

Acid/Base Behavior and Structure

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Background



Acid/Base Behavior and Structure

Factors that Affect Acid Strength

- The H-* bond * = **Some other atom or molecule**
- There are 3 factors that we need to keep track of to understand acidic strength
 - The **polarity** of the H-* bond (how shifted it is)
 - The more polar the bond, the weaker the bond and the stronger the acid
 - The **strength** of the H-* bond (how strong the attraction is)
 - The weaker the bond, the stronger the acid
 - The **stability** of the conjugate base (*-)
 - The more stable the conjugate base, the stronger the acid

Acid/Base Behavior and Structure

General Trends

- Binary Acids
 - An acid composed of hydrogen and another atom type (often a halogen)
 - HX acids
 - The strength of the binary acids depends most on HX bond strength
 - The *stronger* the HX bond, the *weaker* the acid
 - Within a group, the HX bond weakens as X increases in size = stronger acid
 - Which will be stronger
 - HCl or HF?
 - H₂S or H₂O?
 - The strength of the binary acids also depends on bond polarity
 - The strength of the acid *increases* as the electronegativity of X *increases*
 - Which will be stronger
 - NH₃ or CH₄?
 - NH₃ or SiH₄
 - *The strength of binary acids is more dependent on bond strength than polarity*

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General Trends

- Oxyacids
 - Acids which contain 1 or more OH groups
 - These OH groups also exists in many bases and alcohols
 - What determines when the OH group will be acidic, basic or alcoholic?
 - To understand this, let consider species Y bonded to an OH (and other atoms)

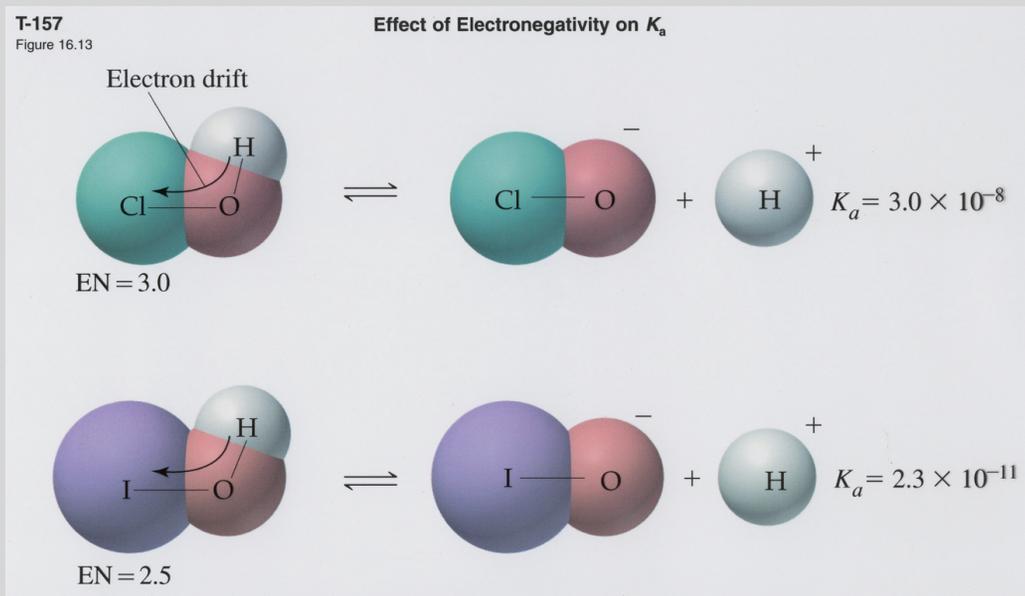


- If Y is a metal
 - Low electronegativity
 - Electrons are completely transferred to O
 - Ionic OH⁻ is formed
 - Basic

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General Trends

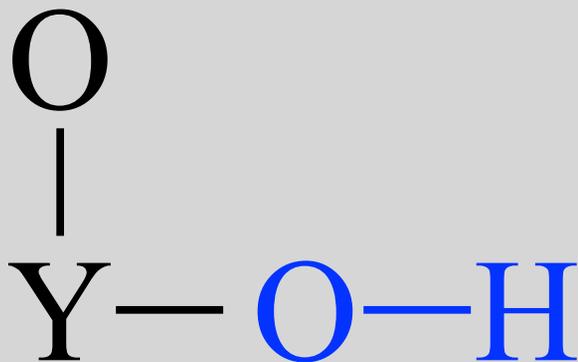
- If Y is a nonmetal
 - The Y-O bond is covalent
 - OH⁻ is not formed readily
 - These substances are either acidic or neutral (alcohols)
 - As the electronegativity of Y increases, the acidity increases, due to drift
 - The O-H bond becomes more polar



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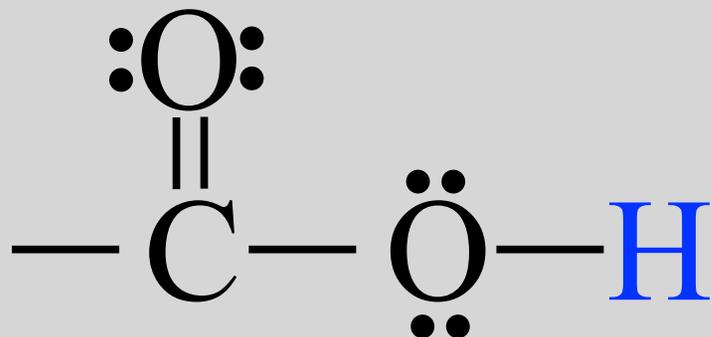
General Trends

- Many times, Y is bonded to more oxygen atoms
 - These additional oxygen (with high electronegativities) make the O-H bond more polar
 - This increased polarity creates stronger acids



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A Special Example of an Oxyacid



- Carboxylic Acid
 - Carboxyl group
 - COOH
 - Largest category of organic acids
 - Acetic acid
 - Formic acid
 - Acetylsalicylic acid
 - Two factors make COOH acidic
 - The additional oxygen makes the O-H bond more polar
 - The COO⁻ anion is resonance stabilized, and therefore more stable

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A Word on Lewis Acids/Bases

- Rather than focus on the transfer of protons, Lewis (as you might suspect, or remember) defined acids and bases by their ability to accept or donate electron pairs
 - A Lewis base is an electron pair donator
 - A Lewis acid is an electron pair acceptor
- These definitions make intuitive sense, since the B/L definitions define acid as proton (+) donors and bases as proton (+) acceptors.
 - Every substance we have identified as an acid or base fits within the Lewis definition
 - The Lewis definition increases the number of species that qualify as acids or bases.
- See the end of chapter 16 for more

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A Word on Lewis Acids/Bases

Lewis Acid-Base Theory

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Homework

- 16.87 - How does the acid strength of an oxyacid depend on (a) the electronegativity of the central atom; (b) the number of non-protonated oxygen atoms in the molecule?
- 16.88 - (a) Why is NH_3 a stronger base than H_2O ? (b) Why is NH_3 a stronger base than CH_4 ?
- 16.93 / 16.95 / 16.97 / 16.98