



# **Chapter 5**

## **Acids and Bases**



1. What are Arrhenius acids and bases?
2. What are Brønsted-Lowry acids and bases?
3. How do we measure the strength of an acid or base?
4. How do we determine the position of equilibrium in an Acid-base reaction?
5. What are the relationships between acidity and molecular structure?
6. What are Lewis acids and bases?
7. What are electrophiles and nucleophiles ?
8. How do we judge the strength of electrophiles and nucleophiles ?
9. How to classify the organic reactions?



# Acidity of Organic Compounds



酸



Which is more acidic, lemon or vinegar?



## The development of acid-base theory

### ✓ 早期酸碱理论

- ◆ 1663年 Boyle, R.
- ◆ 18世纪后期, 从物质内在性质认识酸碱
- ◆ 19世纪初, HCl和HI先后被发现

酸具有酸味, 可以使蓝色石蕊变成红色

Lavoisier 认为酸是一类含氧化合物

Davy 提出氢是酸的基本元素

### ✓ 近代酸碱理论 (19世纪中后期形成)

- ◆ 1889年 Arrhenius 提出水—离子论
- ◆ Bronsted, J. N. 和Lowry, T. M.提出质子论
- ◆ Lewis, G. N. 提出电子论
- ◆ Pearson, R. G. 提出软硬酸碱理论

在水中电离出 $H^+$ 的是酸,  $OH^-$ 的是碱

能给出质子的是酸, 接收质子的是碱

能接受电子的是酸, 给出电子的是碱

体积、电荷数、可极化性等方面定义



# 1. Arrhenius acids and bases

**Arrhenius acid**: A substance that dissolves in water to produce  $\text{H}^+$  ions.

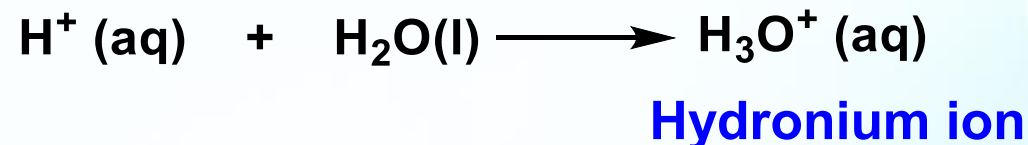
**Arrhenius base**: A substance that dissolves in water to produce  $\text{OH}^-$  ions.

The definitions were put forward by **Svante Arrhenius** (1859-1927) in 1884; **Nobel Prize** in Chemistry 1903.

In **nonaqueous solution**, what are acids and bases?

In **aqueous solution**:

**$\text{H}^+$  ion does not exist in water.**





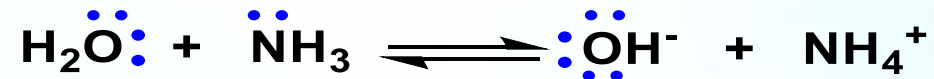


## 2. Brønsted-Lowry acids and bases

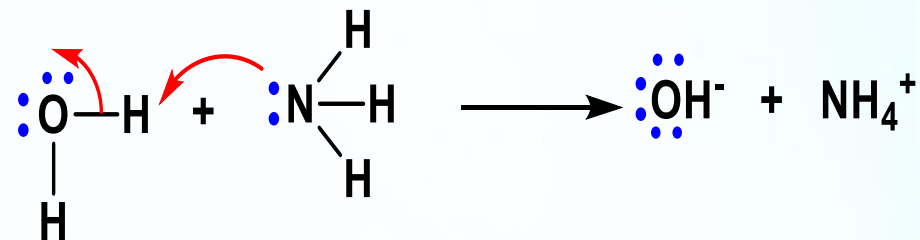
In 1923, the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry independently proposed the definitions.

An acid is a molecule which can provide a proton.

A base is a molecule which can accept that proton.



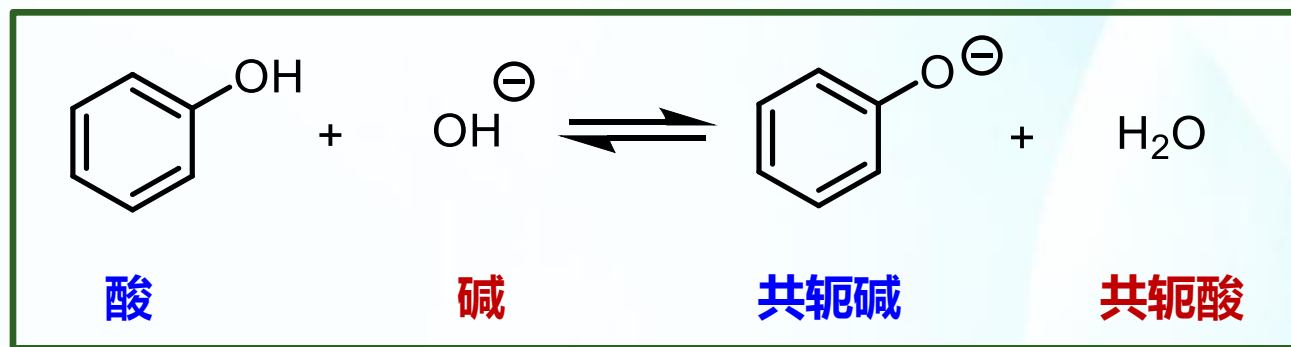
An acid-base reaction is a proton-transfer reaction.



Water loses a proton and is an acid. Ammonia accepts that proton and is the base.

## ◆Bronsted—Lowry 质子论

- 酸：能给出质子的分子或离子 (HA)
- 碱：能结合质子的分子或离子 (A)

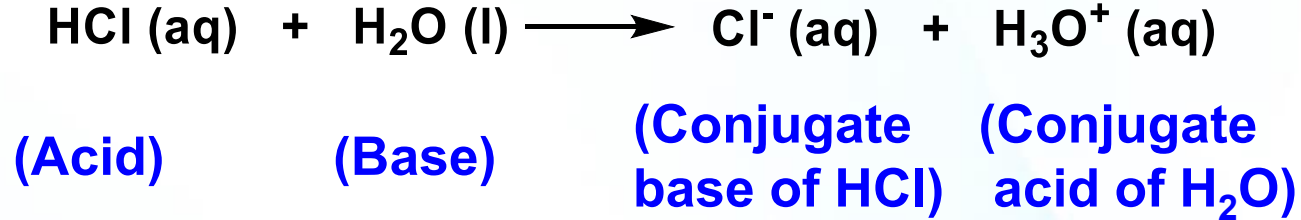


- 质子酸碱的强弱可以用pKa的大小进行比较：

✓ pKa越大，则酸性越弱

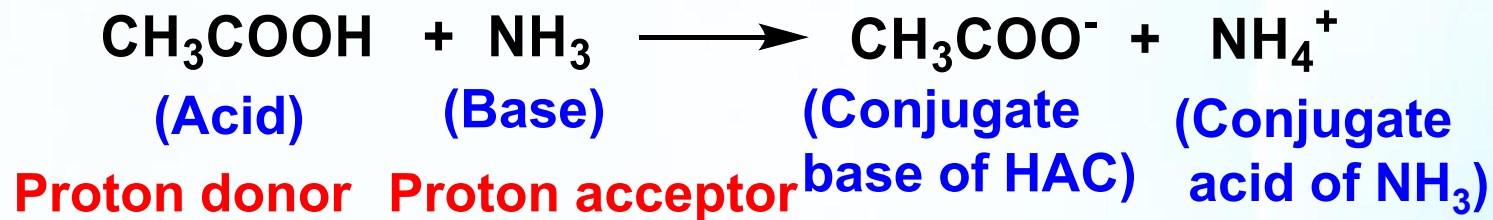
✓ pKa越小，则酸性越强

有机化合物中含有大量的C-H, O-H, N-H, S-H, P-H等化学键，根据质子酸碱理论都可以表现出酸性



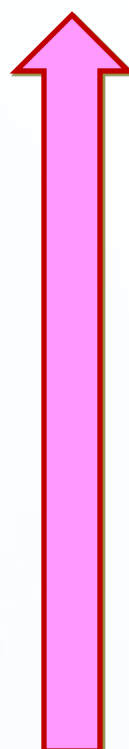
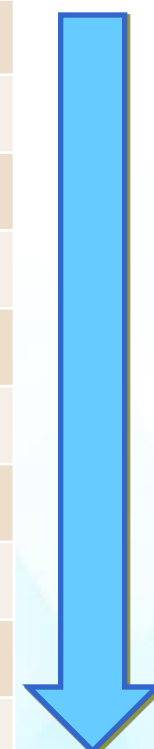
When an acid transfers a proton to a base, the acid is converted to its conjugate base.

When a base accepts a proton, the base is converted to its conjugate acid.



The stronger the acid, the weaker is its conjugate base.



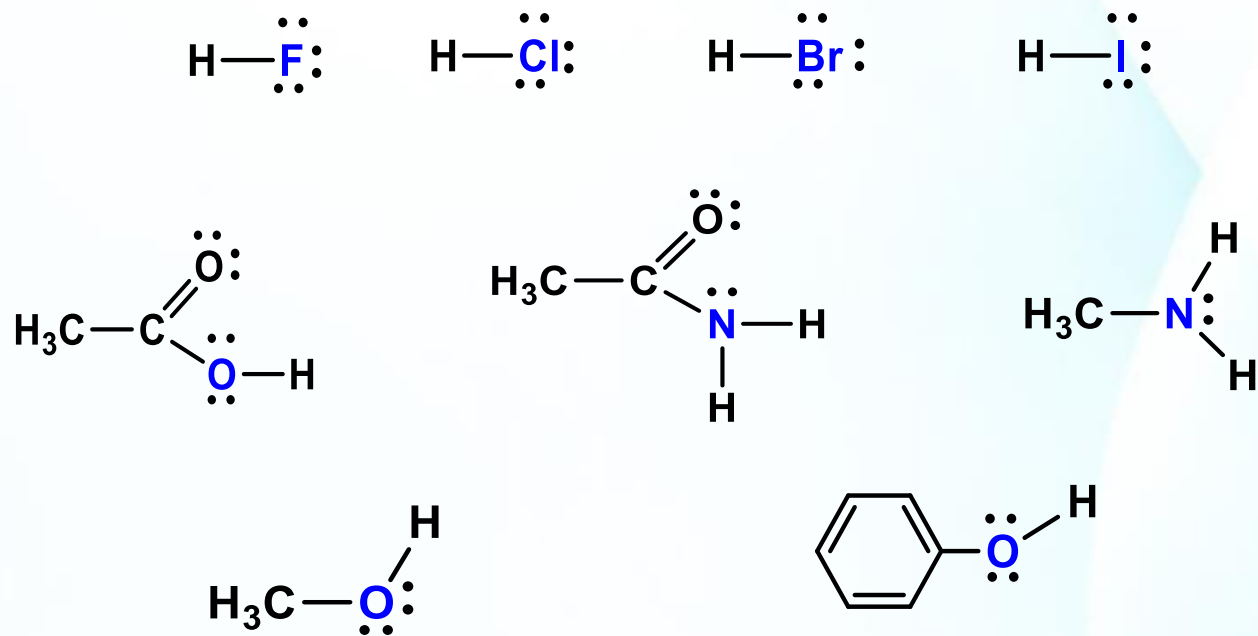



Acid		Conjugate base
HI	-9	I <sup>-</sup>
HCl	-7	Cl <sup>-</sup>
H <sub>2</sub> SO <sub>4</sub>	-5.2	HSO <sub>4</sub> <sup>-</sup>
H <sub>3</sub> O <sup>+</sup>	-1.74	H <sub>2</sub> O
H <sub>3</sub> PO <sub>4</sub>	2.1	H <sub>2</sub> PO <sub>4</sub> <sup>2-</sup>
CH <sub>3</sub> COOH	4.76	CH <sub>3</sub> COO <sup>-</sup>
H <sub>2</sub> CO <sub>3</sub>	6.36	HCO <sub>3</sub> <sup>-</sup>
NH <sub>4</sub> <sup>+</sup>	9.24	NH <sub>3</sub>
C <sub>6</sub> H <sub>5</sub> OH	9.95	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>
NH <sub>4</sub> <sup>+</sup>	9.24	NH <sub>3</sub>
C <sub>2</sub> H <sub>5</sub> OH	15.9	C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>
NH <sub>3</sub>	38	NH <sub>2</sub> <sup>-</sup>
C <sub>2</sub> H <sub>6</sub>	51	CH <sub>3</sub> CH <sub>2</sub> <sup>-</sup>

Weak acids

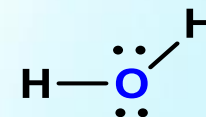
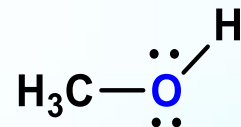
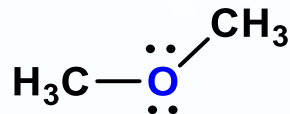
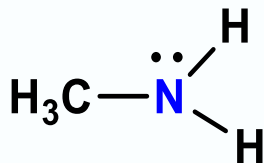
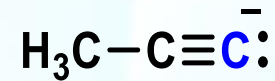
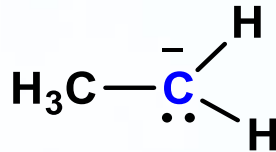
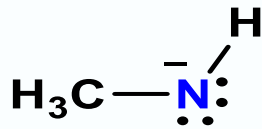
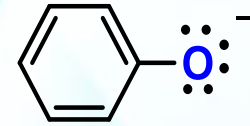
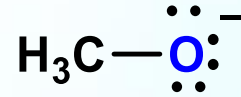
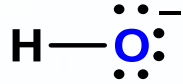
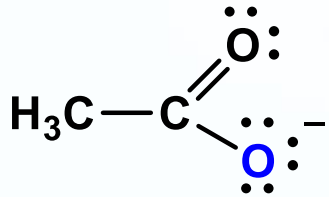
Strong bases

A Brønsted-Lowry acids is a molecule which contains an acidic hydrogen.



This is possible if hydrogen is attached to an electronegative atom such as a halogen, oxygen, or nitrogen.

A Brønsted-Lowry bases is a molecule which can form a bond to a proton, including negatively charged ions and neutral molecules containing oxygen or nitrogen.



How do we measure the strength of an acid ?



- pH: 自于拉丁文pondus hydrogenii的缩写，直译为氢的计量，引申为现在对pH的解释为水溶液中氢离子浓度的量度。

$$\text{pH} = -\lg [\text{H}^+]$$

✓ pH越大，则酸性越弱

✓ pH越小，则酸性越强

碳酸

$$\text{pH}_{\text{饱和碳酸}} = 3.88$$

盐酸

$$\text{pH}_{\text{HCl}} = 4 \quad (c = 0.1 \text{ mM})$$

pH 受浓度影响，这意味着弱酸实际上可以比稀强酸有更低的pH值



✓  $K_a$ 是指一个特定的平衡常数，以代表一种酸离解氢离子的能力。

$$K_a = \frac{[\text{H}^+]\cdot[\text{A}^-]}{[\text{HA}]}$$

对于一些即若的解离过程， $K_a$ 值会特别小，不方便不直观比较酸性强弱

$pK_a$ 是酸式解离常数（ $K_a$ ）的负对数。数值越小，酸性越强，提供质子的能力也越强，是描述酸或碱的强弱的指标。

$$pK_a = -\lg (K_a)$$

- 质子酸碱的强弱可以用 $pK_a$ 的大小进行比较： ✓  $pK_a$ 越小，则酸性越强



## 2.1 Acids Strength

**A strong acid or strong base is one that ionized completely in aqueous solution.**

**A weak acid or weak base is one that only partially ionizes in aqueous solution.**



98.7%



**In an acid-base reaction, the position of equilibrium always favors reaction of the stronger acid and stronger base to form the weaker acid and weaker base.**





What are the relationships between acidity and molecular structure?

### 1) Electronegativity

The more electronegative the atom, the more acidic the proton will be.

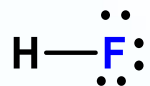
The greater the electronegativity of A, the greater the stability of the anion  $A^-$ , and the stronger the acid HA.

	$H_3C-H$	$H_2N-H$	$HO-H$	$F-H$
pKa	50	38	15.7	3.5
Electronegativity of A in A-H	2.5	3.0	3.5	4.0

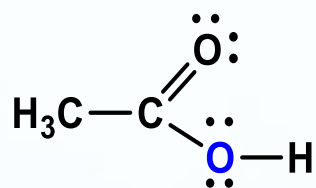
The more electronegative an atom is, the greater its ability to sustain electron density around itself.



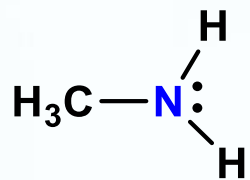
## 2.1 Acids Strength



Hydrofluoric acid has the most acidic proton since the hydrogen is attached to a strongly **electronegative** fluorine. Once the proton is lost, the fluoride ion can stabilize the resulting negative charge.



Acetic acid is more acidic than methylamine but less acidic than hydrofluoric acid. This is because the electronegativity of oxygen lies between that of a halogen and that of a nitrogen atom.

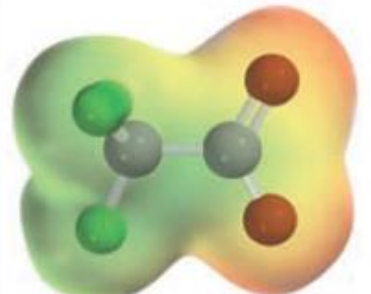
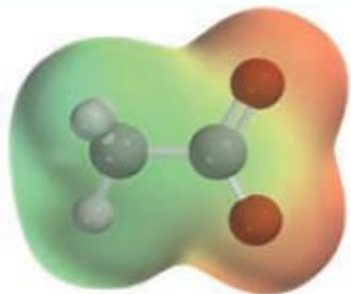
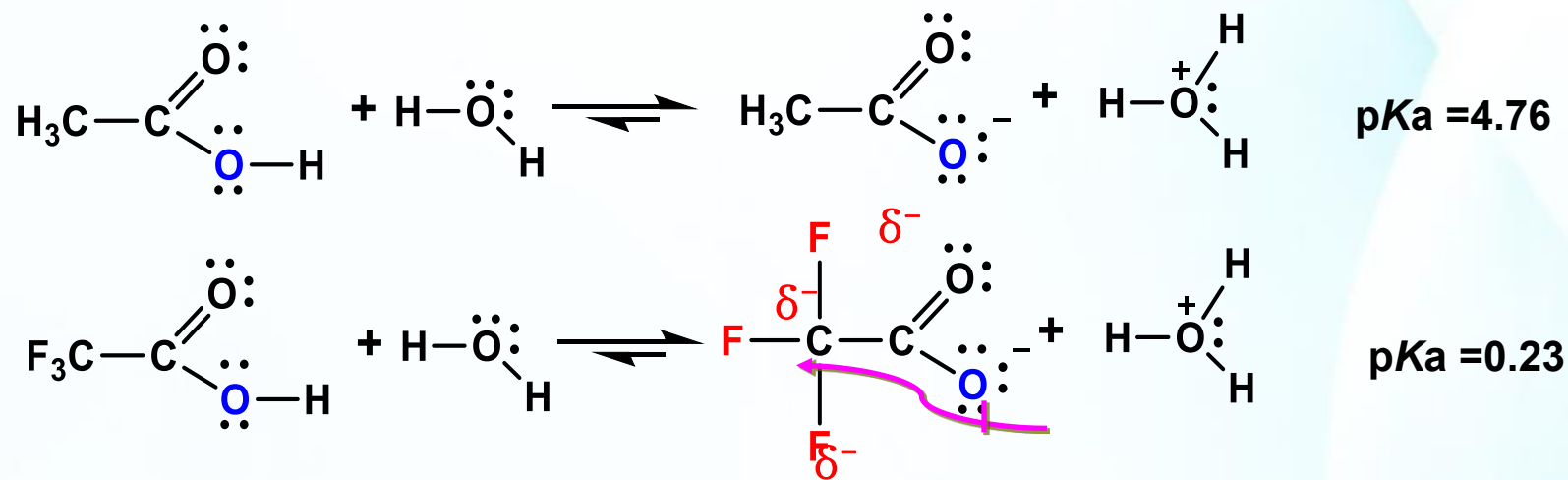


Methylamine is a much weaker acid than hydrogen fluoride. The N-H bonds are less polarized, and the protons are less electron deficient.



## 2) The inductive effect (诱导效应)

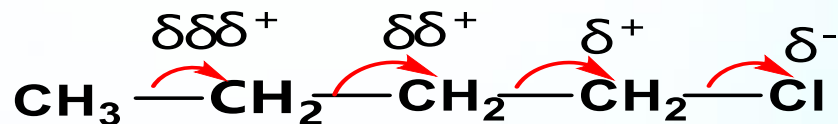
The inductive effect is the polarization of electron density transmitted through covalent bonds by a nearby atom of **higher electronegativity**.



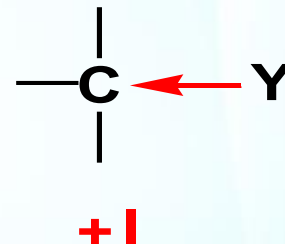
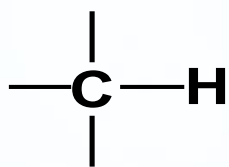
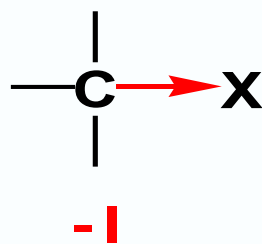


## 2.1 Acids Strength

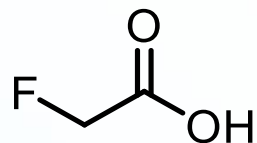
This inductive effect will continue to be felt through the various bonds of the structure. It will decrease through the bonds but it is still significant enough to be felt at the negatively charged atom.



以C—H作标准 { 电负性>H的基团引起-**I**效应 (吸电子作用)  
电负性<H的基团引起+**I**效应 (斥电子作用)

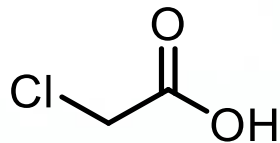


## 影响化合物酸性的因素：电子效应——诱导效应

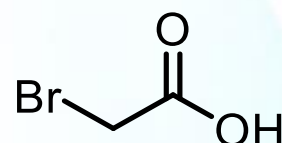


**pKa**

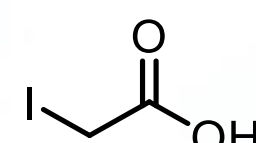
**2.66**



**2.86**

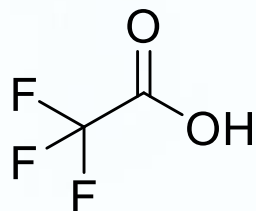


**2.90**



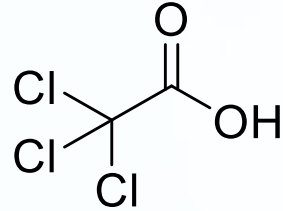
**3.16**

◆ 电负性越强，吸电子诱导效应越强，则酸性越强

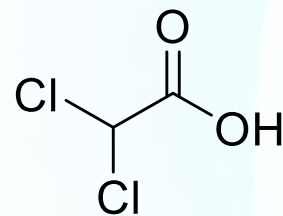


**pKa**

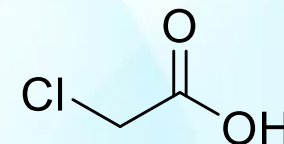
**-0.25**



**0.65**



**1.29**

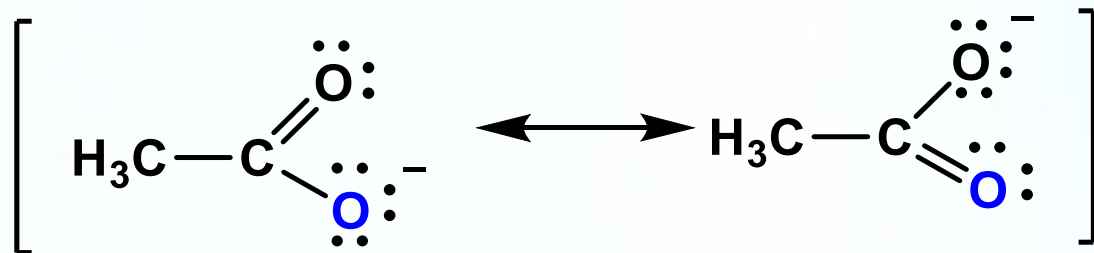
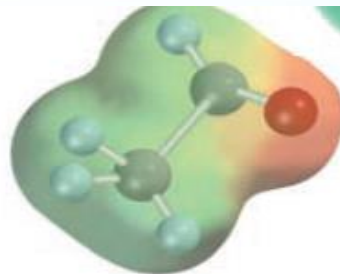
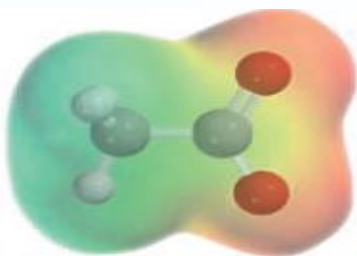


**2.86**

**量变与质变!**



### 3) Resonance effect



The negative charge of the anion is delocalized; it is spread evenly over the two oxygen atoms.

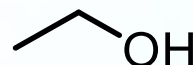
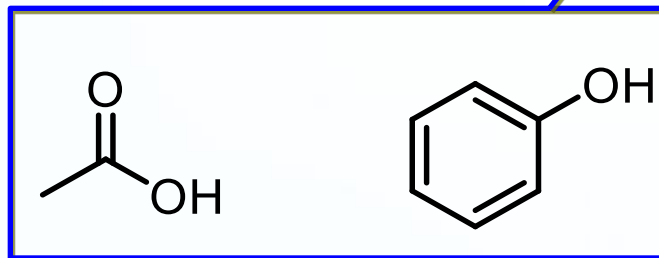




## 2.1 Acids Strength

The negative charge of the conjugate base is delocalized

含氧化合物



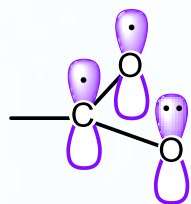
$pK_a$

4.75

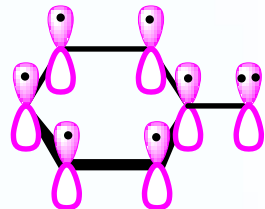
9.96

16

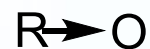
共轭碱



p- $\pi$ 共轭



p- $\pi$ 共轭



同为O-H键，酸性差别为何如此之大？

共轭碱稳定性越小，酸性越弱

#### 4) Size and the delocalization of charge in $A^-$

HF , HCl , HBr , HI ?

电负性: H (2.2)

F (4.0)      Cl (3.0)      Br (2.8)      I (2.5)

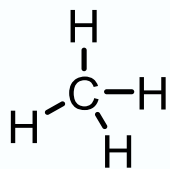
The more stable the anion, the greater the acidity of the acid.

$I^- > Br^- > Cl^- > F^-$

The larger the volume over which the charge of an anion (or cation) is delocalized, the greater the stability of the anion.

$HF < HCl < HBr < HI$

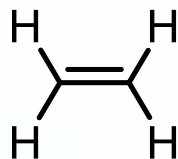
烃类化合物



**pKa**

**56**

**sp<sup>3</sup>杂化**



**48**

**sp<sup>2</sup>杂化**

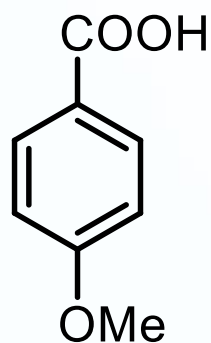


**25**

**sp杂化**

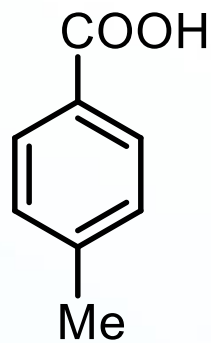
**碳骨架上氢原子酸性为何不同?**

## 影响化合物酸性的因素：电子效应——共轭效应

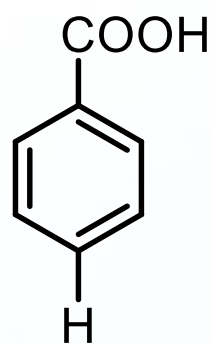


**pKa**

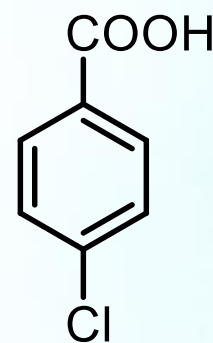
**4.47**



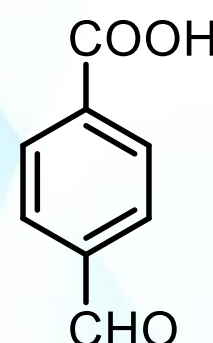
**4.34**



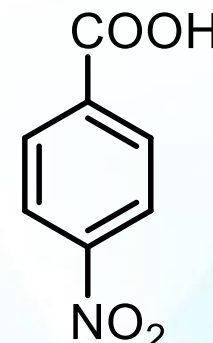
**4.20**



**3.97**



**3.70**



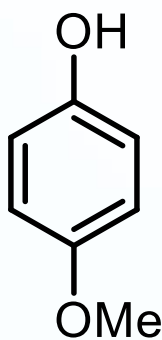
**3.44**

◆ 给电子共轭效应，增强共轭体系电子云密度，则酸性降低

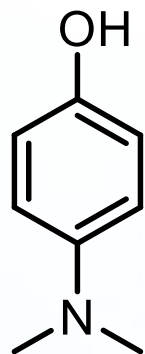
◆ 吸电子共轭效应，降低共轭体系电子云密度，则酸性增强



随堂练习：将下列化合物按照酸性从强到弱的顺序排列



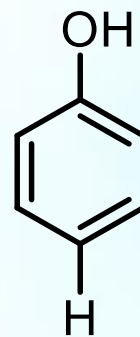
A



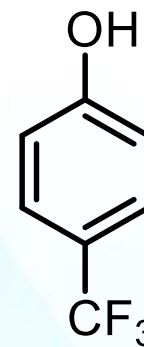
B



C



D



E

◆ 给电子共轭作用：B > A > C

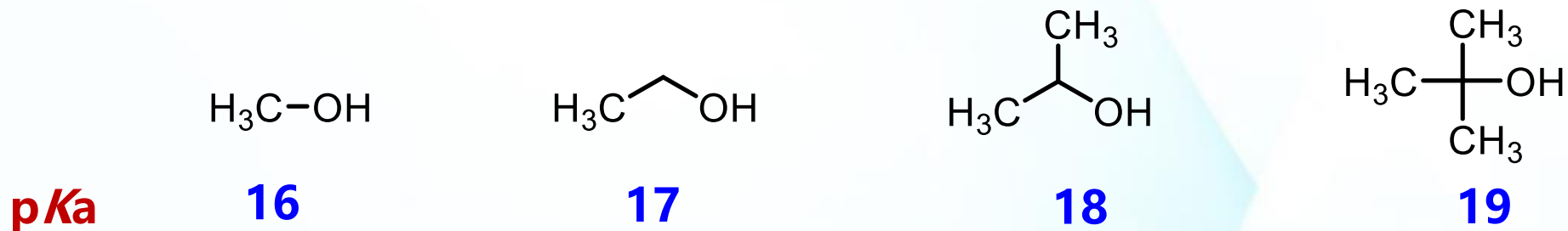
◆ 吸电子诱导作用：C

◆ 吸电子共轭作用：E

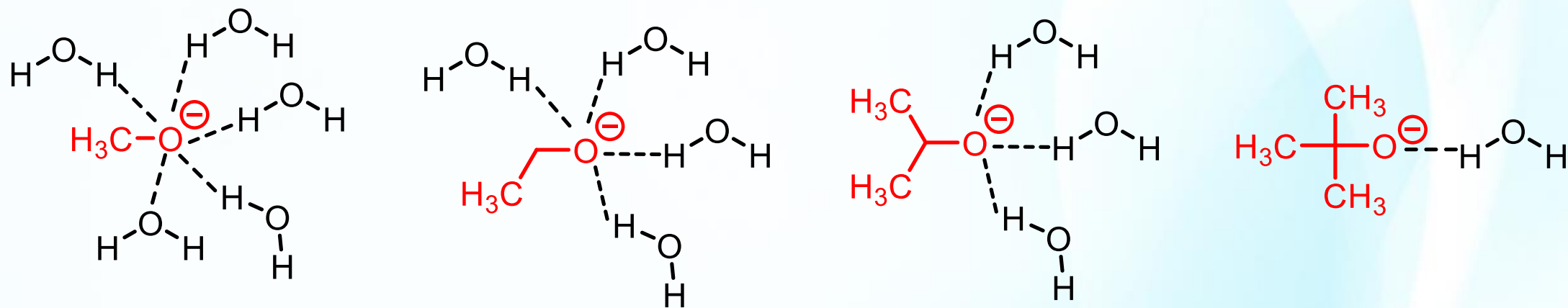
综合作用电子云密度：B > A > D > C > E

酸性由强到弱：E > C > D > A > B

## 影响化合物酸性的因素：空间效应



醇的共轭碱 $\text{RO}^-$ 容易被水溶剂化，共轭碱稳定性越强，则醇的酸性越强

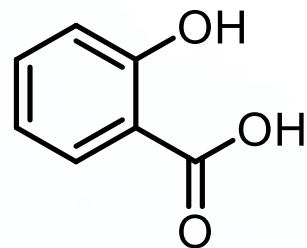






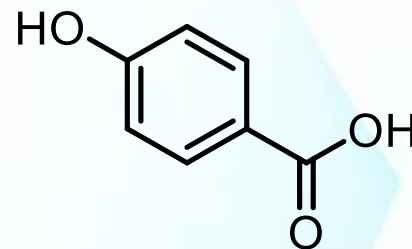
## 2.1 Acids Strength

影响化合物酸性的因素：空间效应

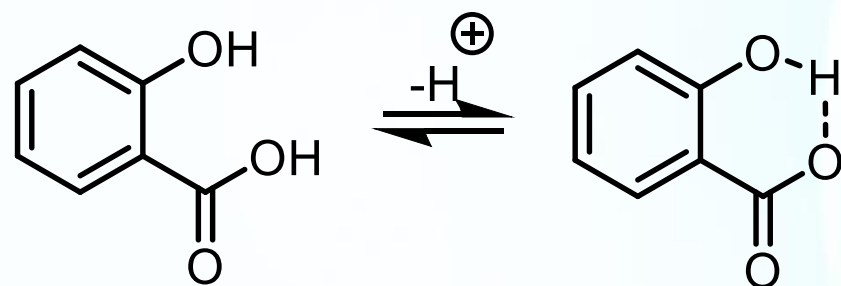


**pKa**

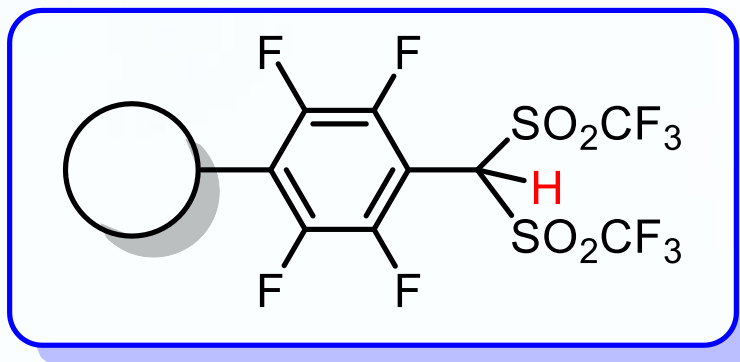
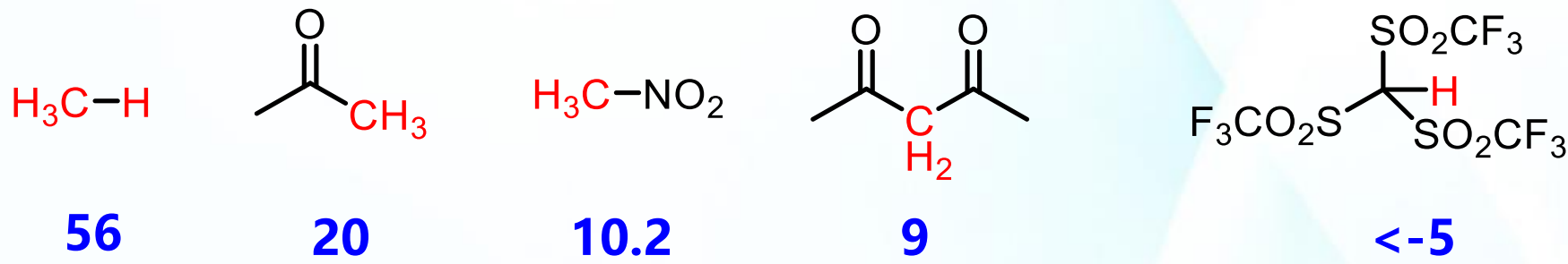
**2.81**



**4.58**



## 有机化合物通过结构改造可以调控其酸性



## 聚苯乙烯骨架的固体超强酸

- ◆ 环境友好，使用便利
- ◆ 可循环使用，催化性能优异



The basicity of neutral molecules can be explained by comparing the stability of their positively charged conjugate acids.

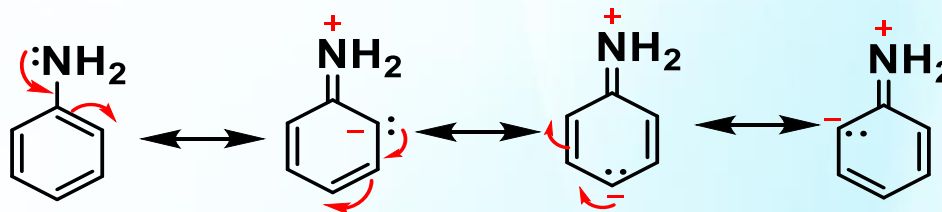
Amines are more basic than alcohols since nitrogen is less electronegative than oxygen and more capable of stabilizing a positive charge.

Alkyl halides are extremely weak bases because the resulting cations are poorly stabilized by a strongly electronegative halogenatom.

Ammonia  $pK_a = 33$     Ethylamine  $pK_a = 40$

actamide  $pK_a = 15$

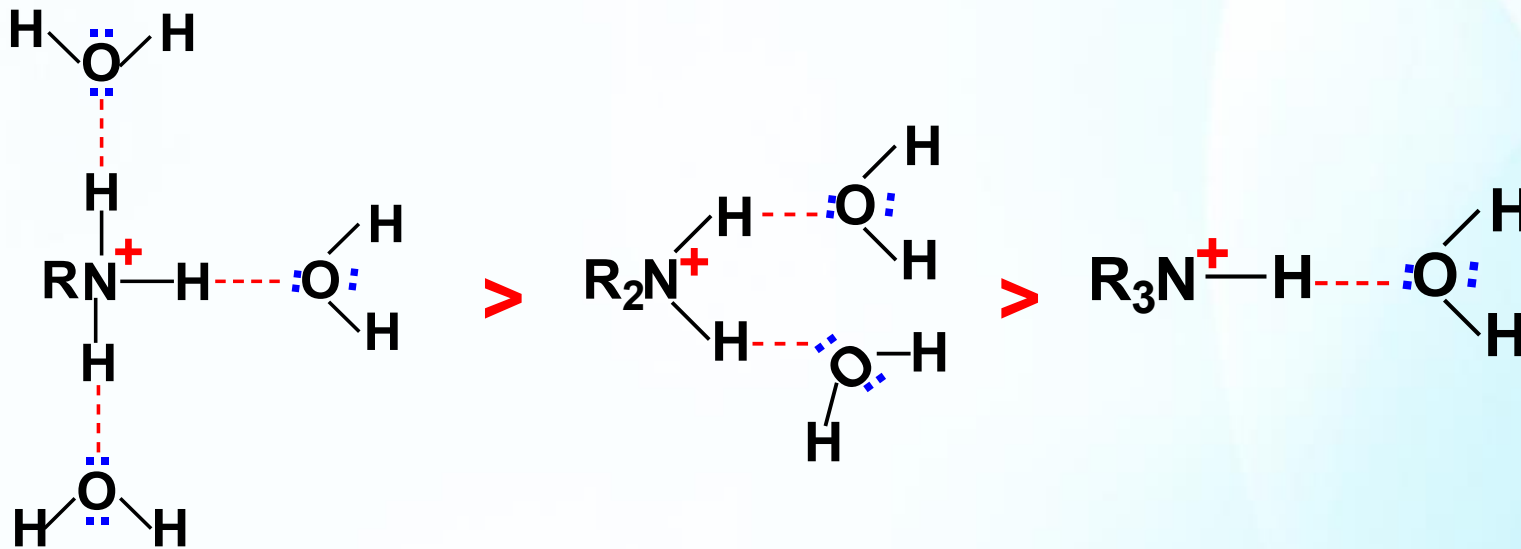
Phenylamine  $pK_a = 15$



The **basicity** of negatively charged compounds depends on the **electronegativity** of the atoms bearing the negative charge.

Electronegative atoms **prefer to have a negative charge rather than a positive charge.**

**Solvation affects basic strength.**

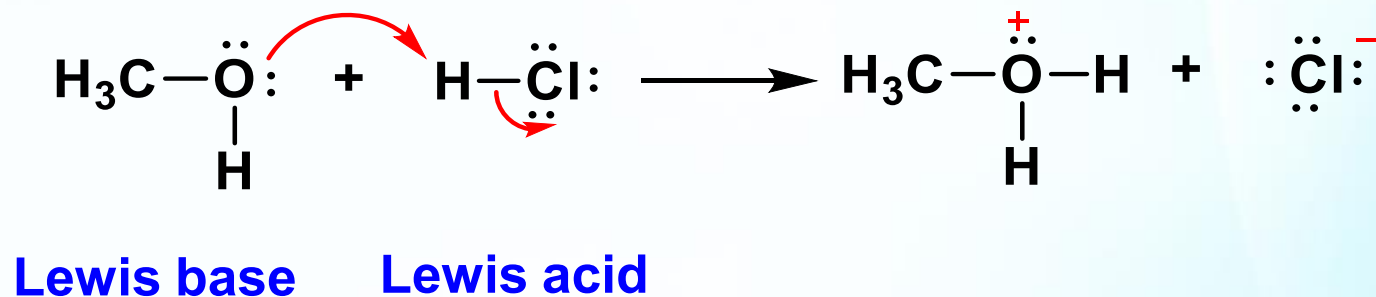
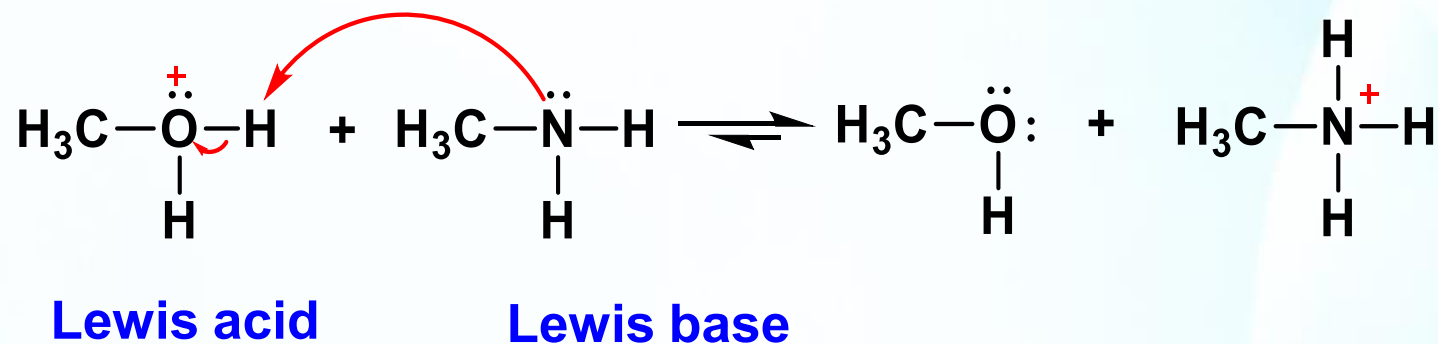




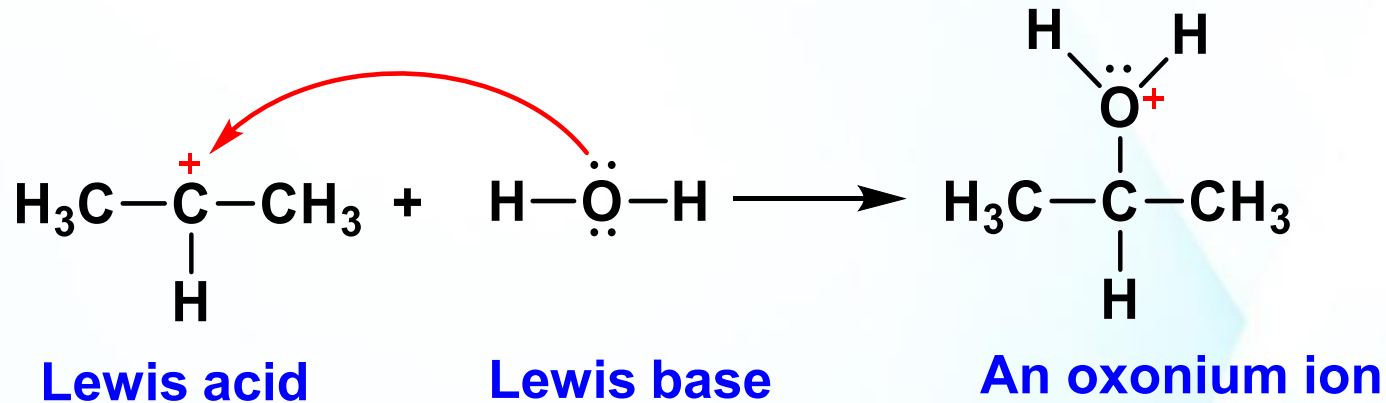
### 3. What are Lewis acids and bases?

**Lewis acid** is a species that can form a new covalent bond by accepting a pair of electrons.

**Lewis base** is a species that can form a new covalent bond by donating a pair of electrons.



### 3. What are Lewis acids and bases?



**Lewis bases** are ions or neutral molecules containing an atom with a lone pair of electrons.

**Lewis acids** are ions or electron deficient molecules with an unfilled valence shell.

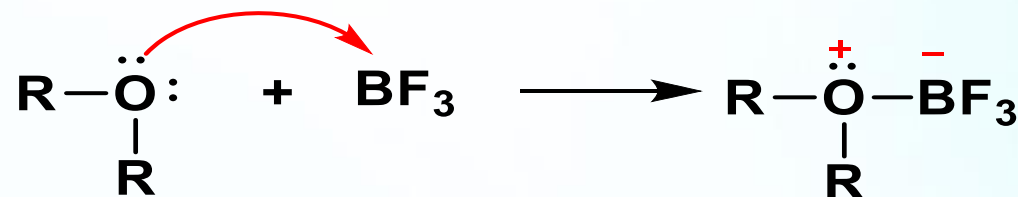
**BF<sub>3</sub>** and **AlCl<sub>3</sub>** are examples of Lewis acids.

Many **transition metal** compounds can also act as Lewis acids (e.g. TiCl<sub>4</sub> and SnCl<sub>4</sub>)



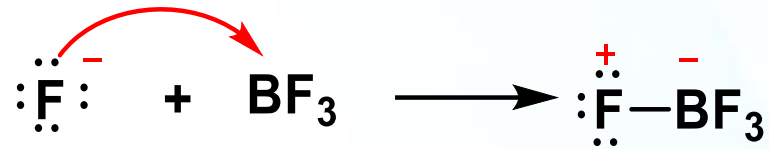


Both Al and B are in Group 3A of the periodic table and have three valence electrons in their outer shell. They means that these elements can form three bonds.



Lewis base    Lewis acid

Boron is surrounded by six electrons. However, boron's valence shell can accommodate eight electrons and so a fourth bond is possible if the fourth group can provide both electrons for the new bond.



Lewis base    Lewis acid

A **Lewis base** can be a negatively charged group or a neutral molecule, as long as there is an atom present with a lone pair of electrons (i.e. O, N, or a halogen.)

Therefore, all negatively charged ions and all functional groups containing a **nitrogen, oxygen, or halogen atom** can act as Lewis bases.

**All the Brønsted-Lowry bases** discussed earlier can also be defined **as Lewis bases**.



**Nucleophiles**: Nucleophiles are electron-rich molecules and react with electrophiles.

**Nucleophilic center**: The nucleophilic center of a nucleophile is the specific atom or region of the molecule which is electron rich.

The easiest nucleophiles to identify are negatively charged ions with lone pairs of electrons, but neutral molecules can also act as nucleophiles if they contain electron-rich functional groups (e.g. an amine).

The nucleophilic center of a neutral molecule is usually an atom with a lone pair of electrons (e.g. nitrogen or oxygen), or multiple bond (e.g. alkene, alkyne, aromatic ring).



- 同一周期的原子作为亲核中心时，试剂的亲核性与碱性一致，试剂碱性强，亲核性就强。



- 同一种元素的亲核试剂，亲核性与碱性的强弱一致。



The more electronegative the atom (e.g. F), the more tightly it holds on to its electrons and the less available these electrons are for forming new bonds (less nucleophilic).



- 亲核试剂的空间位阻如果很大，会影响其接近中心碳，亲核性会减弱。



- In aprotic solvents nucleophilic strengths more closely match relative basicity.
- In protic solvents, anions having large nucleophilic centers (atoms lower down the periodic table) are less solvated and are stronger nucleophiles.

In protic solvents such as water or alcohol, the stronger nucleophiles are those which have a large nucleophilic center, that is, an atom lower down the periodic table (e.g. **S**<sup>-</sup> is more nucleophilic than **O**<sup>-</sup> but is less basic.)



This is because protic solvents can form hydrogen bonds to the anion.  
The smaller the anion, the stronger the solvation and the more difficult it is for the anion to react as a nucleophile.

In protic solvents, the order of nucleophilicity of some common anions is as follows:



When an organic solvent is used which is incapable of forming hydrogen bonds to the anion (e.g. DMF or DMSO), the order of nucleophilicity changes to more closely match that of basicity.

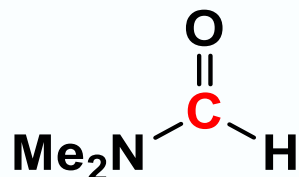
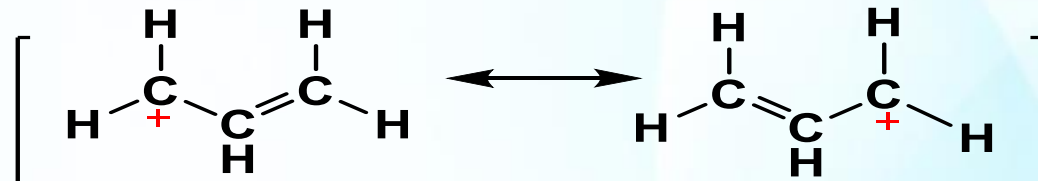
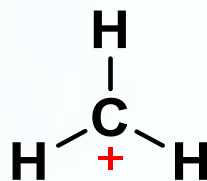
The order of nucleophilicity of the halides in DMSO:



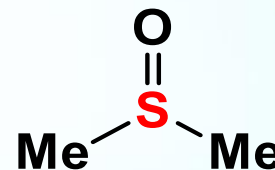


**Electrophiles:** Positively charged ions (cation), easily be identified as electrophiles but neutral molecules can also act as electrophiles if they contain certain types of functional groups (e.g. carbonyl groups or alkyl halides)

**Electrophilic center:** The electrophilic center of an electrophile is the specific atom or region of the molecule which is electron deficient.



DMF



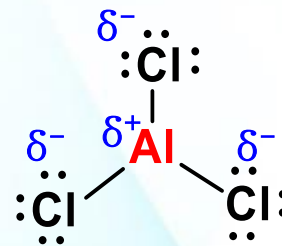
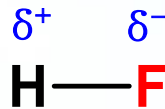
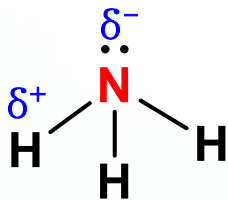
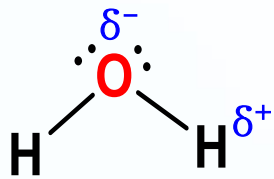
DMSO





## Electrophilic strength

The electrophilic strength of hydrogen atoms depends on the electronegativity of the neighboring atom.

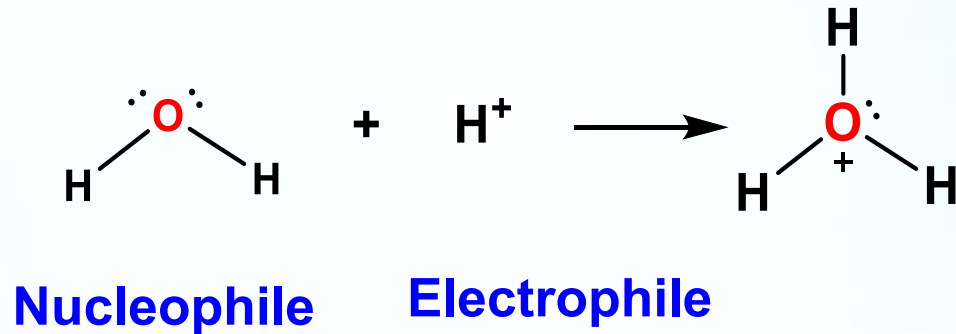
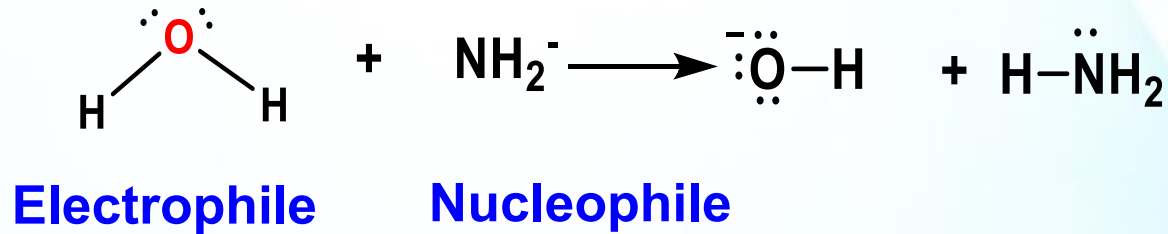


The hydrogen in ammonia is a very weak electrophilic center since the anion formed is unstable. As a result, nitrogen anions are only formed with very strong bases.

Molecules such as hydrogen fluoride or aluminum chloride prefer to react as electrophiles.

This is because the nucleophilic centers in both these molecules are weak, whereas the electrophilic centers (H or Al) are strong.

Water is a molecule which can react equally well as a nucleophile or as an electrophile.



Water reacts as a nucleophile with a proton and as an electrophile with an anion.



## How to identify the nucleophilic and electrophilic centers?

C-H

nonpolar covalent

Neither carbon nor hydrogen is a nucleophilic or electrophilic center.

C-C

C-N

polar covalent

The carbon atom can usually be ignored as an electrophilic center.

N-H

O-H

polar covalent

Nitrogen and oxygen are strong nucleophilic centers. Hydrogen is a weak electrophilic center.

C=O

C=N

C≡N

polar covalent

The O and N are nucleophilic centers and the carbon is an electrophilic center.

C-O

polar covalent

C-X

The oxygen atom is moderately nucleophilic whereas the halogen atom is weakly nucleophilic. The carbon atom is an electrophilic center.

H-X

polar covalent

Hydrogen atoms attached to halogens are more electrophilic than hydrogen atoms attached to oxygen. Hydrogen atoms attached to nitrogen are very weakly electrophilic.

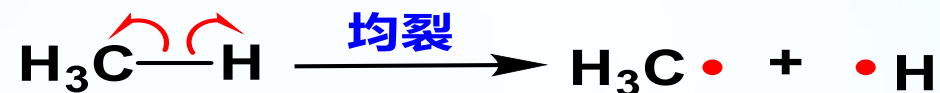


Most organic reactions involve the reaction between a molecule which is rich in electrons (nucleophiles) and a molecule which is deficient in electrons (electrophiles).

## Classification of reactions

有机反应涉及旧键的断裂和新键的形成。键的断裂有均裂和异裂两种方式：

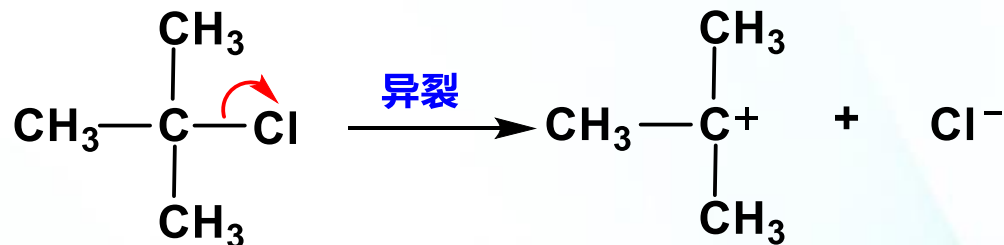
1) 均裂 ——> 自由基反应



经过均裂生成自由基的反应叫作自由基反应。一般在光、热或过氧化物存在下进行。

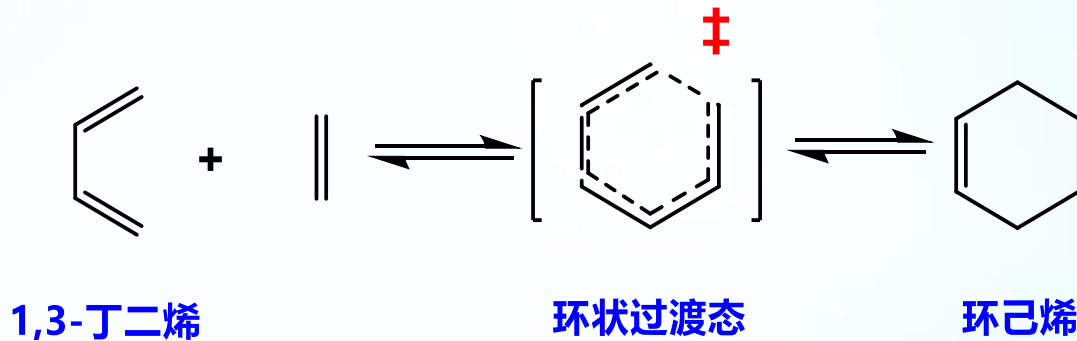


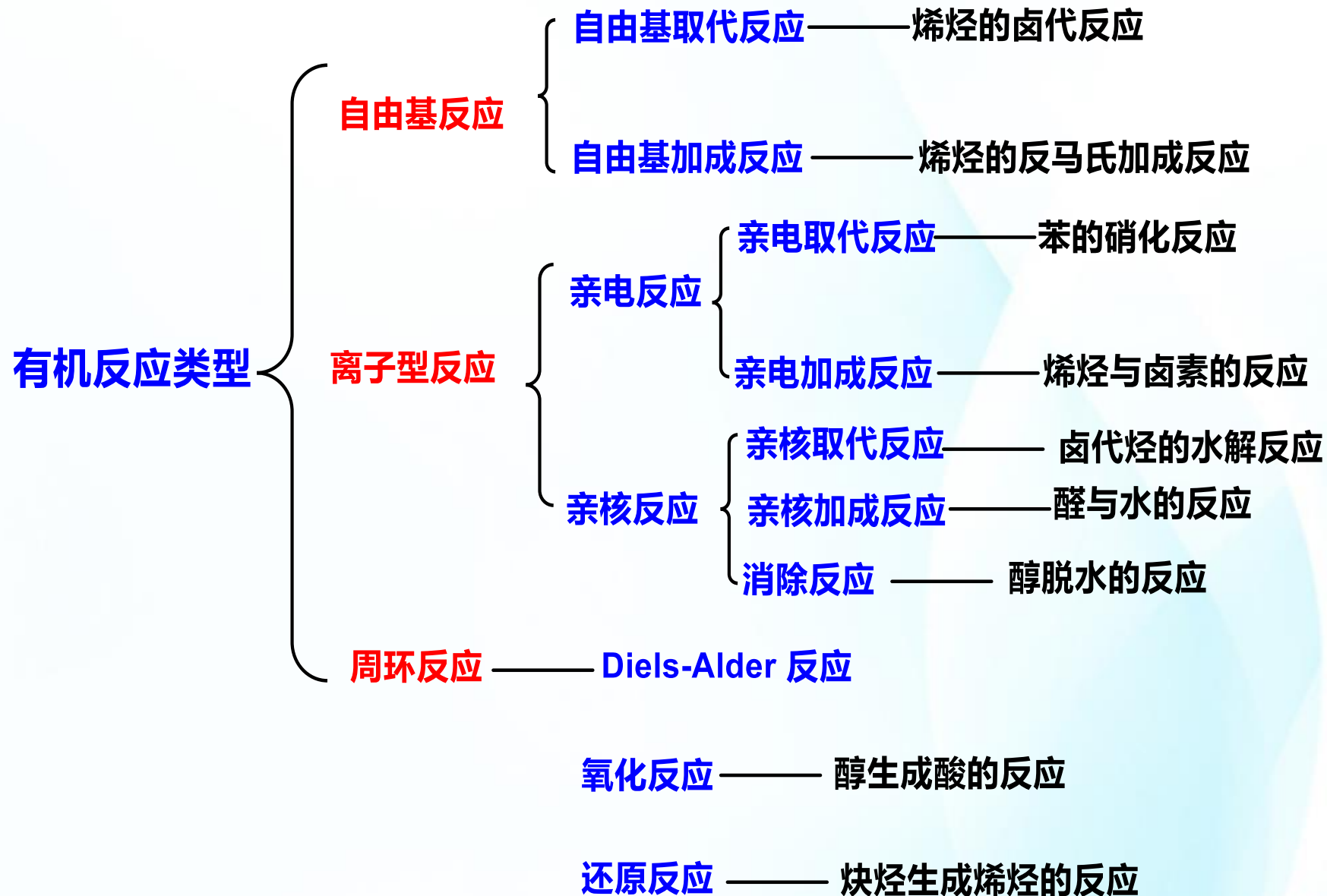
## 2) 异裂 ——> 离子型反应



发生异裂的**反应条件**是有催化剂、极性试剂、极性溶剂存在。异裂的**结果**产生了带正电荷或负电荷的离子。发生共价键异裂的反应，叫做**离子型反应**或异裂反应。

## 3) 周环反应 ——> 反应经环状过渡态，旧键的断裂和新键的生成同时进行的**反应**。

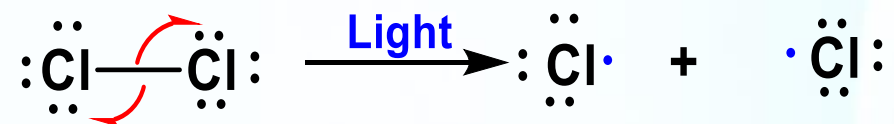






A **mechanism** describes how a reaction takes place by showing **what is happening to valence electrons** during **the formation and breaking of bonds**.

Curly arrows are used to show **what happens to valence electrons** during the making and breaking of bonds.







1963年Pearson提出软硬酸碱理论，并提出 “硬亲硬，软亲软” 经验规则。

✓ 该理论利用“软”和“硬”来形容酸碱抓住电子的松紧程度，即释放和获取电子的难易；

✓ 抓电子紧的酸(碱)称为硬酸(碱)，反之称为软酸(碱)；

✓ 硬酸中心原子的体积小、正电荷数高、可极化性低；而软酸则相反；

✓ 硬碱给予体的原子电负性高，可极化性低，不易被氧化，不易失去外层电子；而软碱则反之。



## 常见的软硬酸碱

	硬	交界	软
酸	$\text{H}^+$ , $\text{Li}^+$ , $\text{Na}^+$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ , $\text{Al}^{3+}$ , $\text{Cr}^{3+}$ , $\text{Fe}^{3+}$ , $\text{BF}_3$ , $\text{Al}(\text{CH}_3)_3$ , $\text{AlCl}_3$ , $\text{SO}_3$ , $\text{RCO}^+$ , $\text{CO}_2$ , $\text{HX}$ (能形成氢键的分子)	$\text{Fe}^{2+}$ , $\text{Cu}^{2+}$ , $\text{Zn}^{2+}$ , $\text{B}(\text{CH}_3)_3$ , $\text{SO}_2$ , $\text{R}_3\text{C}^+$ , $\text{C}_6\text{H}_5^+$	$\text{RX}$ , $\text{ROT}_s$ , $\text{Cu}^+$ , $\text{Ag}^+$ , $\text{RS}^+$ , $\text{Br}^+$ , $\text{I}^+$ , $\text{HO}^+$ , $\text{Br}_2$ , $\text{I}_2$ , 卡宾
碱	$\text{H}_2\text{O}$ , $\text{HO}^-$ , $\text{F}^-$ , $\text{Cl}^-$ , $\text{AcO}^-$ , $\text{PO}_4^{3-}$ , $\text{SO}_4^{2-}$ , $\text{ClO}_4^-$ , $\text{NO}_3^-$ , $\text{ROH}$ , $\text{R}_2\text{O}$ , $\text{RO}^-$ , $\text{NH}_3$ , $\text{RNH}_2$ , $\text{N}_2\text{H}_4$	$\text{PhNH}_2$ , $\text{C}_5\text{H}_5\text{N}$ , $\text{N}_3$ , $\text{Br}^-$ , $\text{NO}_2^-$ , $\text{SO}_3^{2-}$ , $\text{N}_2$	$\text{RSH}$ , $\text{R}_2\text{S}$ , $\text{RS}^-$ , $\text{I}^-$ , $\text{SCN}^-$ , $\text{CN}^-$ , $\text{R}_3\text{P}$ , $\text{C}_2\text{H}_4$ , $\text{C}_6\text{H}_6$ , $\text{R}^-$ , $\text{H}^-$



也许有一天, 不知不觉, 你将渐渐活出写满答案的人生!