Topic IV

Hard-Soft Acid-Base and Donor-Acceptor Concepts of Transition Metals

IV.1 Module 24: Acid-Base Chemistry

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- Brønsted-Lowry Acid-Base Theory of Acids and Bases (1923).
  - Acid: Any chemical species (molecule or ion) that is able to lose, or "donate," a hydrogen ion (proton).
  - Base: Any chemical species that is able to gain, or "accept", a proton.
    - A base must have a pair of electrons available to share with the proton; this is usually present as an unshared pair, but sometimes is in a π orbital.
  - Acid-base reactions: The transfer of a proton from an acid to a base.

$$\mathrm{A{-}H} + \mathrm{:BH} \rightleftharpoons \mathrm{A:} + \mathrm{BH_2}$$

    - Protons do not exist free in solution but must be attached to an electron pair.
  - Water is amphoteric.
- In the Brønsted-Lowry paradigm, we cannot separate the acids/bases from the solvent (no protons; only *solvated* protons). In a non-aqueous medium such as DMSO, however, we have much broader scope of acids and bases.
- **Carbon acid**: Any molecule containing a C–H bond can lose a proton forming the carbanion.
- Carborane ($\mathrm{H(CHB_{11}Cl_{11})}$) is a superacid one million times stronger than sulfuric acid since it's conjugate basis is incredibly stable (super easy to delocalize the charge).
- The base dissociation constant or K_b is a measure of basicity. $\mathrm{p}K_\mathrm{b}$ is the negative log of K_b and related to the $\mathrm{p}K_\mathrm{a}$ by the simple relationship $\mathrm{p}K_\mathrm{a} + \mathrm{p}K_\mathrm{b} = 14$. The larger the $\mathrm{p}K_\mathrm{b}$, the more basic the compound.
- **Superacid**: An acid with acidity greater than that of 100% pure sulfuric acid.
  - In water, the strongest acid you can have is $\mathrm{H_3O^+}$.
  - The strongest superacids are prepared by the combination of two components, a strong Lewis acid and a strong Brønsted-Lowry acid.
  - Fluoroantimonic acid $\mathrm{HF{-}SbF_5}$ is 2×10^{19} stronger than 100% sulfuric acid.

  - Olah's magic acid ($FSO_3H–SbF_5$) can dissolve paraffin (candle wax; extremely inert), converting methane into the t-butyl carbocation.

- **Hammett acidity function**: Can replace the pH in concentrated solutions. *Also known as* $\boldsymbol{H_0}$.

$$H_0 = \mathrm{p}K_{\mathrm{BH^+}} + \log \frac{[\mathrm{B}]}{[\mathrm{BH^+}]}$$

  - Let BH^+ be the conjugate acid of a very weak base B, with a very negative $\mathrm{p}K_{\mathrm{BH^+}}$. In this way, it is rather as if the pH scale has been extended to very negative values.
  - Hammett originally used a series of anilines with EWGs for the bases.

- **Superbase**: A compound that has a high affinity for protons.
  - Again, these do not exist in water.
  - Often destroyed by water, CO_2, and O_2.
  - A superbase has been defined as an organic compound whose basicity is greater than that of proton sponge, which has conjugate $\mathrm{p}K_\mathrm{a}$ of 12.1.
  - These are valuable in organic chemistry, which abounds in very weak acids.
  - A common superbase is lithium diisopropylamide.