

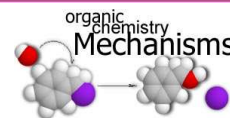
CHEM 344

ORGANIC REACTION MECHANISM

FOR CHEMISTRY' STUDENTS, COLLEGE OF SCIENCE

PRE-REQUISITES COURSE; CHEM 241

CREDIT HOURS; 2 (2+0+0)



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INTRODUCTION

ACIDS AND BASES

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ACID-BASE REACTIONS

- Many of the reactions that occur in organic chemistry are either acid-base reactions themselves or they involve an acid-base reaction at some stage
- Arrhenius regarded acid-base reactions as occurring only in water,
 - An **Arrhenius acid** is a source of H^+ ion.
 - An **Arrhenius base** is a source of OH^- ion.

The Arrhenius acid-base theory provided a good start toward understanding acid-base chemistry, but it proved much too limited in its scope.



- Two classes of acid-base reactions are fundamental in organic chemistry:
 - Brønsted-Lowry**
 - Lewis acid-base reactions**

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THE STRENGTH OF BRØNSTED-LOWRY ACIDS AND BASES

ACIDITY AND pK_a

- Relative Strength of Selected Acids & Their Conjugate Bases

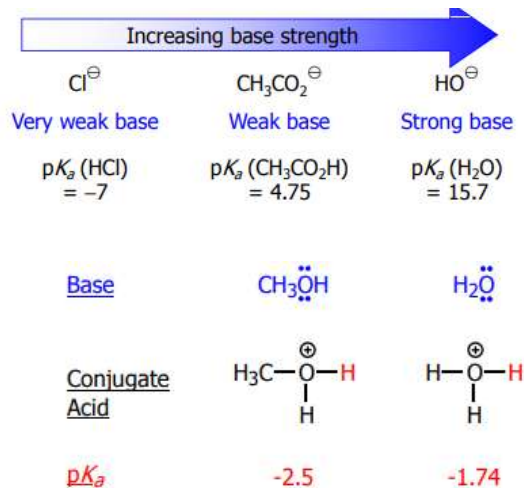
	Acid	pK_a	Conjugate base
 Increasing acidity of the acid	H-Cl	-7	Cl^-
	CH_3COO-H	4.8	CH_3COO^-
	HO-H	15.7	HO^-
	CH_3CH_2O-H	16	$CH_3CH_2O^-$
	$HC\equiv CH$	25	$HC\equiv C^-$
	H-H	35	H^-
	H_2N-H	38	H_2N^-
	$CH_2=CH_2$	44	$CH_2=\bar{C}H$
	CH_3-H	50	CH_3^-
			 Increasing basicity of the conjugate base

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THE STRENGTH OF BRØNSTED-LOWRY ACIDS AND BASES

PREDICTING THE STRENGTH OF BASES

- The stronger the acid, the weaker its conjugate base
- The larger the pK_a of the conjugate acid, the stronger the base
- Since $\text{CH}_3\text{O}^+\text{H}_2$ is a stronger acid than H_3O^+ , H_2O is a stronger base than CH_3OH



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FACTORS AFFECTING ACID STRENGTH

RELATIONSHIPS BETWEEN STRUCTURE AND ACIDITY

- The stronger the H-X bond, the weaker the acid.

- The strength of H-X bond

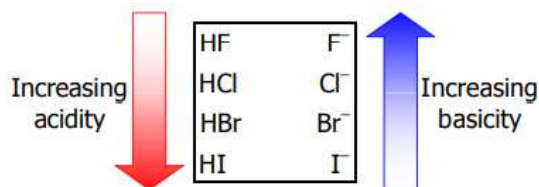


	H-F	H-Cl	H-Br	H-I
Bond Length (Å)	0.92	1.28	1.41	1.60
pK_a	3.2	-7	-9	-10

Increasing acidity

- The stronger the acid, the weaker the conjugate base.

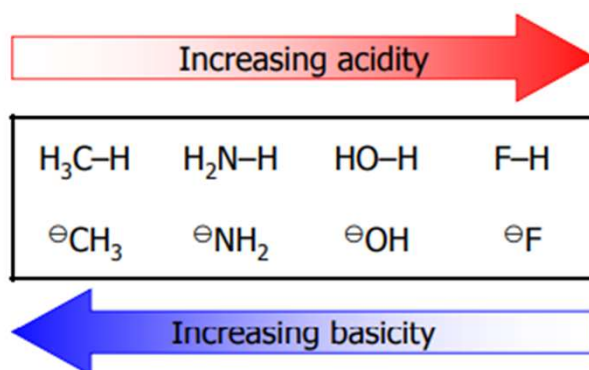
- Thus acidity increases as we descend a vertical column in a group in the Periodic Table



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FACTORS AFFECTING ACID STRENGTH RELATIONSHIPS BETWEEN STRUCTURE AND ACIDITY

- The higher the electronegativity of an atom, the easier it will acquire a negative charge.
 - Thus acidity increases from left to right when we compare compounds in the same row of the Periodic Table



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FACTORS AFFECTING ACID STRENGTH RELATIONSHIPS BETWEEN STRUCTURE AND ACIDITY

Acidity increases within a given row
(electronegativity effect)

	C	N	O	F
Hydride	$(\text{H}_3\text{C-H})$	$(\text{H}_2\text{N-H})$	(HO-H)	(F-H)
pK_a	48	38	15.7	3.2
			S	Cl
			(HS-H)	(Cl-H)
			7.0	-7
			Se	Br
			(HSe-H)	(Br-H)
			3.9	-9
				I
				(I-H)
				-10

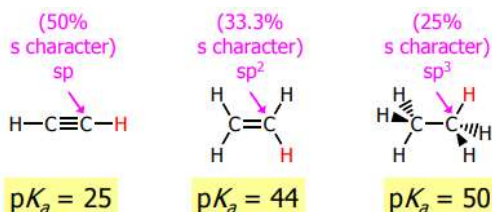
Acidity increases within a given column
(bond strength effect)

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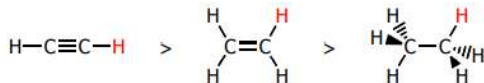
FACTORS AFFECTING ACID STRENGTH

THE EFFECT OF HYBRIDIZATION

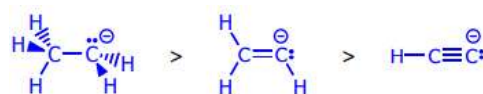
- The higher the percent of **s-character** of the hybrid orbital, the closer the lone pair is held to the nucleus, and the more stable the conjugate base.



- Relative acidity of the hydrocarbons



- Relative basicity of the carbanions

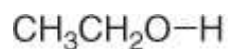


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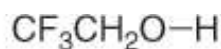
FACTORS AFFECTING ACID STRENGTH

INDUCTIVE EFFECTS

- The **inductive effect** of a group can be *electron donating* or *electron withdrawing*
- When electron density is pulled away from the negative charge through σ bonds by very electronegative atoms, it is referred to an **electron withdrawing inductive effect**.



ethanol

 $\text{p}K_a = 16$ 

2,2,2-trifluoroethanol

 $\text{p}K_a = 12.4$

← stronger acid

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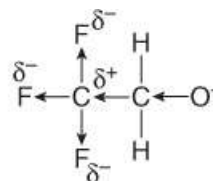
FACTORS AFFECTING ACID STRENGTH

INDUCTIVE EFFECTS

- More electronegative atoms stabilize regions of high electron density by an electron withdrawing inductive effect.
- The more electronegative the atom and the closer it is to the site of the negative charge, the greater the effect.
- The acidity of H—A increases with the presence of electron withdrawing groups in A.



No additional electronegative atoms stabilize the conjugate base.



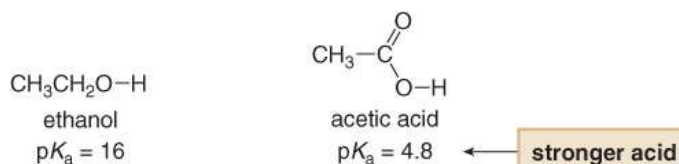
CF_3 withdraws electron density, stabilizing the conjugate base.

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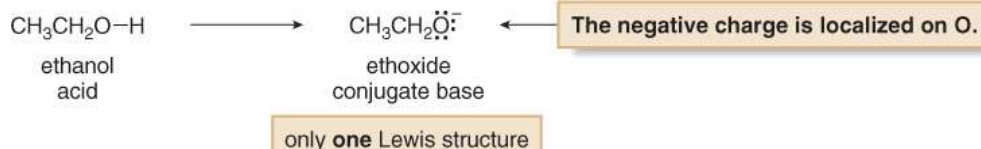
FACTORS AFFECTING ACID STRENGTH

RESONANCE EFFECTS

- when we compare the acidities of ethanol and acetic acid, we note that the latter is more acidic than the former.



- When the conjugate bases of the two species are compared, it is evident that the conjugate base of acetic acid enjoys resonance stabilization, whereas that of ethanol does not.

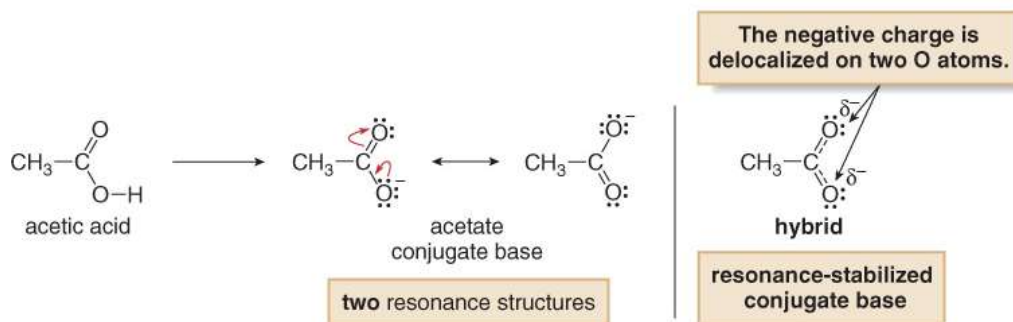


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FACTORS AFFECTING ACID STRENGTH

RESONANCE EFFECTS

- Resonance delocalization makes CH_3COO^- more stable than $\text{CH}_3\text{CH}_2\text{O}^-$, so CH_3COOH is a stronger acid than $\text{CH}_3\text{CH}_2\text{OH}$.



- The acidity of $\text{H}-\text{A}$ increases when the conjugate base A^- is resonance stabilized.

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FACTORS AFFECTING ACID STRENGTH

SUMMARY OF THE FACTORS THAT DETERMINE ACIDITY

Factor	Example																
1. Element effect: The acidity of $\text{H}-\text{A}$ increases both left-to-right across a row and down a column of the periodic table.	<div style="text-align: center;"> <p>Increasing acidity →</p> <table style="margin: auto;"> <tr> <td>$\text{C}-\text{H}$</td> <td>$\text{N}-\text{H}$</td> <td>$\text{O}-\text{H}$</td> <td>$\text{H}-\text{F}$</td> </tr> <tr> <td></td> <td></td> <td>$\text{S}-\text{H}$</td> <td>$\text{H}-\text{Cl}$</td> </tr> <tr> <td></td> <td></td> <td></td> <td>$\text{H}-\text{Br}$</td> </tr> <tr> <td></td> <td></td> <td></td> <td>$\text{H}-\text{I}$</td> </tr> </table> <p style="text-align: right;">↓ Increasing acidity</p> </div>	$\text{C}-\text{H}$	$\text{N}-\text{H}$	$\text{O}-\text{H}$	$\text{H}-\text{F}$			$\text{S}-\text{H}$	$\text{H}-\text{Cl}$				$\text{H}-\text{Br}$				$\text{H}-\text{I}$
$\text{C}-\text{H}$	$\text{N}-\text{H}$	$\text{O}-\text{H}$	$\text{H}-\text{F}$														
		$\text{S}-\text{H}$	$\text{H}-\text{Cl}$														
			$\text{H}-\text{Br}$														
			$\text{H}-\text{I}$														
2. Inductive effects: The acidity of $\text{H}-\text{A}$ increases with the presence of electron-withdrawing groups in A .	<table style="margin: auto;"> <tr> <td>$\text{CH}_3\text{CH}_2\text{O}-\text{H}$</td> <td>$\text{CF}_3\text{CH}_2\text{O}-\text{H}$</td> </tr> <tr> <td></td> <td style="text-align: center;">more acidic</td> </tr> </table>	$\text{CH}_3\text{CH}_2\text{O}-\text{H}$	$\text{CF}_3\text{CH}_2\text{O}-\text{H}$		more acidic												
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	more acidic																
3. Resonance effects: The acidity of $\text{H}-\text{A}$ increases when the conjugate base A^- is resonance stabilized.	<table style="margin: auto;"> <tr> <td>$\text{CH}_3\text{CH}_2\text{O}-\text{H}$</td> <td>$\text{CH}_3\text{COO}-\text{H}$</td> </tr> <tr> <td></td> <td style="text-align: center;">more acidic</td> </tr> </table>	$\text{CH}_3\text{CH}_2\text{O}-\text{H}$	$\text{CH}_3\text{COO}-\text{H}$		more acidic												
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4. Hybridization effects: The acidity of $\text{H}-\text{A}$ increases as the percent s-character of A^- increases.	<table style="margin: auto;"> <tr> <td>CH_3CH_3</td> <td>$\text{CH}_2=\text{CH}_2$</td> <td>$\text{H}-\text{C}\equiv\text{C}-\text{H}$</td> </tr> <tr> <td colspan="3" style="text-align: center;">→ Increasing acidity</td> </tr> </table>	CH_3CH_3	$\text{CH}_2=\text{CH}_2$	$\text{H}-\text{C}\equiv\text{C}-\text{H}$	→ Increasing acidity												
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→ Increasing acidity																	

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ACID-BASE REACTIONS

HOW TO USE CURVED ARROWS IN ILLUSTRATING REACTIONS

- show the direction of electron flow in a reaction mechanism
- point from the source of an electron pair to the atom receiving the pair
- always show the flow of electrons from a site of higher electron density to a site of lower electron density
- never show the movement of atoms. Atoms are assumed to follow the flow of the electron

