings**.

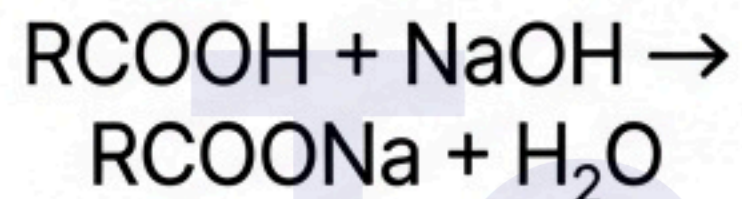
# Chemical Proof of Acidity

## Electropositive Metals



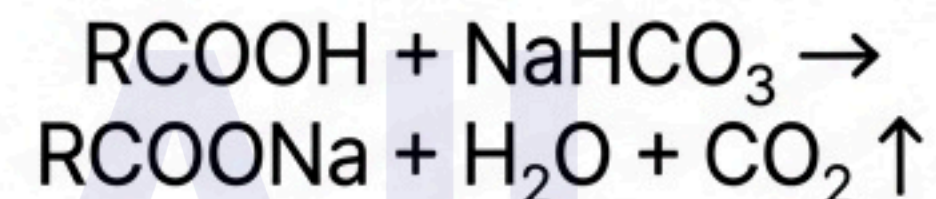
Reacts to form salt and liberates hydrogen gas.

## Alkalies



Reacts to form salt and water (similar to phenols).

## Carbonates & Bicarbonates



Reacts to form salt, water, and liberates carbon dioxide.



**Diagnostic Marker:** The Carbonate Test distinguishes carboxylic acids from phenols. Weaker bases like  $\text{NaHCO}_3$  cannot react with phenols, making the evolution of  $\text{CO}_2$  a definitive identifier.

# The Mathematics of Acidity (pKa)



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$K_a$  = Acid Dissociation Constant

**Strong**

pKa < 1

**Moderate**

pKa 1 to 5

**Weak**

pKa 5 to 15

**Extremely Weak**

pKa > 15

**Smaller pKa = Stronger Acid**

**Example:**

Trifluoroacetic acid,  
pKa = 0.23

**Example:**

Benzoic acid,  
pKa = 4.19

**Example:**

Acetic acid,  
pKa = 4.76

**Example:**

Acetic acid,  
pKa = 4.76

Carboxylic acids are weaker than mineral acids (pKa  $\approx$  -7) but significantly stronger than alcohols (pKa  $\approx$  16) and simple phenols (pKa  $\approx$  10).



# You've Learned the Theory. Let's Test Them Now.

$$E=mc^2$$



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## Key Highlights

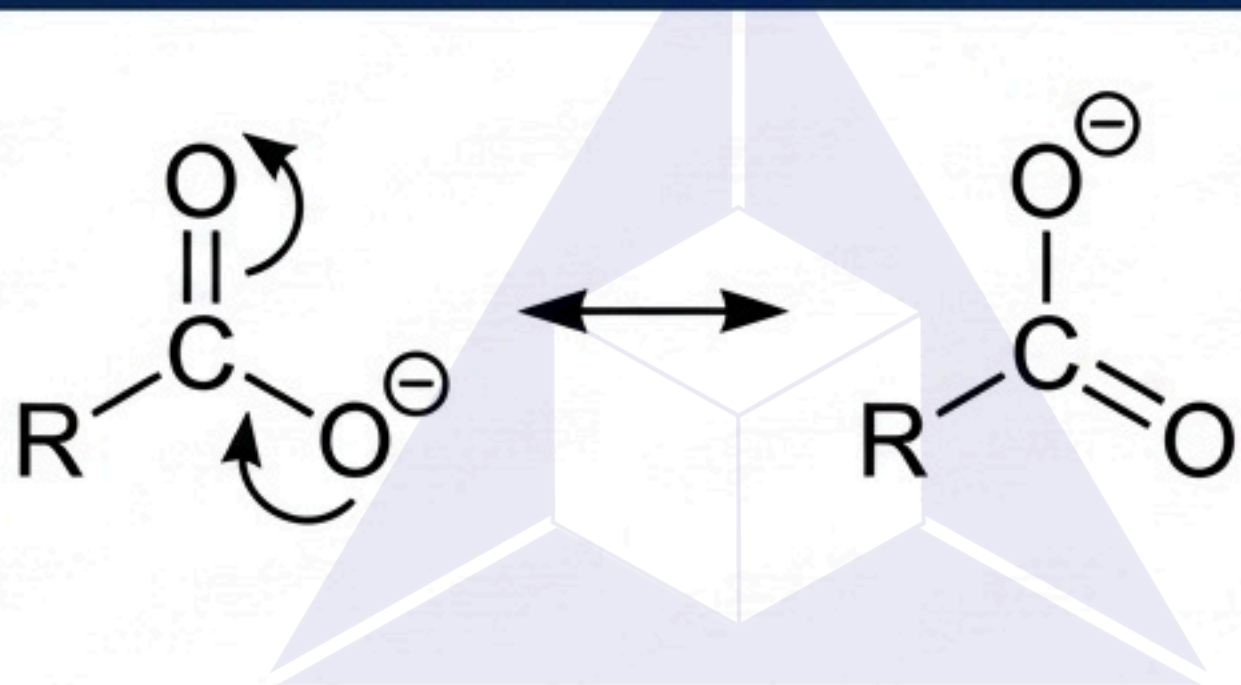
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# The Secret to Stability: Resonance

Acidity depends on the stability of the conjugate base.

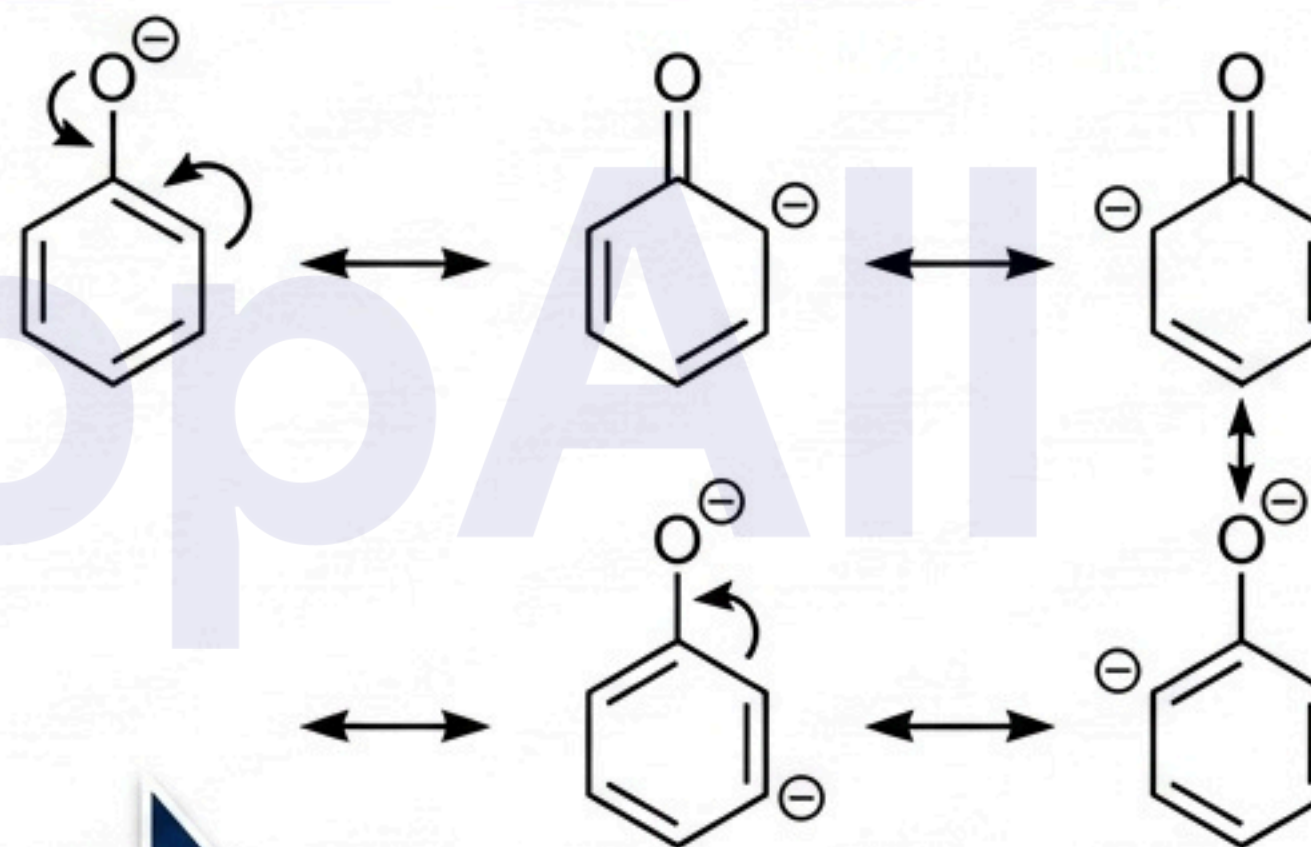
## Carboxylate Ion (Highly Stable)



### ✓ Equivalent Structures

The negative charge is perfectly delocalized over two highly electronegative oxygen atoms.

## Phenoxide Ion (Less Stable)

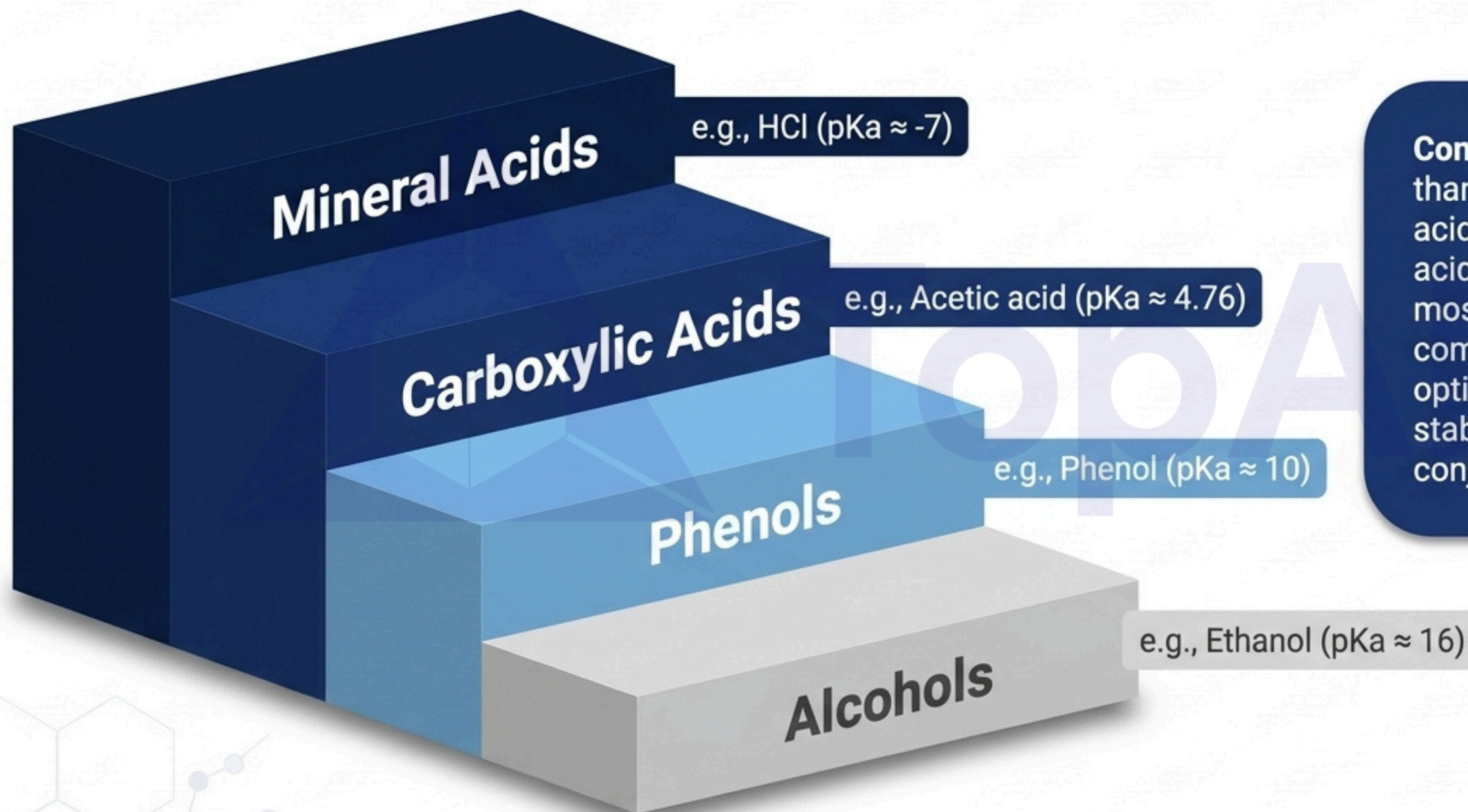


### Non-Equivalent Structures

The negative charge is less effectively delocalized onto less electronegative carbon atoms.

Greater delocalization on  
electronegative atoms  
= Stronger Acid

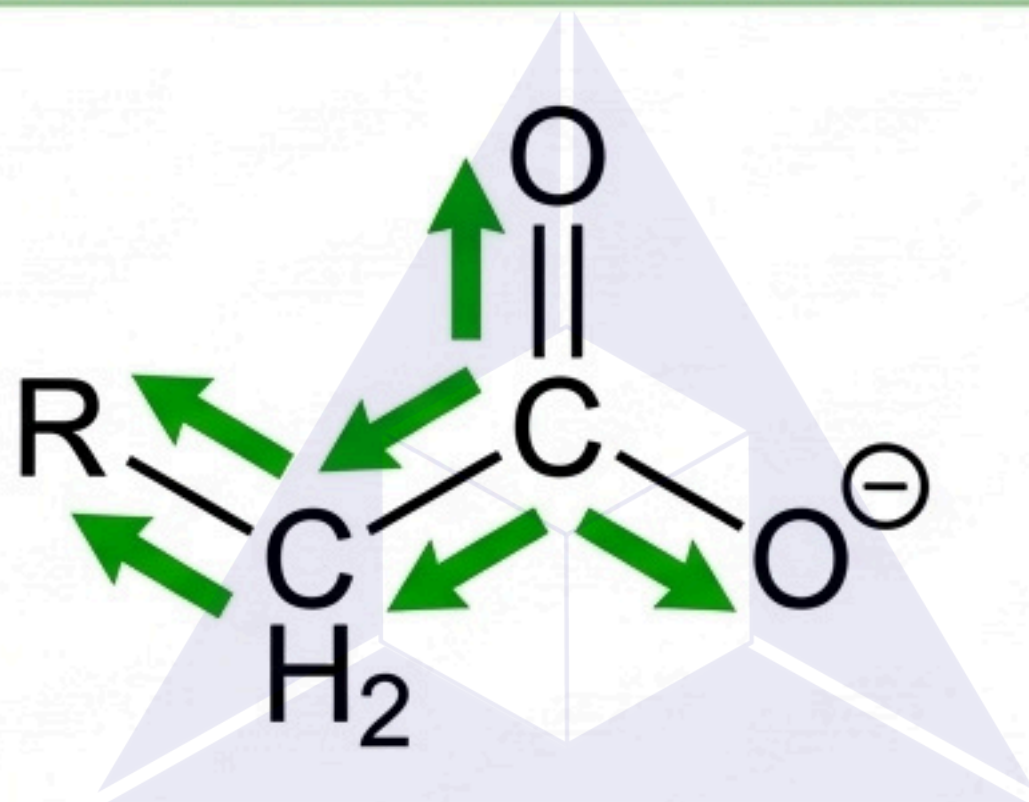
# The Acidity Hierarchy Matrix



**Context:** While weaker than inorganic mineral acids, carboxylic acids are the most acidic organic compounds due to optimal resonance stabilization in their conjugate base.

# The Substituent Effect: Inductive Tug-of-War

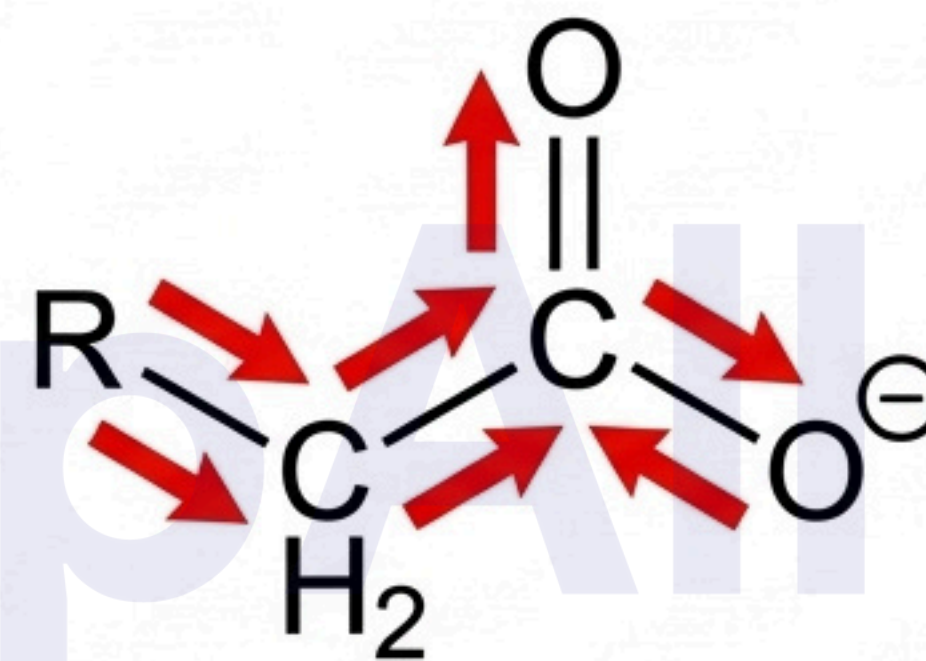
## Electron Withdrawing Groups (EWG)



**Mechanism:** Stabilizes the carboxylate anion through delocalization of the negative charge.

**Result: Strengthens Acid**

## Electron Donating Groups (EDG)

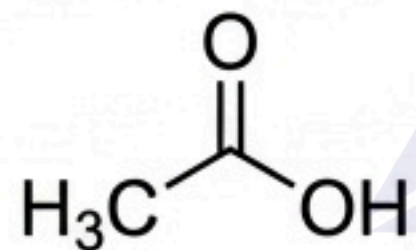


**Mechanism:** Destabilizes the carboxylate anion by intensifying the negative charge.

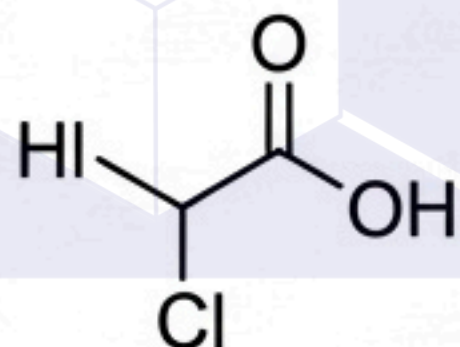
**Result: Weakens Acid**

# Inductive Power Ranking

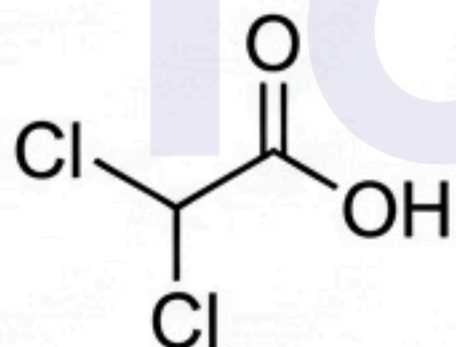
The strength sequence of Electron Withdrawing Groups (EWG)



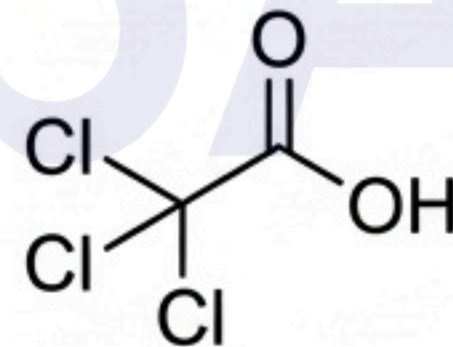
**CH<sub>3</sub>COOH**  
(Weakest)



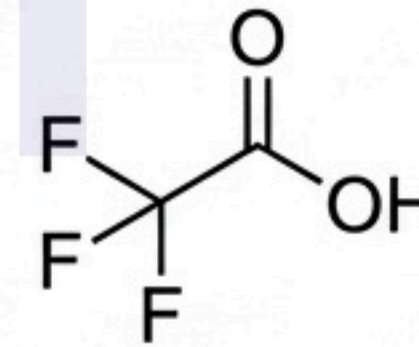
**CH<sub>2</sub>ClCOOH**



**CHCl<sub>2</sub>COOH**



**CCl<sub>3</sub>COOH**

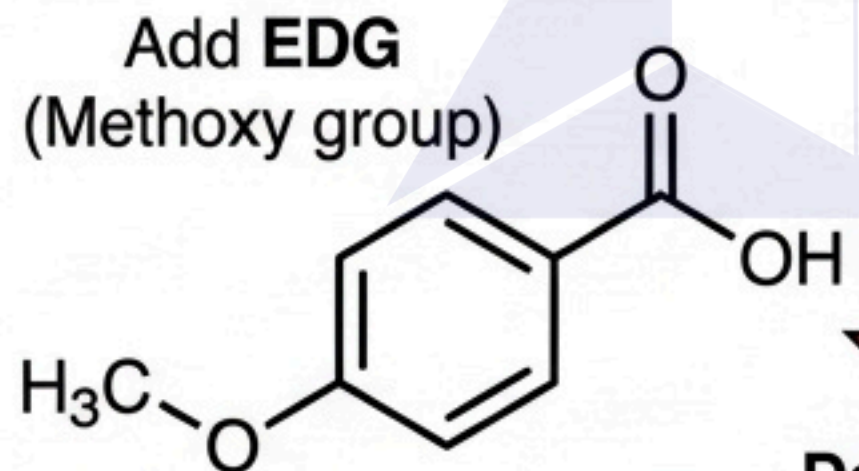


**CF<sub>3</sub>COOH**  
(Strongest)

Replacing hydrogen atoms with highly electronegative fluorine or chlorine atoms drastically stabilizes the conjugate base, plummeting the **pKa**.

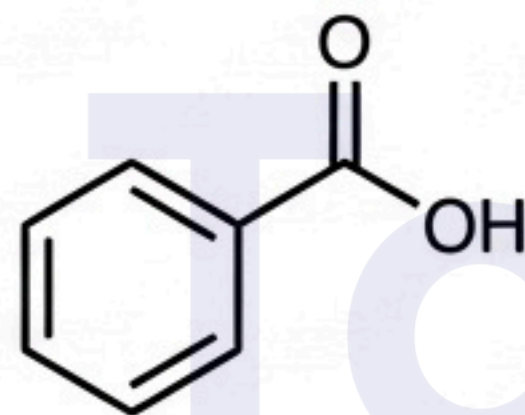
# Application: Aromatic Carboxylic Acids

Direct attachment to an  $sp^2$  hybridized carbon (phenyl ring) increases acidity due to higher electronegativity.



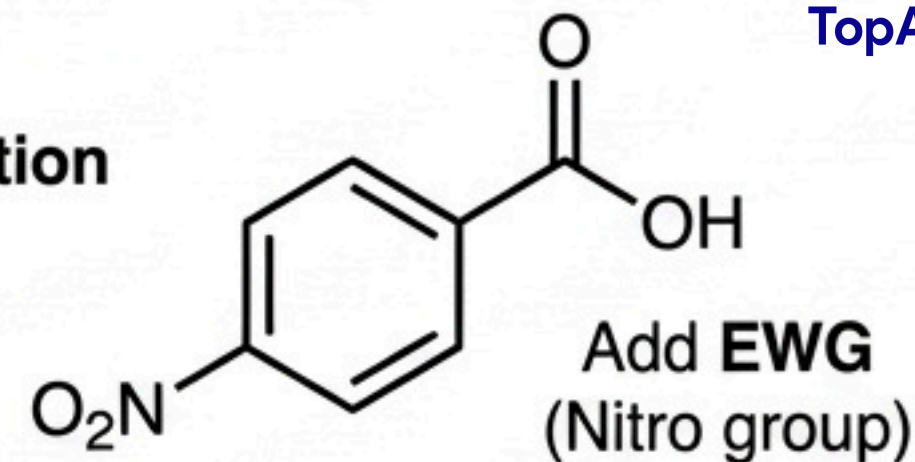
pKa = 4.46 (Weaker Acid)

Destabilization



Benzoic acid  
(pKa = 4.19)

Stabilization



pKa = 3.41 (Stronger Acid)

The presence of EWGs on the phenyl ring pulls electron density away from the carboxylate, while EDGs push density into it, dictating the ultimate acid strength.



# You've Learned the Theory.

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