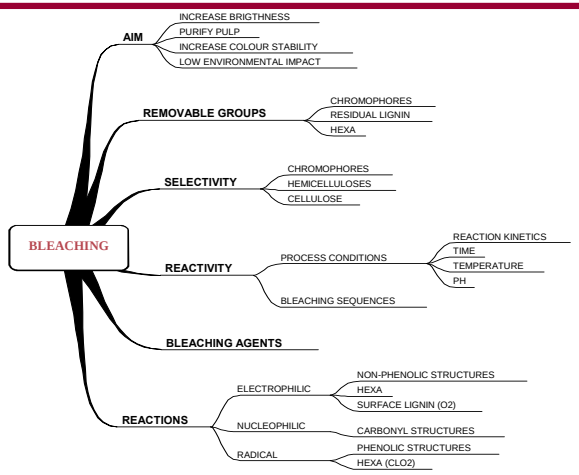
Bleaching chemicals

Lecture 10

Outline



Bleaching agents

Designation	Bleaching agent	Formula
C	Chlorine	Cl_2
O	Oxygen	O_2 (HO^-, HOO^-)
D	Chlorine dioxide	ClO_2 (Cl_2, HOCl, ClO^-)
Z	Ozone	O_3 (H_2O_2)
P	Peroxide	HO_2^- (HO^-)
Paa	Peracetic acid	AcOOH
E	Alkali (extraction)	HO^-
X	Enzyme	xylanase
A	Acid	H_3O^+
Q	Chelant	EDTA, DTPA

peracetic acid = peretikkahappo; chelate = kelaatti

Classification of bleaching agents

RADICALS	ELECTROPHILES	NUCLEOPHILES
O_2	Cl_2	HO_2^- (H_2O_2)
ClO_2	HOCl	ClO^-
	O_3	Peroxyacids
	Peroxyacids	

Reactions involve a transfer of an unpaired electron (i.e radical) and these radicals are oxidants

Reactions involve a transfer of a pair of electrons
- electrophiles accept a pair of electrons (oxidants)
- nucleophiles donate a pair of electrons (reductants)

Electrophiles

- According to IUPAC *"an electrophile is a reagent that forms a bond to its reaction partner by accepting both bonding electrons from that reaction partner"*
- Main electrophilic bleaching agents are
  - chlorine (Cl_2), hypochlorous acid (HOCl), peracetic acid (HOOAc) and ozone (O_3)

hypochlorous acid = alikloorihapoke

Electrophiles

- Electrophilic bleaching agents react with all unsaturated structures:
  - Phenolic
  - Non-phenolic

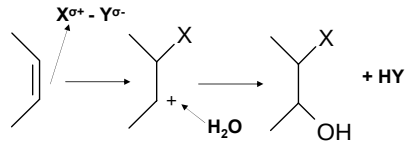
  } lignin structures
  - Hexenuronic acid groups
  - Extractives

Reactivity of electrophilic bleaching agents

Reactivity

Compound	Charge distribution	Leaving group	Acid
O_3	$^{+}O\text{-}O\text{-}O^{-}$		
Cl_2	$Cl^{\delta+}\text{-}Cl^{\delta-}$	Cl^-	HCl
HOCl	$HO^{\delta+}\text{-}Cl^{\delta-}$	Cl^-	HCl
$HOOMoO_3^-$	$HO^{\delta+}\text{-}^{\delta-}OMoO_3^-$	MoO_4^{2-}	$HMoO_4^-$
$HOOSO_3^-$	$HO^{\delta+}\text{-}^{\delta-}OSO_3^-$	SO_4^{2-}	HSO_4^-
HOOAc	$HO^{\delta+}\text{-}^{\delta-}OAc$	AcO^-	AcOH

Basic reaction mechanism of Cl_2, HOCl and peroxyacids

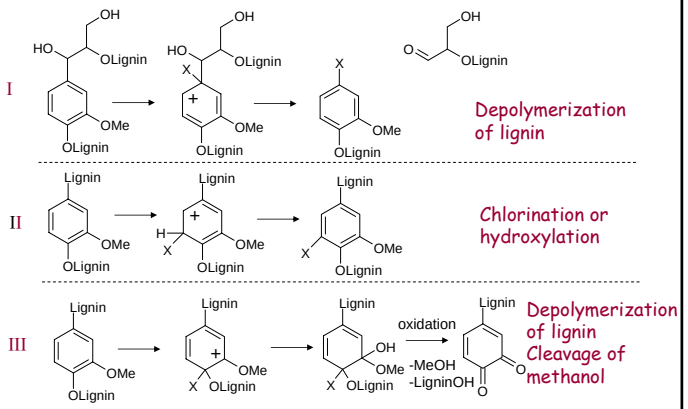


- X is a electrophilic part
  - Cl (Cl_2) or HO (AcOOH and HOCl)
- Y is a leaving group
  - Cl (Cl_2 and HOCl) or AcO (AcOOH)
- HCl is a stronger acid than AcOH

➡ HOCl is a better electrophile than AcOOH

➡ Affects bleaching conditions (temperature and time)

Reactions of electrophiles (Cl_2, HOCl and peroxyacids) and non-phenolic lignin structures

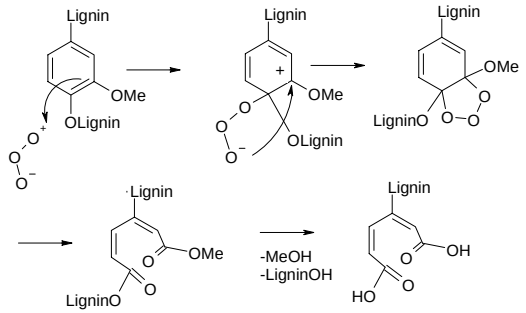


Reactions of electrophiles (O_3) and unsaturad structures

- Formation of a otsonide, which is a *nucleophile*
- Reactions of ozone are controlled by diffusion

  ➡ reactions are fast
- Depolymerization of lignin happens via hydrolysis of ester

Reactions of electrophiles (O_3) and unsaturad structures



Nucleophiles

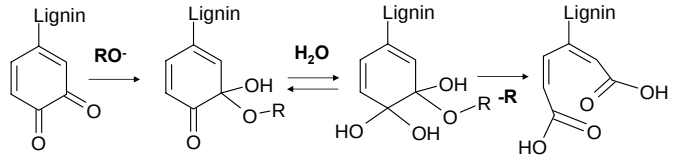
- According to IUPAC *"a nucleophile is a reagent that forms a bond to its reaction partner by donating both bonding electrons"*
- Nucleophilic group of nucleophilic bleaching agents is oxygen atom
- Nucleophiles react with carbonyl structures of chromophores, such as quinones and stilbene quinones (selective reaction)

Reactivity of nucleophilic bleaching agents

Bleaching agent		Leaving group
Hypochlorite	ClO^-	Cl^-
Peroxyacids	$HOOSO_3^-$	SO_4^-
	$HOOMoO_3^-$	MoO_4^-
	HOOAc	AcO^-
Hydrogen peroxide	H_2O_2	HO^-

Reactivity

Reactions of nucleophilic bleaching agents



- two-step nucleophilic reaction with conjugated carbonyl structures
  - Step 1: nucleophilic addition
  - Step 2: cleavage of a leaving group
  - R is the leaving group (Cl^-, SO_4^-, MoO_4^-, AcO^- or HO^-)

Radicals

- IUPAC: ”a radical is a molecule possessing an unpaired electron”
- Radical bleaching agents:

  Chlorine dioxide, ClO_2 (O=Cl-O·)

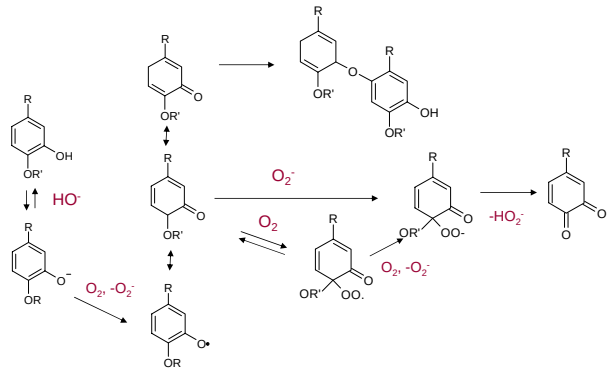
  Oxygen, O_2 (·O-O·)

  Reactivity
- Radical bleaching agents react mainly with *phenolic lignin* structures
  - ClO_2 also reacts with HexA

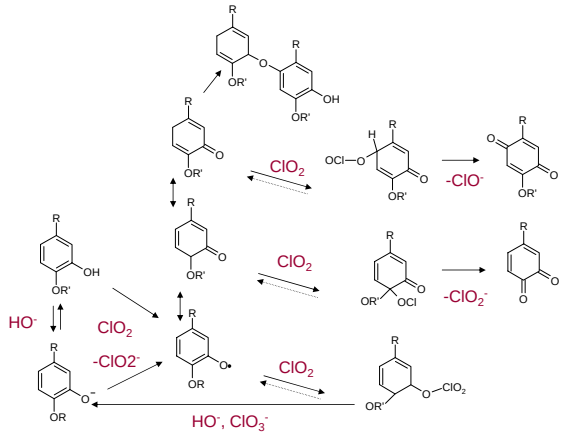
Radicals

- New radicals are also formed during bleaching
  - Oxygen delignification
    - hydroxy (OH·) and peroxy (HO_2·) radicals
  - ClO_2 bleaching
    - Cl· radicals
- Cl· and OH· radicals are very reactive
  - reactions with lignin and carbohydrate structures
    - oxidation and depolymerization of cellulose chains

Reaction mechanism, O_2



Reaction mechanism, ClO_2



Auxiliary bleaching chemicals

Chemical	Function
ACID	Acid hydrolysis of HexA
ALKALI	Solubilize lignin residue after acid stage
CHELANT	Removal of transition metals (Cu, Fe, Mn) which degrade peroxides
XYLANASE ENZYME	Degradation of LC complexes on the surface of fibres

Bleaching sequences

- A single bleaching treatment or stage is not sufficient to remove all chromophores from pulp
  ⇒ bleaching sequence
- Order and type of bleaching stages has an effect on
  - consumption of bleaching chemicals
  - amount of organic material dissolved during bleaching

Some examples of bleaching sequences for kraft pulps

- Conventional sequences
  - C_D-EO-D-E-D
  - C-E-D-EP-D
- Elemental Chlorine Free (ECF)
  - O-D-E_O-D-E-D
  - D-E_O-D-E-D
- Total Chlorine Free (TCF)
  - O-A-Z-Q/P-Paa

Bleaching sequences

- Which one of these bleaching sequences is better and why?

a) O – A – Z – Q/P – Paa

b) O – Z – A – Q/P – Paa