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| Reaction of Alcohols with Hydrogen Halides | Chapter 14: Alcohols, Thiols and Ethers |

**This handout will help you with 3 components: 1) Overall reaction (REQUIRED and on the Test); 2) Answering a lab question from Polymer Lab; 3) Extra Credit question (Mechanism on p.2) on the Test**:

**Reaction of Alcohols with Hydrogen Halides**   
Overall reaction (MUST KNOW FOR TEST):

Substitution of alcohols using HX

**Reaction type: Nucleophilic Substitution**

Summary:

* When treated with HBr or HCl alcohols typically undergo a nucleophilic substitution reaction to generate an alkyl halide and water.
* Alcohol relative reactivity order : 3o > 2o > 1o > methyl.
* Hydrogen halide reactivity order : HI > HBr > HCl > HF (paralleling acidity order).
* Reaction usually proceeds via an [SN1 mechanism](http://www.mhhe.com/physsci/chemistry/carey/student/olc/graphics/carey04oc/ref/ch04nucle.html#1) (\*don’t have to learn the specifics until Organic Chem with Cody, **unless you want points on the Extra Credit question on upcoming Test**) which proceeds via a [carbocation intermediate](http://www.mhhe.com/physsci/chemistry/carey/student/olc/graphics/carey04oc/ref/ch04nucle.html#carb), that can also undergo rearrangement.
* Methanol and primary alcohols will proceed via an [SN2 mechanism](http://www.mhhe.com/physsci/chemistry/carey/student/olc/graphics/carey04oc/ref/ch04nucle.html#2) (\*will learn with Cody) since these have highly unfavorable carbocations.
* The reaction of alcohols with HCl in the presence of ZnCl2 (catalyst) forms the basis of the Lucas test for alcohols.(\****Don’t have to know the Lucas test***)

\*See next page for mechanism. Remember: nucleophile attacks electrophile!

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| **(SN1) MECHANISM FOR REACTION OF ALCOHOLS WITH HX (Ex: HBr)**  **Step 1:**  This step is very fast and reversible. OH (nucleophile) attacks H+ of HBr. *FYI (but not on test): This is an acid/base reaction. Protonation of the alcoholic oxygen to make it a better leaving group. The lone pairs on the oxygen make it a Lewis base.*          **NOTE THE OXONIUM ION!**  **Step 2:**  Cleavage of the C-O bond allows the loss of the good *leaving group*, a neutral water molecule, to give a carbocation intermediate.            **Step 3:**  Attack of the nucleophilic bromide ion on the electrophilic carbocation creates the alkyl bromide. | http://www.mhhe.com/physsci/chemistry/carey/student/olc/graphics/carey04oc/ch15/figures/sn1roh.gif |