

# Chemistry 2000 Slide Set 19a: Organic acids

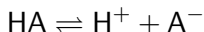
## Structural determinants of acidity

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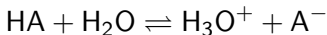
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## The acid dissociation constant, $K_a$

- The strength of an acid HA is measured by the **acid dissociation constant**,  $K_a$ , the equilibrium constant for the dissociation of the acid into a proton and its **conjugate base**:



- It is sometimes useful to think of  $K_a$  as the equilibrium constant for the reaction of an acid with water:



- Larger  $K_a \implies$  stronger acid

$pK_a$ 

- $K_a$  values range over many orders of magnitude, so they are not very convenient for some purposes (e.g. comparisons between acids).
- Define

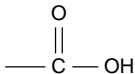
$$pK_a = -\log_{10} K_a$$

- Smaller  $pK_a \implies$  stronger acid
- Strong acids may have negative  $pK_a$  values (dissociate completely in water).

## Organic acids

	Functional group	$pK_a$
Stronger acid	Carboxylic acids	3–5
	Phenols	1–10
	Water	14 ( $pK_w$ )
Weaker acid	Alcohols	15–18

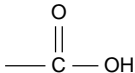
## Acidity of carboxylic acids



- Carboxylic acids are among the most acidic organic compounds.
- Acid strength depends on
  - the polarity of the bond to the dissociable hydrogen (in this case the O-H bond), and
  - the stability of the conjugate base.

# Acidity of carboxylic acids

## Polarity of the O-H bond

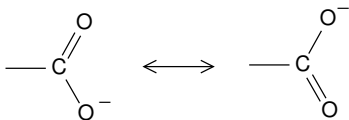


- The carbonyl group is **electron withdrawing**: Because of the large electronegativity of oxygen, electron density is pulled away from the carbon atom. This in turn pulls electron density away from the hydrogen atom, increasing the partial positive charge on this atom.

# Acidity of carboxylic acids

## Stability of carboxylate ions

- Carboxylate anions are **resonance stabilized**:



The negative charge is therefore spread over a larger region of the molecule, which tends to stabilize the anion.

- How would this manifest itself in an MO description?

- Substituents on the adjacent carbon to the carboxylic acid functional group can have a substantial effect on the  $pK_a$ .
- Consider the following series:

Molecule	$\text{CH}_3\text{COOH}$	$\text{FCH}_2\text{COOH}$	$\text{F}_2\text{CHCOOH}$	$\text{F}_3\text{CCOOH}$
$pK_a$	4.67	2.66	1.24	0.23

- The fluorine atom is very electronegative and “pulls” electron density to itself. This decreases the negative charge carried by the carboxylate group, which stabilizes the conjugate base.

Base	$\text{CH}_3\text{COO}^-$	$\text{FCH}_2\text{COO}^-$	$\text{F}_2\text{CHCOO}^-$	$\text{F}_3\text{CCOO}^-$
Charge of O	-0.77	-0.754	-0.739	-0.711

- This is called an **inductive effect**.



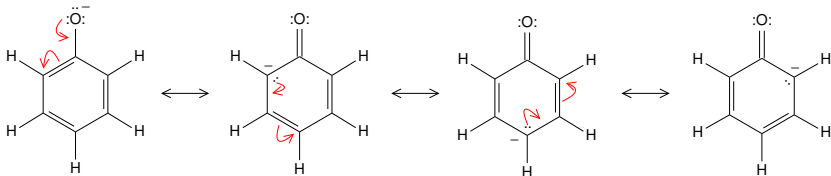
# Alcohols

- Unlike carboxylic acids, most alcohols are only about as acidic as water itself.
- Why?
  - No electron-withdrawing group (in an ordinary alcohol) to increase the polarization of the O-H bond
  - No resonance stabilization of the negative charge of the conjugate base
- Inductive effects can increase the acidity of an alcohol.

Example:	Molecule	$\text{CH}_3\text{CH}_2\text{OH}$	$\text{Cl}_3\text{CCH}_2\text{OH}$
	$\text{p}K_a$	15.9	12.24

# Phenols

- Phenols are much more acidic than ordinary alcohols.
- Phenol itself has a  $pK_a$  of 9.95, vs 17 for cyclohexanol.
- Why? Resonance stabilization of the charge on the phenolate anion:



- Some phenols are even more acidic because the substituents can participate in charge delocalization.

Example: *p*-nitrophenol has a  $pK_a$  of 7.21.

