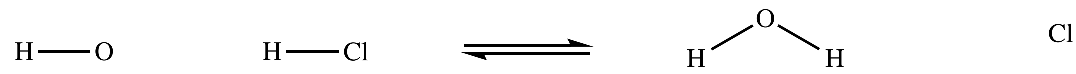
Chapter 3: Acids and Bases

General Principles of Organic Compound Acidity

NaOH
KOH
LiOH



Bronsted base proton (H^+) acceptor	Bronsted acid proton (H^+) donor	conjugate acid	conjugate base
Lewis base electron pair donor	Lewis acid electron pair acceptor		

- *acid-base reactions are equilibria, often favoring one side of the equilibrium or the other*
- *a "strong" Bronsted acid is one that favors giving up a proton such that the equilibrium lies heavily to the right side of the equation*

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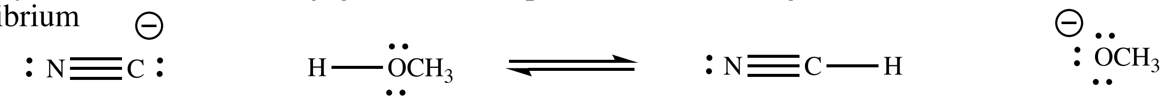
identify the acid/base and conjugate acid/base pairs in the following. Predict the direction of favorable equilibrium

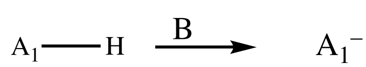


- *the favored direction of a Bronsted acid/base reaction equilibrium can be predicted based on relative pKa's of the reacting acid and the conjugate acid*
- *equilibrium favors formation of the weaker acid*

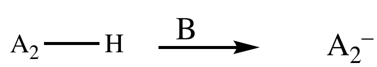
Partial Table of pKa Data

lower pKa value = stronger acid

Acid	pKa
H_2SO_4	-5
HCl	-4
HCN	9
H_2O	15
CH_3OH	16
CH_4	60



strongly stabilized
conjugate base



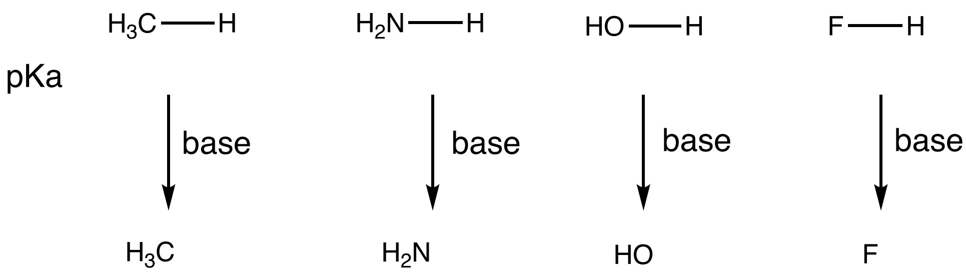
poorly stabilized
conjugate base

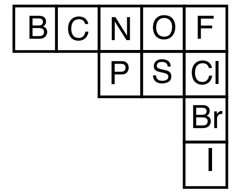
- *an "acidic" compound is one that gives up a proton (H^+) to a base readily*
- *a neutral acid compound forms a negatively charged conjugate base upon giving up the proton (H^+)*
- *usually, differences in acidity can be traced to stabilization of the negative charge on the conjugate base*
- *if the negative charge of the conjugate base is stabilized strongly, it is easily formed, and the acid will be strong*
- *if the negative charge of the conjugate base is NOT stabilized sufficiently, the acid resists giving up the proton and the acid will be weak*

Problems: 4,5

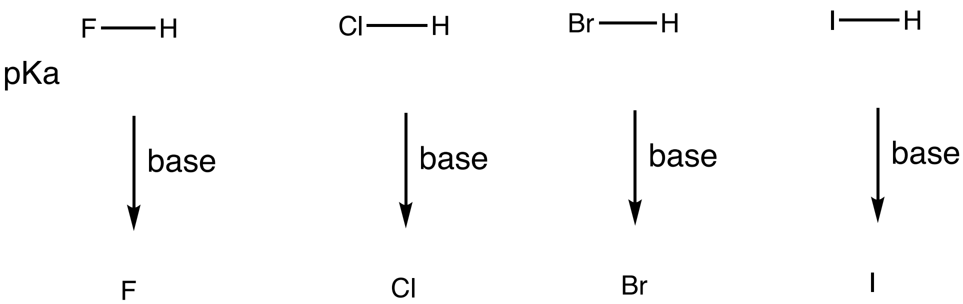
Effect of the Type of **Atom** on Acidity

• *when comparing the acidity of a series of compounds in which the acidic proton is attached to different atoms that are in the* ***same row*** *of the periodic table, acidity increases going from left to right (i.e., correlates with increasing electronegativity)*

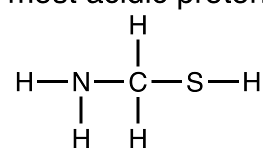




• *when comparing the acidity of a series of compounds in which the acidic proton is attached to different atoms that are in the* ***same column*** *of the periodic table, acidity increases going down the column (i.e., correlates with increasing size of the atom bearing the negative charge)*
• *increasing size of the atom means the charge is delocalized (spread out) over a larger surface area*
• *delocalization of charge results in stabilization of that charge*
• *this* ***increased stability*** *means the anion is formed easier, which translates to* ***greater acidity*** *for the starting acid*

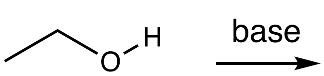


most acidic proton?

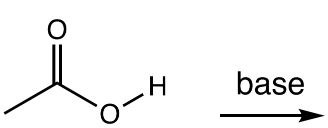


Problems: 1

Effect of **Resonance** on Acidity



ethanol
pKa = 16

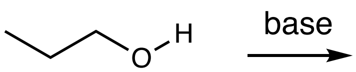


acetic acid
pKa =

hybrid form

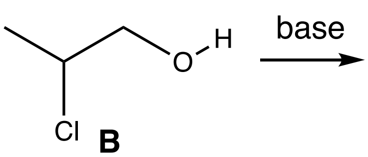
• *resonance interactions spread charge over multiple atoms (delocalization of the charge)*
• *since delocalization of charge stabilizes charge, resonance-stabilized anions are always more stable than non-resonance stabilized anions*
• *acids that give rise to resonance-stabilized conjugate acids are therefore more acidic than similar compounds that cannot engage in resonance*

How the Inductive Effect Affects Acidity



A

pKa = 16

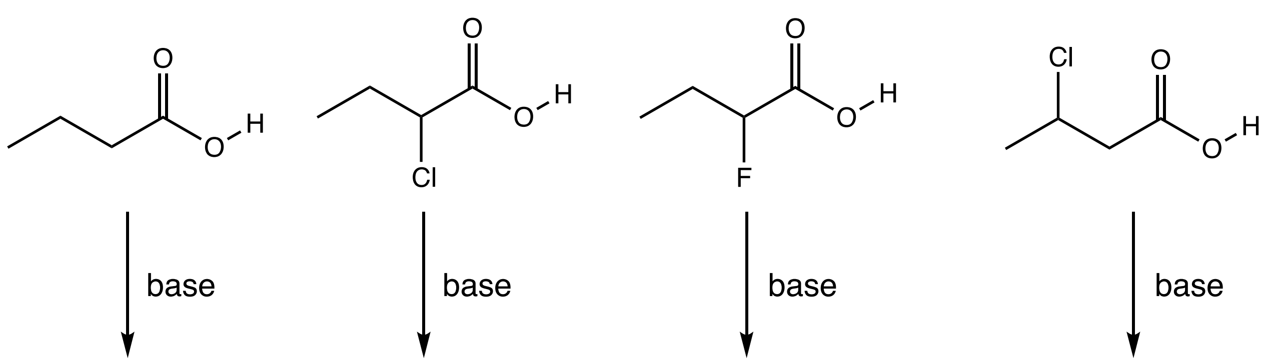


B

pKa = 13

i. pKa of 13 means compound **B** is ____________ acidic than compound **A**
ii. the conjugate base of **B** must be ____________ stable than the conjugate base of A

• *substituents that place partial positive charge next to a negatively charged site due to the effect of polar bonds help to stabilize the negative charge*
• *the substituent acts to "withdraw" electron density away from the negatively charged atoms*
• *withdrawal of electron density in this way is referred to as the "inductive" effect*
• *substituents that inductively withdraw electron density help to stabilize the conjugate base and thereby increase the acidity of the starting acid*



Summary of Factors that Affect Acidity

IMPORTANCE ↑

1. **A**tom: what type of atom is the negative charge placed onto when the proton is removed?
2. **R**esonance: is the resulting negative charge of the conjugate acid stabilized by resonance?
3. **I**nduction: are there any nearby groups that can inductively stabilize the negative charge of the conjugate base?

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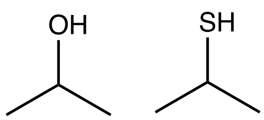
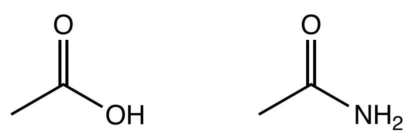
predict the more acidic compound from each pair:

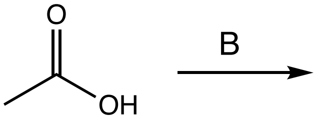
Plan of Attack!

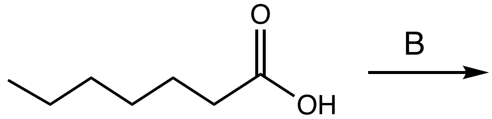
1. View all possible hydrogens on the molecules of interest
2. C-H bonds can typically be ignored unless they are the only types of bonds present
3. Analyze the possible conjugate bases
4. Apply the order of priority to determine the most acidic proton present





Effect on Water Solubility





Problems: 1-3,6-10