How do we determine which molecule is more basic?

One way to determine is by considering molecules' structure, because structure can affect basicity of a molecule.

Let's start with this concept….

Higher electron density within the molecule means that it is…
more likely to share electrons with another molecule
stronger basicity

Lower electron density within a molecule means that it is…
less likely to share electrons with another molecule
weaker basicity

Basically, higher electron density means stronger base and lower electron base means weaker base!

So what features can influence basicity?

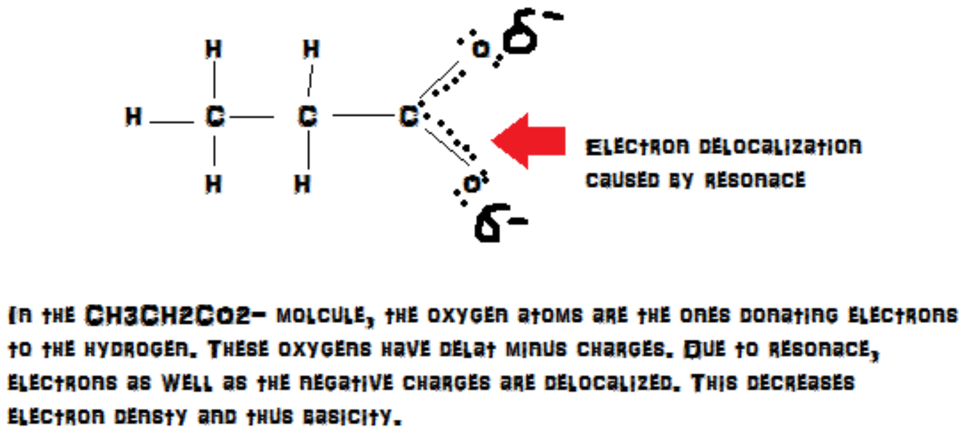
- Resonance
- Electronegativity
- Size of atomic radius
- Inductive effect
- Formal charges

Let's go through all of these features and learn how they influence a molecule's basicity!!!

1. Resonance

   Lets recall from the that resonance delocalizes electrons.
   If an atom is involved in resonance has a negative formal charge, it delocalizes that formal charge.

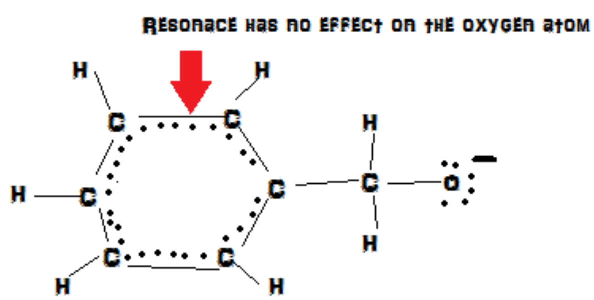
   Ex:

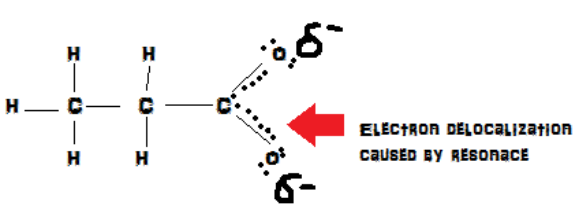


Key point: Resonance usually DELOCALIZES electrons from the atom, thus REDUCING electron density. This causes the molecule to have lower basicity!

But why usually? Why not always?
Because resonance does not ALWAYS reduce basicity. Sometimes it has no effect on it!

Ex:





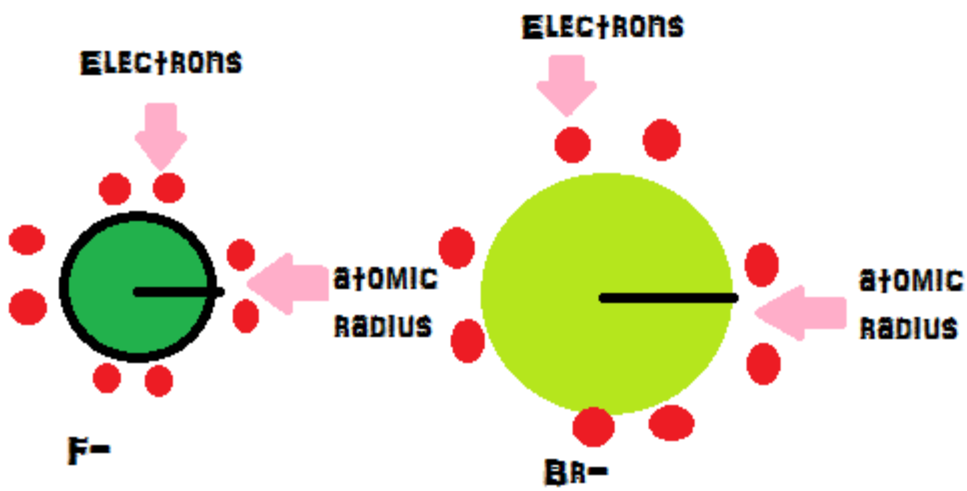
If a basic atom is not involved in resonance, then resonance has no impact on the molecule's basicity! This is because the atom's electron density is not delocalized!

2. Atomic radius

Atoms with smaller atomic radius's will have greater electron density, increasing basicity. Atoms with larger atomic radius's will have less electron density, reducing basicity.

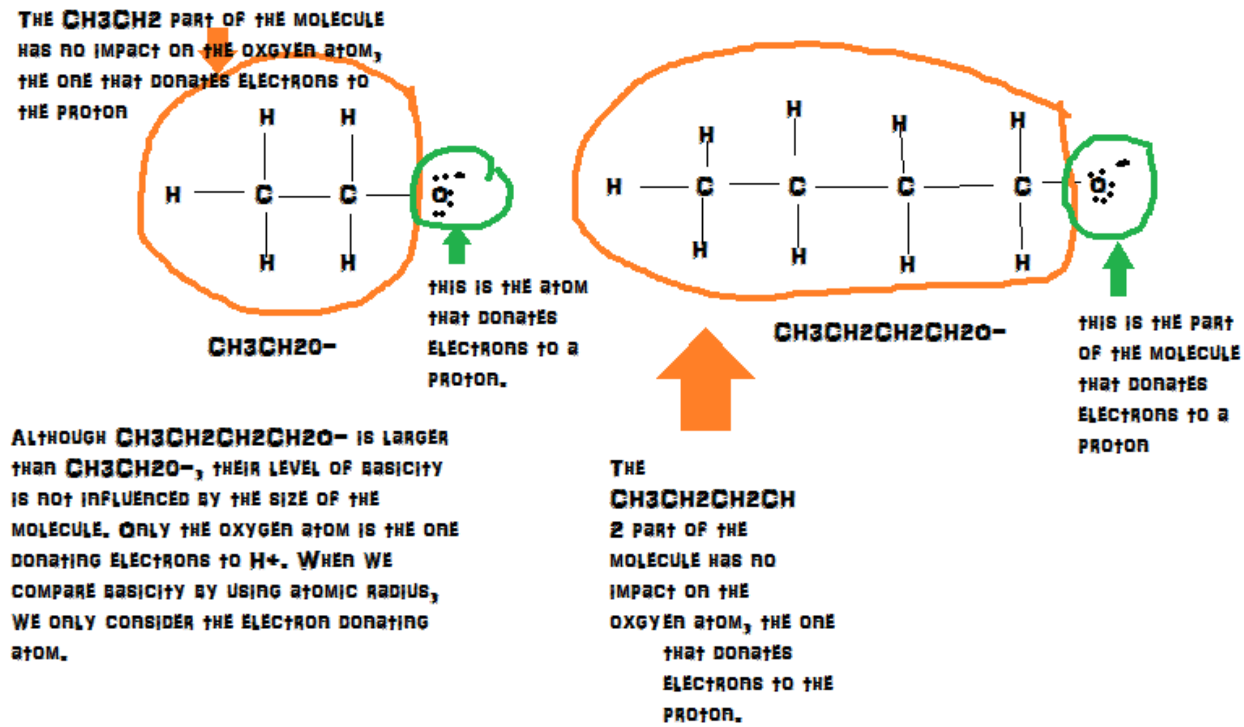
Key point: LARGER atomic radius means LOWER basicity. SMALLER atomic radius means HIGHER basicity.

Ex: Whats the difference between F- and Br-?



Br- has a larger atomic radius than F-.
Notice how the electrons on the F- are covering more of the atom than compared to that of Br.
F- has a greater electron density than Br-
Therefore, Br- is less basic than F-.

But don't get confused!
We only consider atomic radius of the atom that donates electrons to the hydrogen proton.
The atomic radius concept will not work between CH3CH2O- and CH3CH2CH2CH2O-



This is because the carbon hydrogen chain is not the one donating electrons to a proton, the oxygen is..

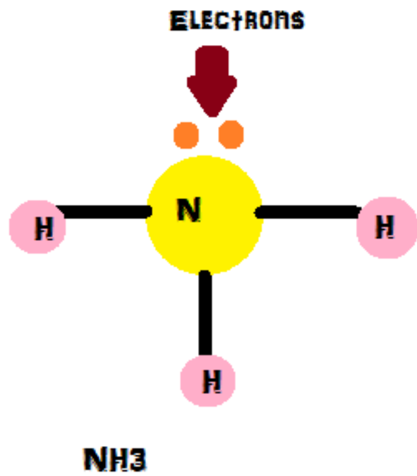
Of course we can say that CH3CH2CH2CH2O- has greater London dispersion forces, but that's a different story.

3. Electronegativity

When an atom has greater electronegativity, this means that the atom is greedier for electrons.
It is less willing to share its electron pairs with a proton, reducing the atom's likelihood to bond to the proton.
This reduces basicity.

Key point: If the atom donating electrons to the proton has a HIGH ELECTRONEGATIVITY, then the molecule containing that atom has a LOWER BASICITY.

Ex: NH3 vs F-



The electron donating atoms are N and F-.
Because F has a higher electronegativity than N, it is less willing to donate electrons to the proton. This reduces the likelihood that F will form bonds with H, meaning that F is the less basic out of the two.

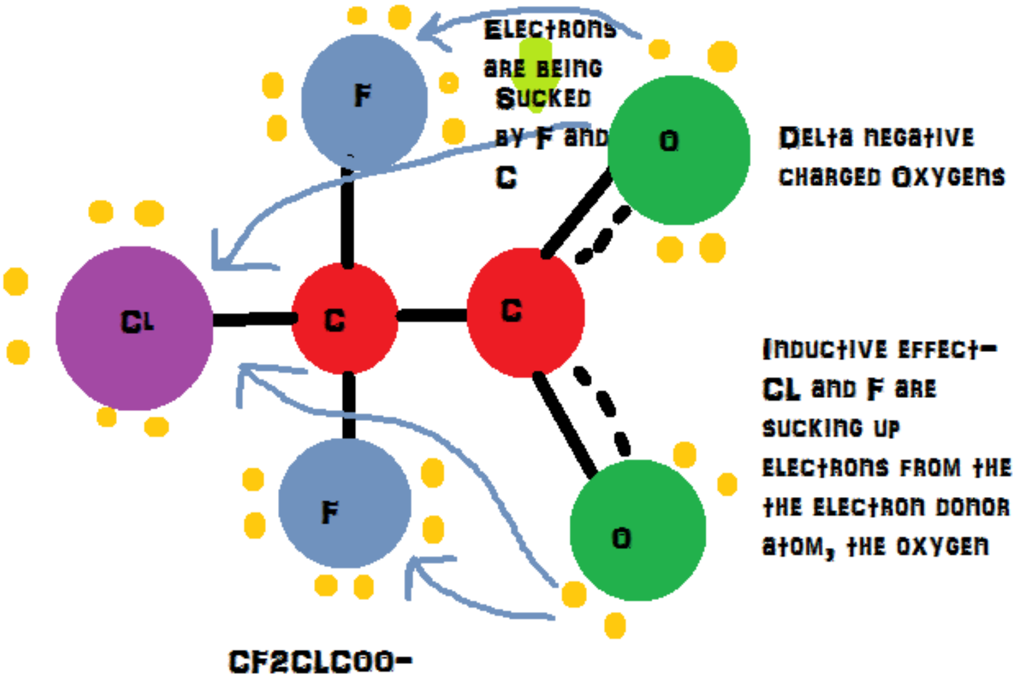
4. Inductive effect

What does this term even mean?!?!?!?!?!

Inductive effect is when other atoms within the molecule can take or give electrons from the atom donating electrons to a proton.

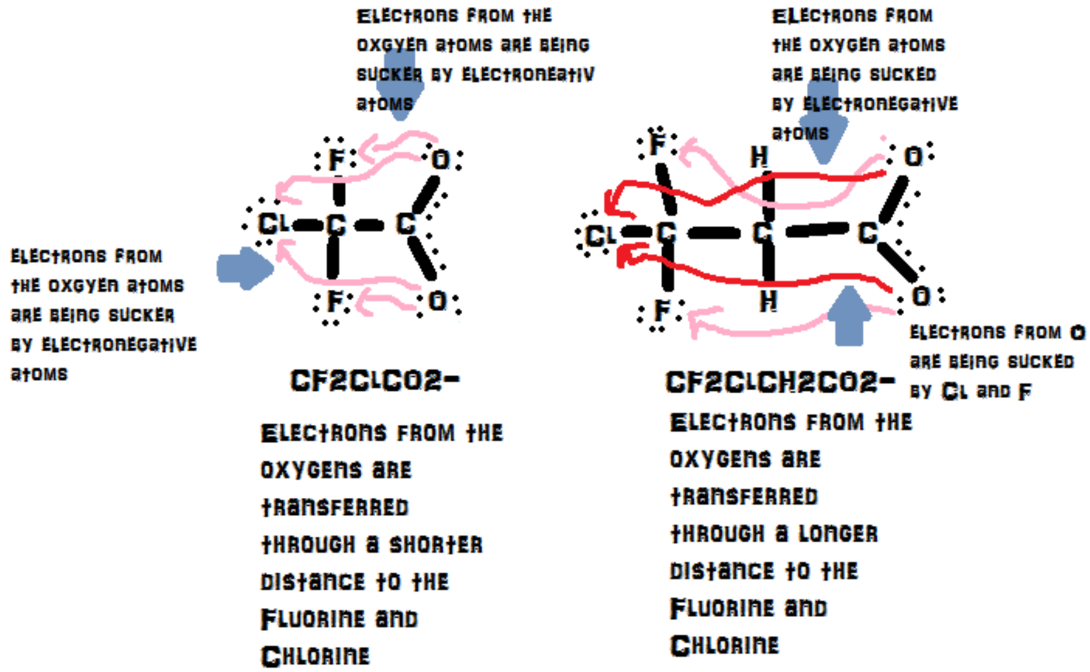
…Atoms that do not donate electrons to protons can influence basicity as well.

Example of inductive effect taking electrons away.
CF2ClCOO-

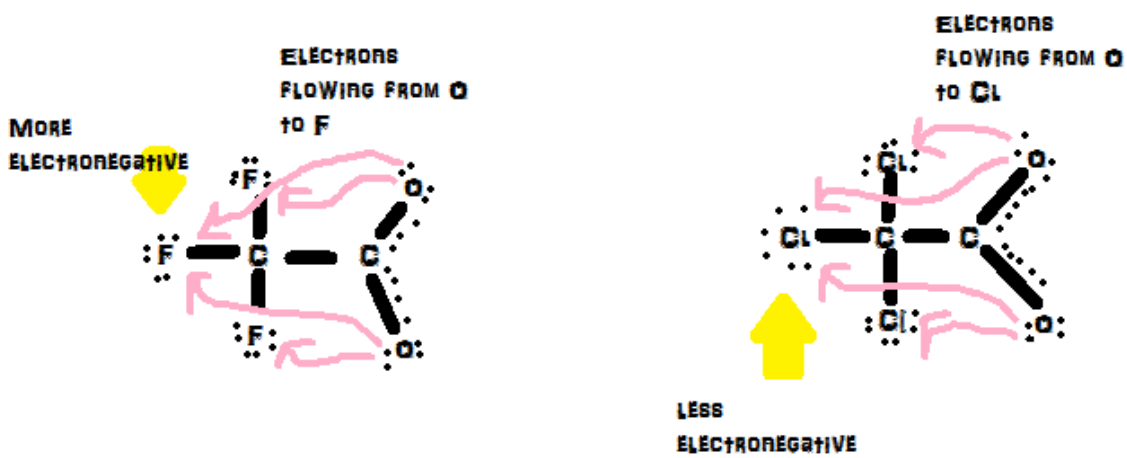


The atoms involved in inductive effect are the F, Cl, Br. Because these atoms are electronegative, they take electrons away from the O-, the electron donating atom.

The closer these atoms are to the electron donating atom, the larger the inductive effect. CF2ClCO2- has a larger inductive effect than CF2ClCH2CO2-



The more electronegative these atoms are, the larger to inductive effect.
$CF_3CO_2^-$ has a larger inductive effect than $CCl_3CO_2^-$



F is more electronegative so it is more electron greedy. This causes it to attract more electrons on the oxygen. Therefore CF3CO2- has a greater inductive effect than CCl3CO2-

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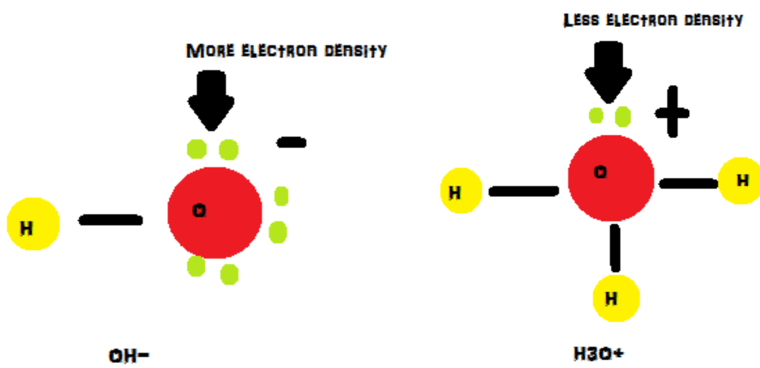
5. Formal charges

Formal charges are either positive or negative.

Key point: A POSTIVE formal charge on the electron donating atom will DECREASE its electron density, making it less likely to form a bond with a hydrogen proton. A NEGATIVE formal charge on the electron donating atom will INCREASE its electron density, making it more likely to form a bond with a hydrogen proton.

Ex: HO- vs H3O+.



Notice that the oxygen atom of the OH- has more electrons than that of H3O+. This illustrates that the oxygen atom of OH- has more electron density.
A negative formal charge usually indicates an increase in electron density while a postive formal charge indicates a decrease in electron density.
An increase in electron density releates to an increase in likely-hood to donate electrons to a proton.
So in this case, OH- is more basic than H3O+
SO a negative formal charge -> increase in basicity

HO- has a negative formal charge, and thus a greater electron density.
However, H3O+ has a positive formal charge, thus a lower electron density.

Now that we discussed the features that influence basicity, lets put them all together!

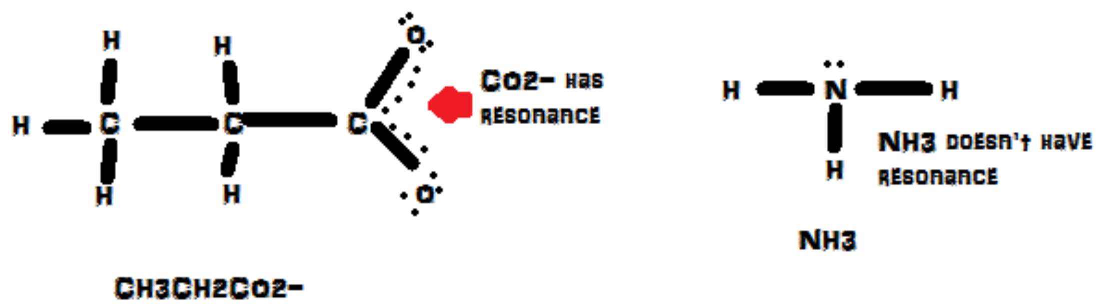
So we went over resonance, atomic radius, electronegativity, formal charge, and inductive effects.
When comparing the basicity of several molecules, which ones should we consider first, second, third, fourth, and last?

Resonance has the greatest effect on basicity.

Atomic radius has the second greatest effect on basicity.
Electronegativity has the third greatest effect on basicity.
Inductive effect has the last greatest effect on basicity.
Formal charges influences are not equal.

In other words.
Resonance> Atomic radius> Electronegativity> Inductive effect.

Lets go through an example.
Which one is more basic, CH3CH2CO2- or NH3



Because CH3CH2CO2- has resonance and NH3 doesn’t, CH3CH2CO2- has more basic.

Work cited:

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