Basic Organic Chemistry L9-2

These are study notes for Basic Organic Chemistry L9-2: Properties, Acid–Base Behavior, and Nucleophilicity of Alcohols.

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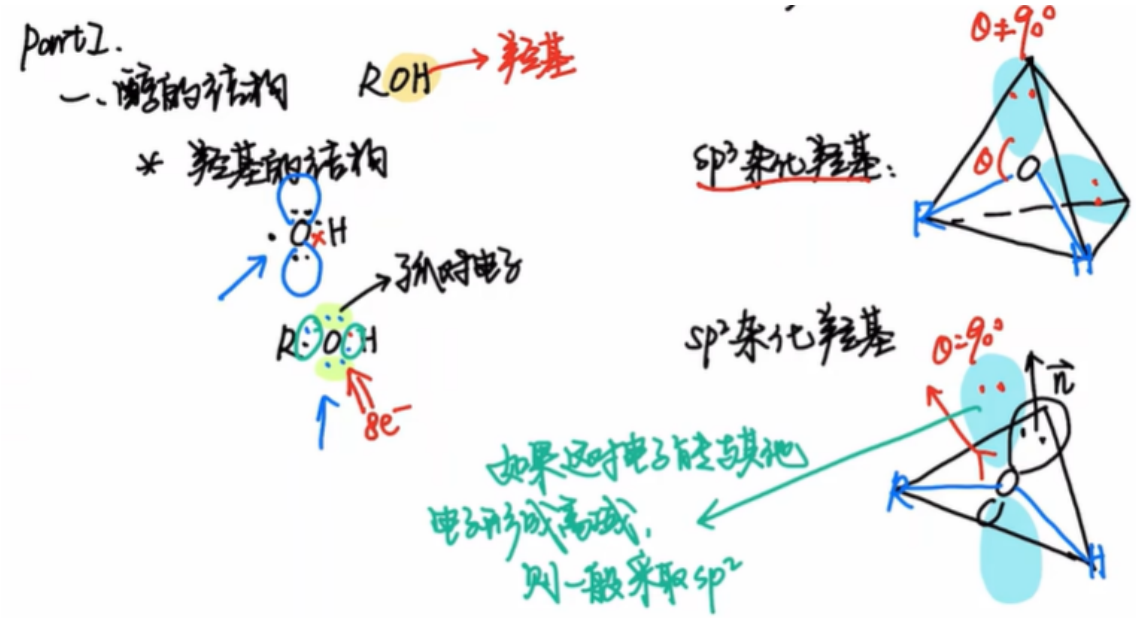
#PartI:Structure of alcohol According to the octet rule, the structure of alcohol is $R-O-H$, in which there are two lone pairs of electrons on the O atom.



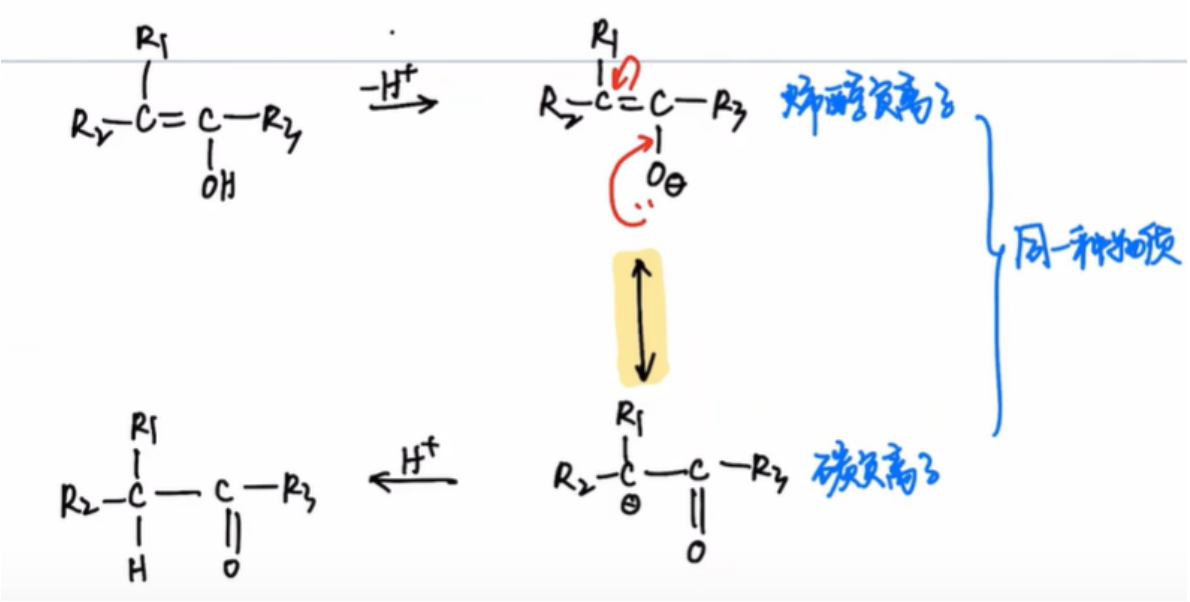
Affected by **electronic effect** and **steric hindrance effect**, the hybridization mode of alcohol hydroxyl oxygen can be sp^3/sp^2

Phenol

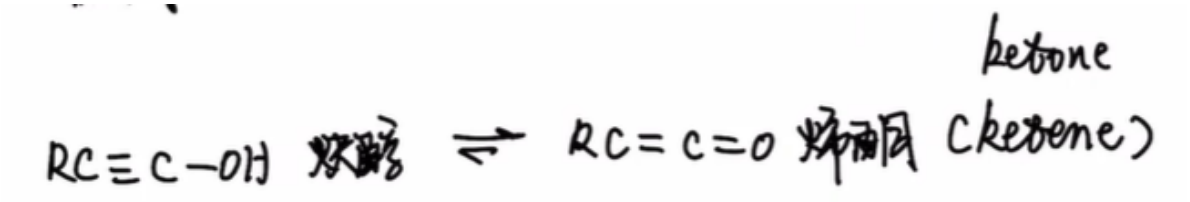
In phenol, the O atom adopts sp^2 hybridization, so that the lone pair of electrons of O can form conjugation with the benzene ring, causing electron delocalization and a decrease in system energy.

Phenol negative ion

In the enol anion, the hydroxyl oxygen also adopts sp^2 hybridization due to $p-\pi$ conjugation.



Alkynyl alcohol-enone



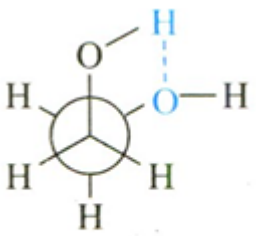
According to the $\alpha - C$ classification, alcohols can be divided into primary/secondary/tertiary alcohols.

Physical properties

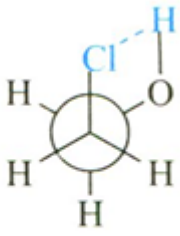
1. Lower alcohols are easily soluble, intermediate alcohols are partially soluble, and higher alcohols are insoluble.
2. With the same number of carbon atoms, branched chain alcohols have lower boiling points.
3. The melting and boiling points of lower alcohols are higher than those of hydrocarbons with the same carbon number.

Stereochemistry

For ethylene glycol and 2-chloroethanol, since the ortho-cross conformation can form intramolecular hydrogen bonds and reduce the conformational energy, they mainly exist in the ** ortho-cross conformation**



乙二醇



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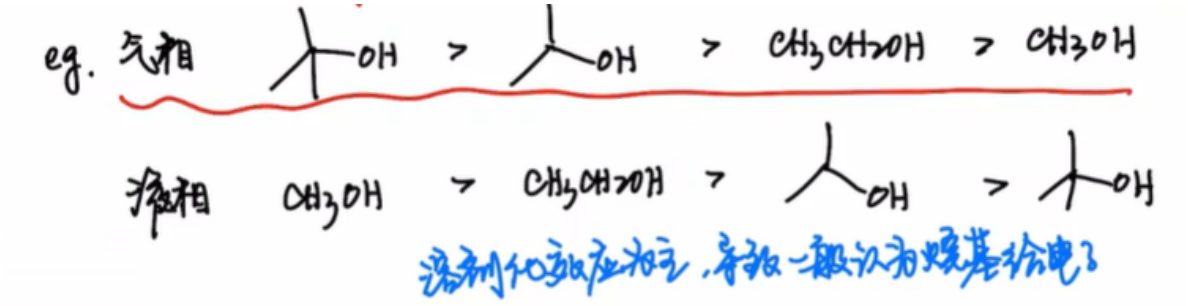
PartII: Acidity and alkalinity of alcohol

Acidic

The more stable the conjugate base, the stronger the acidity.

According to the acid-base order of the alcohol molecule, the electronic effect of the group can be known.

- In the liquid phase, the alkyl group exhibits an electron-donating effect, which is not conducive to the charge dispersion of alkoxy anions. This is because the alkyl group has large air resistance, which is not conducive to the solvation of alkoxy anions.
- In the gas phase, the alkyl group exhibits an electron-withdrawing effect.



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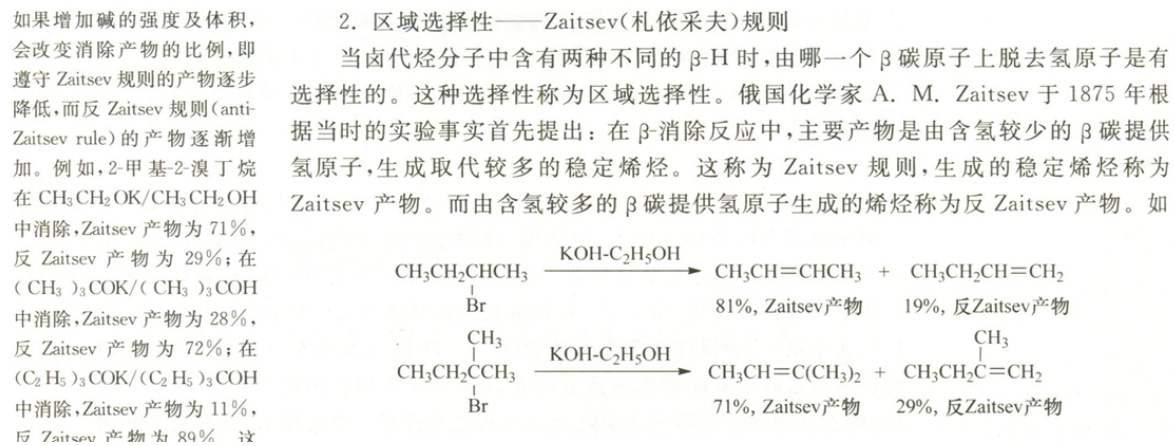
Since most organic reactions occur in the liquid phase, it is generally believed that **alkyl groups are electron-donating groups**.

$$\boxed{\text{alcohol} + \text{reactive metal (K, Na, Mg, Al)} \rightarrow \text{alkoxide} + H_2 \uparrow}$$

Common alkoxides and their uses

-$EtONa$: As a small sterically hindered strong base, as a strong nucleophile -$BuOK$: As a large sterically hindered strong base, as a weak nucleophile

When carrying out β-elimination reaction of halogenated hydrocarbons, strong bases with large steric hindrance give **anti-Zaitsev product**, and weak bases with small steric hindrance give **Zaitsev product**



如果增加碱的强度及体积，会改变消除产物的比例，即遵守 Zaitsev 规则的产物逐步降低，而反 Zaitsev 规则(anti-Zaitsev rule)的产物逐渐增加。例如，2-甲基-2-溴丁烷在 CH_3CH_2OK/CH_3CH_2OH 中消除，Zaitsev 产物为 71%，反 Zaitsev 产物为 29%；在 $(CH_3)_3COK/(CH_3)_3COH$ 中消除，Zaitsev 产物为 28%，反 Zaitsev 产物为 72%；在 $(C_2H_5)_3COK/(C_2H_5)_3COH$ 中消除，Zaitsev 产物为 11%，反 Zaitsev 产物为 89%。这

2. 区域选择性——Zaitsev(札依采夫)规则

当卤代烃分子中含有两种不同的 β-H 时，由哪一个 β 碳原子上脱去氢原子是有选择性的。这种选择性称为区域选择性。俄国化学家 A. M. Zaitsev 于 1875 年根据当时的实验事实首先提出：在 β-消除反应中，主要产物是由含氢较少的 β 碳提供氢原子，生成取代较多的稳定烯烃。这称为 Zaitsev 规则，生成的稳定烯烃称为 Zaitsev 产物。而由含氢较多的 β 碳提供氢原子生成的烯烃称为反 Zaitsev 产物。如

> This is because when the volume and strength of the base increase, β-H with larger steric hindrance is less susceptible to attack, while β-H with smaller steric hindrance and strong acidity is more susceptible to reaction.

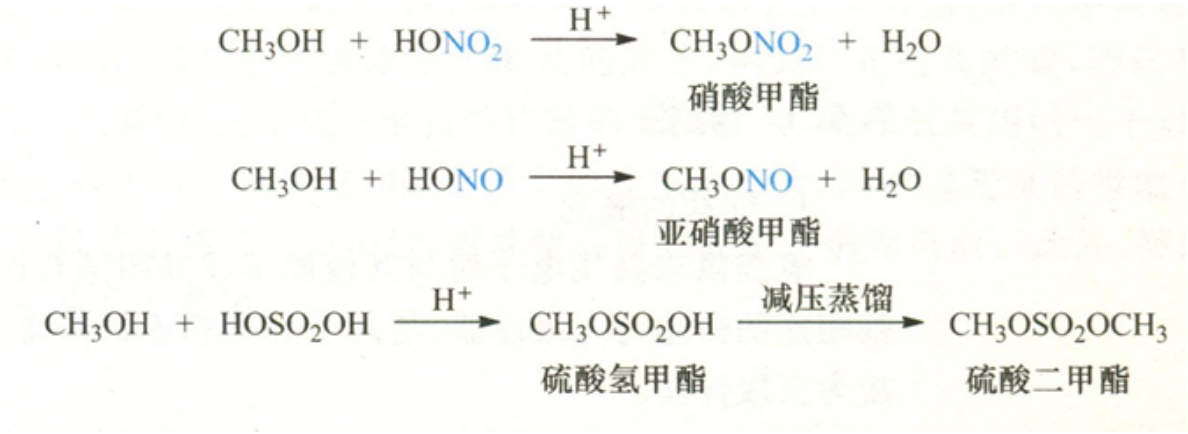
Aluminum isopropoxide can serve as a catalyst for redox reactions.

Basic/Nucleophilic

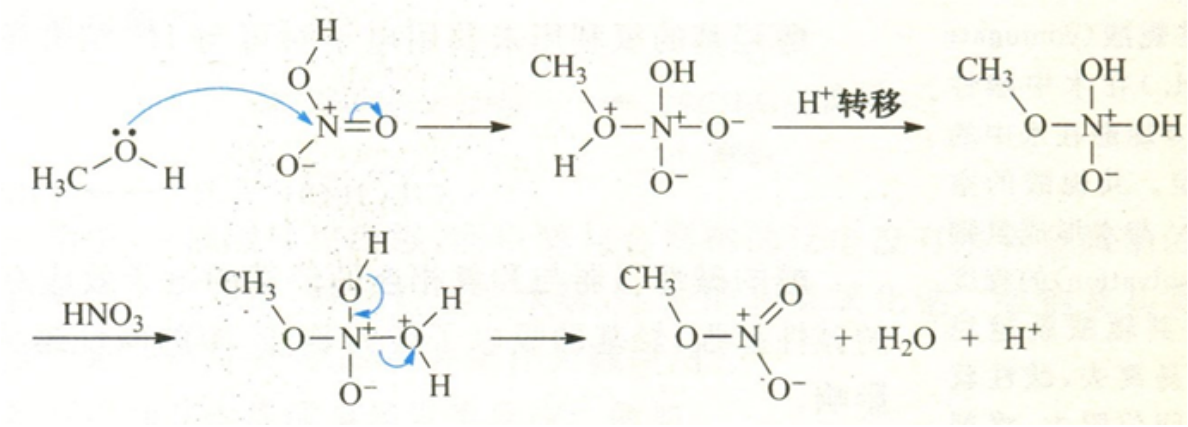
If the lone pair of electrons on the oxygen atom of the alcoholic hydroxyl group is combined with H^+, it will show **alkalinity**. If it is combined with the electrophile E^+, it will show **nucleophilicity**

Also due to the unfavorable reasons for liquid phase solvation, the steric hindrance of the alkyl group will enhance the acidity of the conjugate acid of the alcohol, which means weakening the alkalinity of the alcohol.

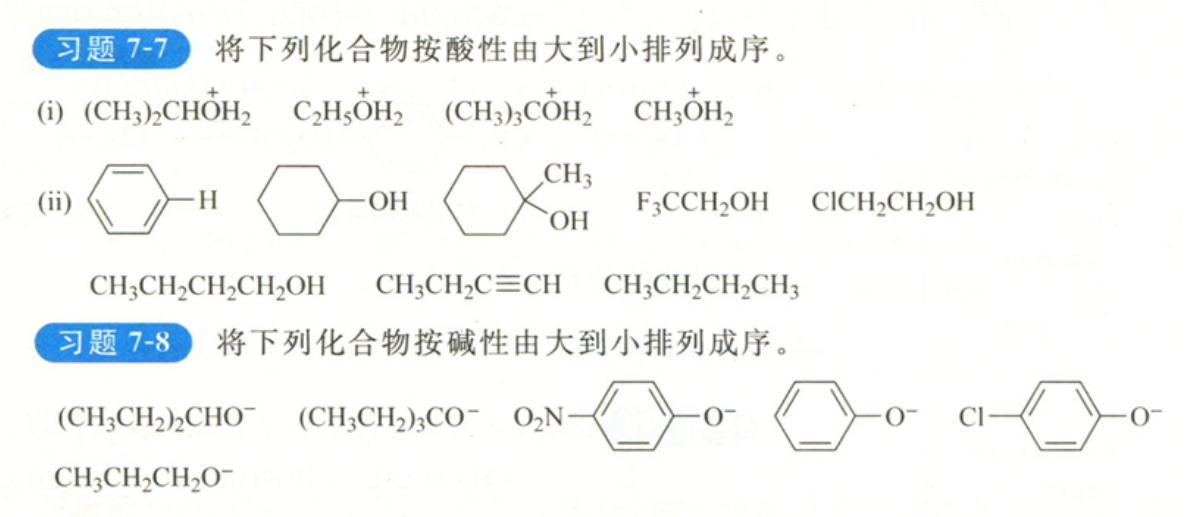
Alcohols can react with oxo inorganic acids, losing a molecule of water and forming inorganic acid esters.



Take the reaction between alcohol and nitric acid as an example: the reaction follows the **addition-elimination mechanism**



Comprehensive judgment



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(i)2,3,1,4

(ii)7,4,5,1,2,3,6,8

7-8 2,1,6,4,5,3