



## Oxidation Number (Ox. State)

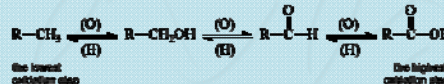
Ox. step	Primary	Secondary	Tertiary	Quaternary
-4	CH <sub>4</sub>			
-3		RCH <sub>3</sub>		
-2	CH <sub>3</sub> OH		R <sub>2</sub> CH <sub>2</sub>	
-1		RCH <sub>2</sub> OH		R <sub>3</sub> CH
0	CH <sub>2</sub> O		R <sub>2</sub> CHOH	R <sub>3</sub> C
+1		RCHO		R <sub>3</sub> COH
+2	HCOOH		R <sub>2</sub> 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 reagent oxidizes. When an organic compound undergoes oxidation, the oxidation reagent 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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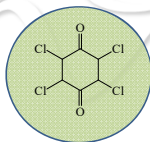
## Oxidation Reagents

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):

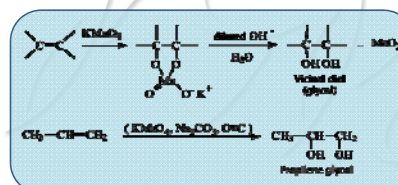
- Heat with Pt, Pd, S or Se
- Substituted quinones (e.g. Chloranil)



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

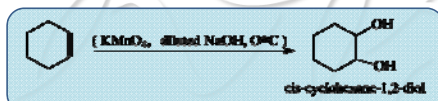
In dilute basic medium and in the cold (0-5°C), KMnO<sub>4</sub> acts to dihydroxylate the double bond and glycols (1,2-diols) are formed.



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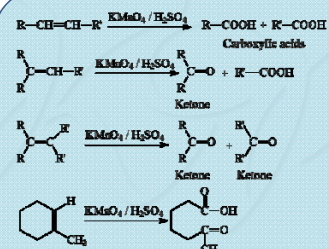
## Oxidation of Ethylenic Double Bond and Aromatic Side Chain with $\text{KMnO}_4$

This reaction takes place as cis-addition in stereochemistry.  
For example; cis-cyclohexane-1,2-diol is formed from cyclohexene.



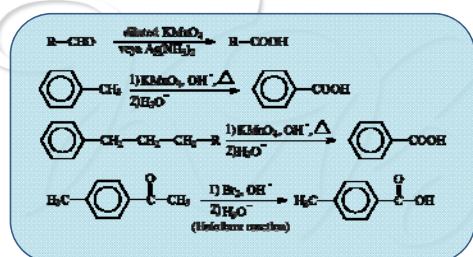
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The acidic permanganate solution leads to ketone or carboxylic acid formation breaking the double bond according to the environment of the double bond carbon...



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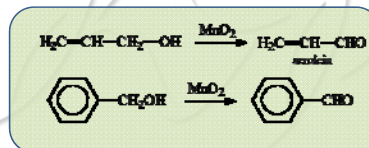
Oxidation in the side chain takes place in the benzylic carbone. Even if there are alkyl groups including multiple "C" atoms, it is always fragmented to benzoic acid...



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## Moderate Oxidation with $\text{MnO}_2$

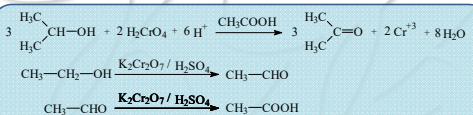
- Freshly prepared  $\text{MnO}_2$  is used in one step oxidation of allylic and benzylic alcohols.
- $\text{MnO}_2 \rightarrow \text{Mn}^{2+}$  is reduced and there is no oxidation to further steps.



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## Oxidation of the secondary alcohols with chromic acid (Obtaining of Acetone)

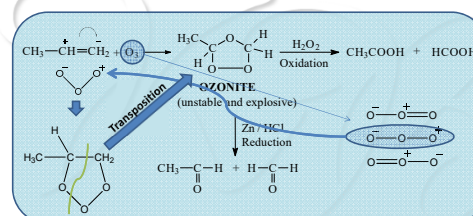
- Acetone is obtained by the addition Chromic acid ( $\text{H}_2\text{CrO}_4$ ),  $\text{CrO}_3$  or  $\text{Na}_2\text{Cr}_2\text{O}_7$  to  $\text{H}_2\text{SO}_4$ . While Cr is reduced from +6 to +3, related compound is oxidized.



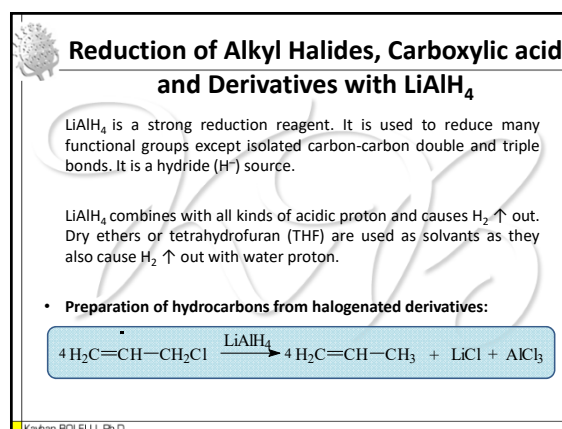
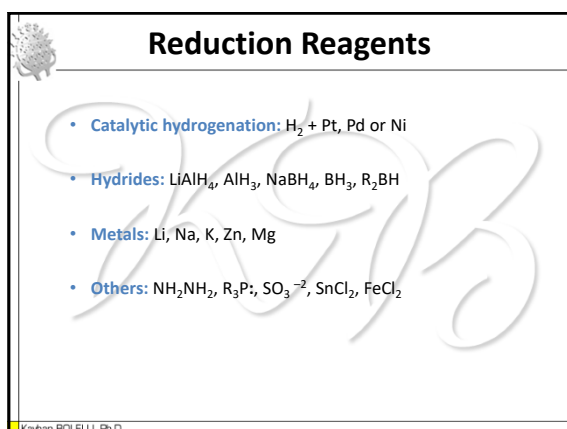
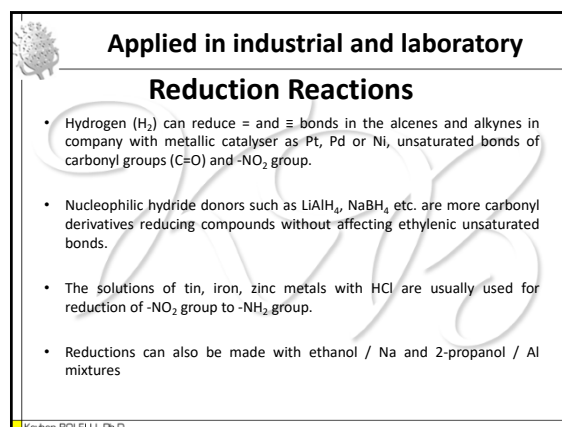
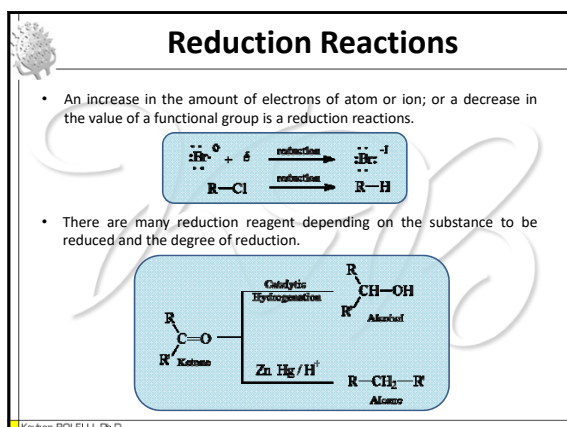
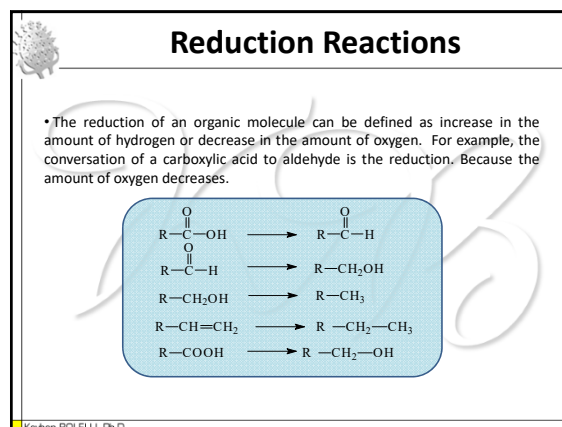
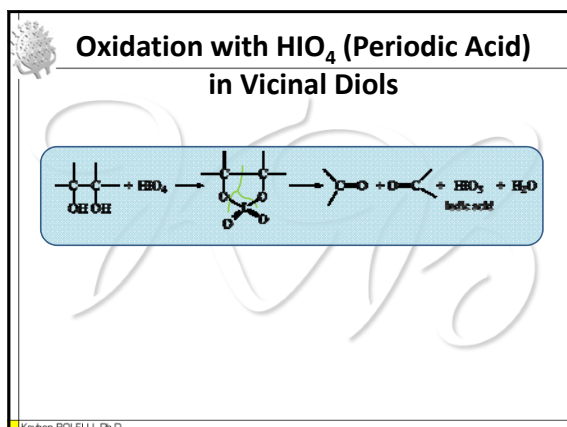
- Other oxidation reagents including Cr (VI)  
 $\text{Na}_2\text{Cr}_2\text{O}_7$  (sodium bichromate),  $\text{Na}_2\text{CrO}_4$  (sodium chromate),  $\text{H}_2\text{CrO}_4$  (chromic acid),  $\text{CrO}_3$  (chromic oxide),  $\text{CrO}_2\text{Cl}_2$  (chromyl chloride)

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## Oxidation of ethylenic compounds with $\text{O}_3$ (Ozonolysis)



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### Preparation of Primary Amines by Action from Amides ve Nitriles

$$\begin{aligned} R-C\equiv N &\xrightarrow{LiAlH_4} R-CH_2-NH_2 \\ R-CONH_2 &\xrightarrow{LiAlH_4} R-CH_2-NH_2 \end{aligned}$$

- LiAlH<sub>4</sub> is converted to alcohols by reducing R-CHO, R<sub>2</sub>C=O, R-COOH, RCH(O)-CH<sub>2</sub>, RCOOR, RCOCl molecules.

$$R-CHO \xrightarrow{LiAlH_4} R-CH_2OH$$

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### Reaction Mechanism of LiAlH<sub>4</sub>

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### Reduction of Carbonyl Derivatives with NaBH<sub>4</sub>

NaBH<sub>4</sub> is a weaker reduction agent than LiAlH<sub>4</sub>. It is used to reduce aldehydes and ketones majorly. The reduction process with NaBH<sub>4</sub> can be carried out in an aqueous medium or alcohol.

$$\begin{aligned} H_2C=CH-CO-CH_3 &\xrightarrow{NaBH_4} H_2C=CH-CH(OH)-CH_3 \text{ (3-hydroxy-1-butene)} \\ R-CHO &\xrightarrow{NaBH_4} R-CH_2OH \end{aligned}$$

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### Catalytic Reduction (Hydrogenolysis)

Hydrogenolysis is called that is opened by hydrogen and a metal catalyser the bond in the ethylenic and acetylenic unsaturated structures and the bond between carbon and heteroatom. These metals are platinum (Pt), rutenium (Ru), palladium (Pd) and nickel (Ni).

$$\begin{aligned} CH_2=CH_2 &\xrightarrow[Pt \text{ or } Pd]{H_2, \text{ pressure}} CH_3-CH_3 \\ R-C\equiv C-R &\xrightarrow[Pt / CaCO_3]{H_2} R-CH=CH-R \text{ (cis-addition)} \\ R-C(=O)-Cl &\xrightarrow[Pt / H_2SO_4]{H_2} R-CH_2-H + HCl \text{ (Rosemund Reaction)} \\ CH_3-CH_2-CH_2-Cl &\xrightarrow[Pt]{H_2} CH_3-CH_2-CH_3 + HCl \\ R-C(=O)-H &\xrightarrow[NH_3, 150^\circ C]{H_2 / Rh, Ni, \text{ pressure}} R-CH_2-NH_2 \end{aligned}$$

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### Examples of Reduction using Metal / Acid System

- It is used Zn, Fe, Sn / HCl, H<sub>2</sub>SO<sub>4</sub> and SnCl<sub>2</sub>, FeSO<sub>4</sub>. When metal is treated with acid, the hydrogen gas is formed on the rise.

$$\begin{aligned} Ar-NO_2 &\xrightarrow{Zn / HCl} Ar-NH_2 \\ Ar-C(=O)-R &\xrightarrow[HCl, \text{ heat}]{Zn-Hg} Ar-CH_2-R \\ R-C(=O)-H &\xrightarrow[\text{conc. HCl, heat}]{Zn-Hg} R-CH_3 \end{aligned}$$

- Zn also reduces in aqueous and alcoholic medium.

$$I-CH_2-CH_2-I \xrightarrow[\text{alcohol}]{Zn} CH_2=CH_2$$

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### Haloform Reaction

- The halogenation of the α-C atom of many ketone compounds can be carried out in the form of total halogenation in a basic medium. So methyl ketones [CH<sub>3</sub>-CO-] contain three halogen atoms in α-C and are formed trihalomethyl ketones.

$$R-C(=O)-CH_3 + X_2 \xrightarrow{\text{basic}} R-COO^- + CHX_3$$

- The haloform reaction takes place via the hypohalogenide derivative of halogens in basic medium.

$$\begin{aligned} X_2 + 2NaOH &\longrightarrow Na^+OX^- + Na^+X^- + H_2O \text{ (hypohalogenite)} \\ Na^+OX^- &\xrightarrow[H_2O]{\text{ketone}} HOX + NaOH \text{ (Hypohalogenous Acid)} \end{aligned}$$

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