

# HYDROLYSIS REACTIONS

Kayhan BOLELU, Ph.D

## HYDROLYSIS REACTIONS

**HYDROLYSIS** means fragmentation by water.  
(Bond rupture by using water)

Organic molecules that can be fragment by water:  
Carboxylic Acid Derivates (Amides, Acid chlorides, Esters, Acid Anhydrides, Nitriles)



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## HYDROLYSIS REACTIONS

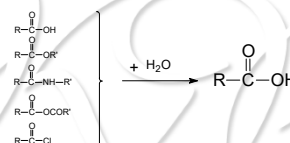
**Hydrolysis** occurs slowly when it is made only with water, but the reaction rate increases if the reaction is in the presence of acid or base. (Hydrolysis is carried out using an acid or base **catalyser** in aqueous medium.)



The task of the catalysers is to facilitate electron transfer by activating the bond electrons.

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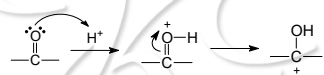
## HYDROLYSIS OF CARBOXYLIC ACID DERIVATIVES



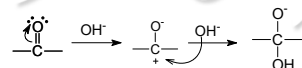
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## HYDROLYSIS OF CARBOXYLIC ACID DERIVATIVES

### • HYDROLYSIS in H<sup>+</sup> medium

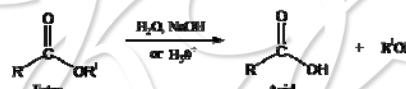


### • HYDROLYSIS in OH<sup>-</sup> medium

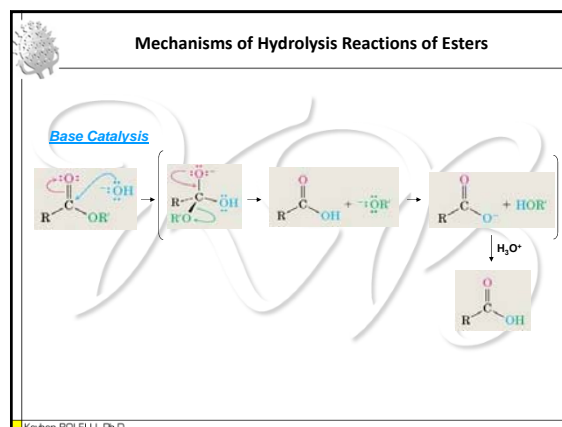
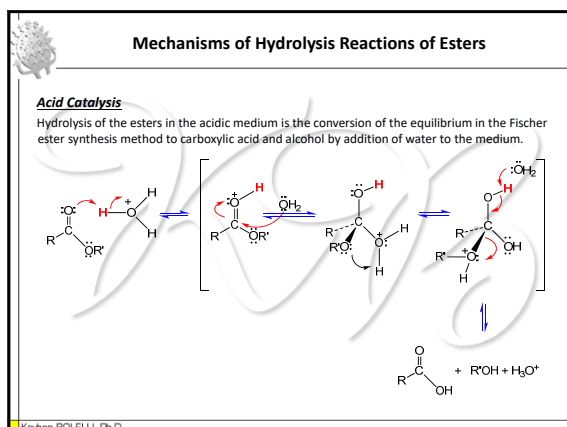


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## HYDROLYSIS OF ESTERS



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### Mechanisms of Hydrolysis Reactions of Esters

When hydrolysis is compared with acid and base catalysis, most significant difference can be summarized as follows:

- \* While water, which is a weak nucleophile in acid-catalyzed hydrolysis, is added to carbonyl group (C=O) increasing electrophilic charge by taking proton; OH<sup>-</sup>, which is a strong nucleophile in base-catalyzed hydrolysis, is added to the weak electrophilic C=O bond.
- \* Carboxylic acid salt and alcohol are formed by base-catalyzed hydrolysis.

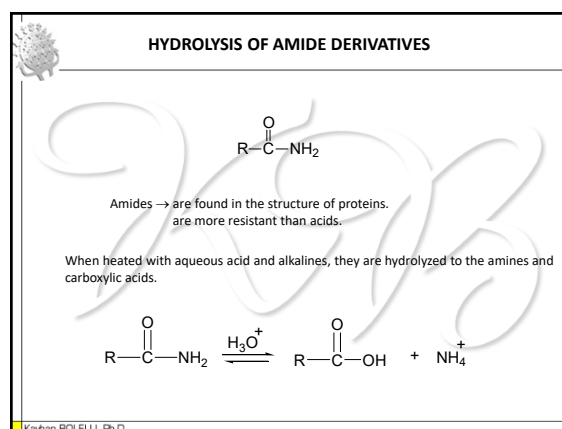
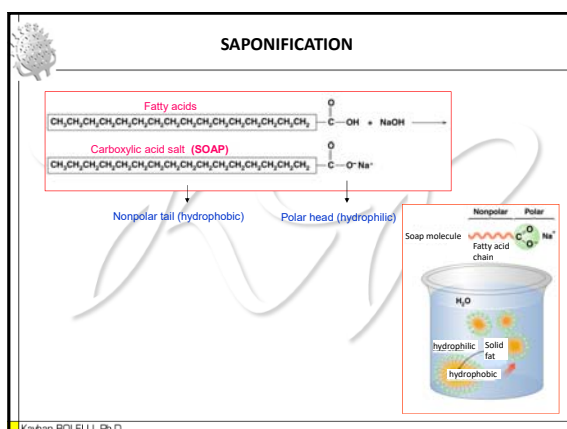
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### SAPONIFICATION

Alkaline hydrolysis → SAPONIFICATION

(Soaps are obtained by alkaline hydrolysis of glycerol esters of high-carbon fatty acids.)

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### HYDROLYSIS OF AMIDE DERIVATIVES

$$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}_2 \xrightleftharpoons{\text{OH}^-} \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- + \text{NH}_3$$

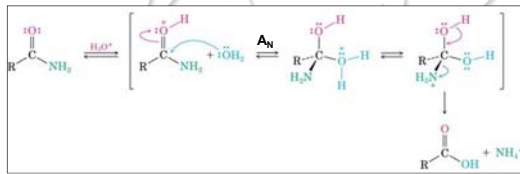
The appearance of ammonia in the basic environment can be understood from the smell or blueness of the litmus paper.

If the amide used is *N*-substituted amide, primary or secondary amines are formed instead of ammonia.

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### Mechanisms of Hydrolysis Reactions of Amides


**ACID CATALYSIS**



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### Mechanisms of Hydrolysis Reactions of Amides

**BASE CATALYSIS**



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### HYDROLYSIS OF ACID HALIDES

- Since acyl halides and acid anhydrides are active molecules, they hydrolyze under neutral conditions.

$$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}$$

Since the electrophilic charge of carbonyl carbon is greater than the alkyl carbon, the substitution of halogen is easier.

- To avoid hydrolysis of these compounds, acyl halides and anhydrides should be stored under dry  $\text{N}_2$ , the used solvents and reagents should be dry.

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### HYDROLYSIS OF ACID HALIDES

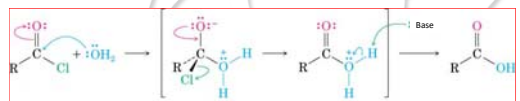
$$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} + \text{H}_2\text{O} \longrightarrow \text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH} + \text{HCl}$$

↓  
pyridine/NaOH (to remove)

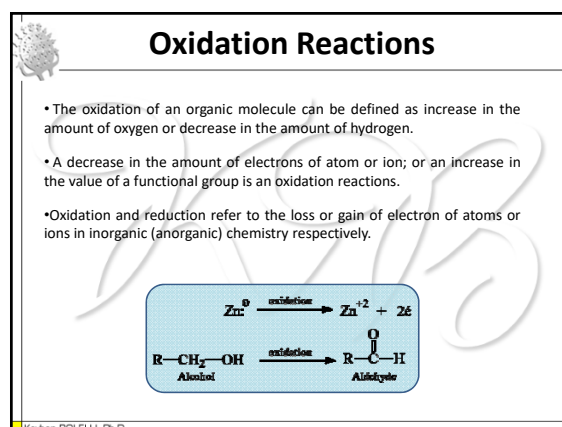
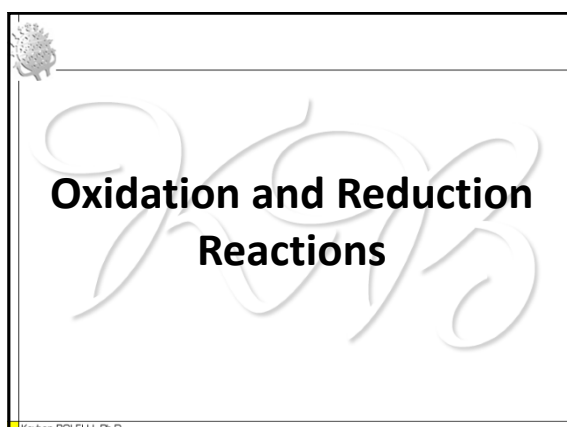
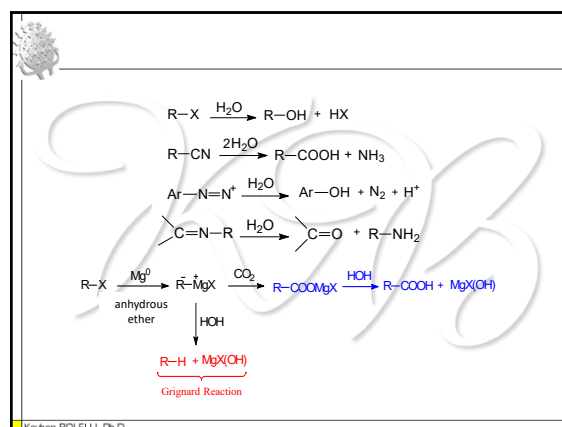
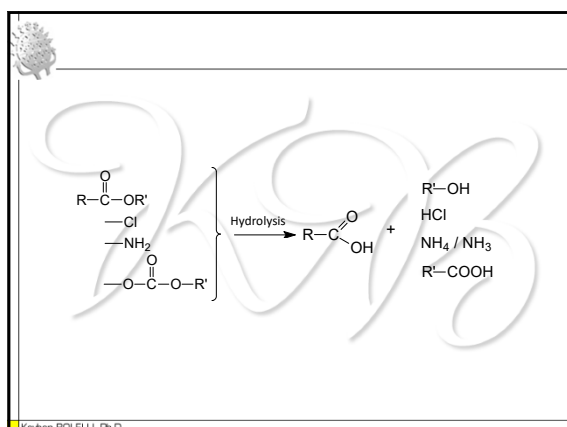
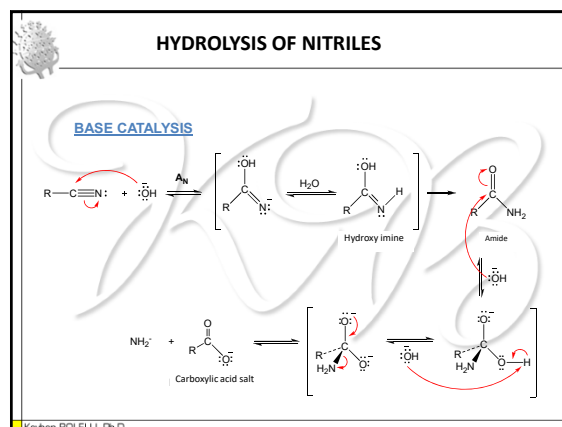
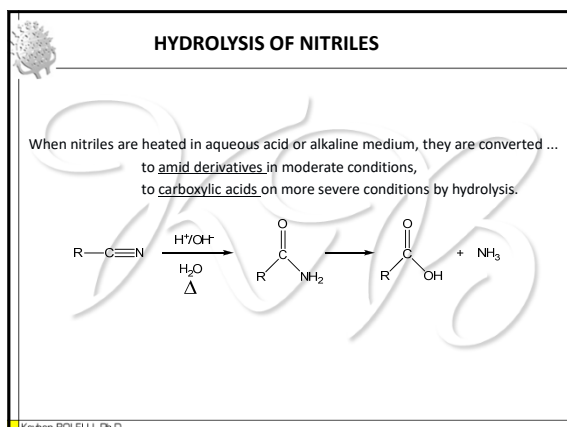
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### HYDROLYSIS OF ACID HALIDES

The hydrolysis reaction of acyl chlorides is nucleophilic acyl substitution.



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## Oxidation Number (Ox. State)

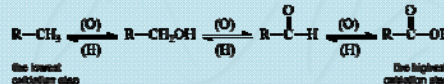
Ox. step	Primary	Secondary	Tertiary	Quaternary
-4	CH <sub>4</sub>			
-3		RCH <sub>3</sub>		
-2	CH <sub>3</sub> OH		R <sub>2</sub> CH <sub>2</sub>	
-1		RCH <sub>2</sub> OH		R <sub>3</sub> CH
0	CH <sub>2</sub> O		R <sub>2</sub> CHOH	R <sub>3</sub> C
+1		RCHO		R <sub>3</sub> COH
+2	HCOOH		R <sub>2</sub> CO	
+3		RCOOH		
+4	CO <sub>2</sub>			

The oxidation number of a free element is always 0. If an element loses the  $n$  number of electrons, it is considered to be oxidized by  $+n$  value, and if it gains, it is considered to be reduced by  $-n$  value. In organic molecules, the oxidation numbers of the "C" atoms can be calculated by considering each "H",  $-1$ ; each "C",  $0$ ; each heteroatoms,  $+1$  values for the 4 bonds of the "C" atoms.

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## Oxidation and Reduction

When an organic compound undergoes reduction, the reduction reactive oxidizes. When an organic compound undergoes oxidation, the oxidation reactive undergoes reduction. Oxidation and reduction reaction take place at the same time.



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## Applied in industrial and laboratory Oxidation Methods

- Oxidation in air or with pure oxygen. (These reactions can be accomplished by biologically catalyzing homogeneous or heterogeneous catalysers.)
- Catalytic dehydrogenation at high temperature. (Vanadium oxides)
- Oxidation with some inorganic substances outside oxygen. (The most commonly used reagents: Sodium dichromate + H<sub>2</sub>SO<sub>4</sub> (sulfochromic mixture), in neutral, basic or acidic medium KMnO<sub>4</sub>, concentrated nitric acid, hydrogen peroxide, ozone, some metallic oxide and peroxides, some oxygenated salts.)
- Oxidation with some organic substances or peroxides and peracides.

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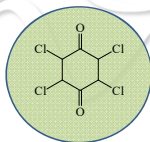
## Oxidation Reagents

O <sub>2</sub>	HNO <sub>3</sub>	SO <sub>3</sub>	Cl <sub>2</sub>	Ag <sub>2</sub> O	MnO <sub>2</sub>
O <sub>3</sub>	RO-NO	(CH <sub>3</sub> ) <sub>2</sub> S <sup>+</sup> -O <sup>-</sup>	Br <sub>2</sub>	HgO	MnO <sub>4</sub> <sup>-</sup>
H <sub>2</sub> O <sub>2</sub>	Ø-N <sub>2</sub>	SeO <sub>2</sub>	I <sub>2</sub>	Hg(OAc) <sub>2</sub>	CrO <sub>3</sub>
t-BuO-OH	H <sub>2</sub> NCl		NBS	Pb(OAc) <sub>4</sub>	CrO <sub>2</sub> Cl <sub>2</sub>
R-COO-OH	H <sub>3</sub> N <sup>+</sup> -OSO <sub>3</sub> <sup>-</sup>		t-BuOCl	FeCl <sub>3</sub>	OsO <sub>4</sub>
	R <sub>3</sub> N <sup>+</sup> -O <sup>-</sup>			Fe(CN) <sub>6</sub> <sup>-3</sup>	IO <sub>4</sub> <sup>-</sup>

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## Dehydrogenation (-2H):

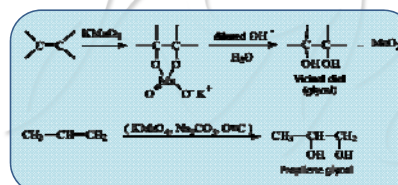
- Heat with Pt, Pd, S or Se
- Substituted quinones (e.g. Chloranil)



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## Oxidation of Ethylenic Double Bond and Aromatic Side Chain with KMnO<sub>4</sub>

In dilute basic medium and in the cold (0-5°C), KMnO<sub>4</sub> acts to dihydroxylate the double bond and glycols (1,2-diols) are formed.



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