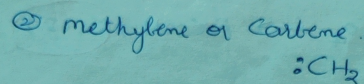


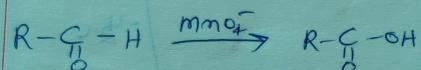
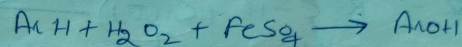
Radicals:

* When a substance has two unpaired electrons per molecule it is called a biradical.



⑤ oxidation of aldehydes to carboxylic acids: - Terry March 701

[Hydrogen Peroxide and ferrous sulfate = Fenton's reagent]



* Oxidation of aldehydes to carboxylic acids is one of the most common oxidation rxn.

* Many oxidizing agents are used - ① Permanganate in acid, basic or neutral soln

② Chromic acid.

③ Bromine.

④ Silver oxide is specific oxidizing agent for aldehydes.

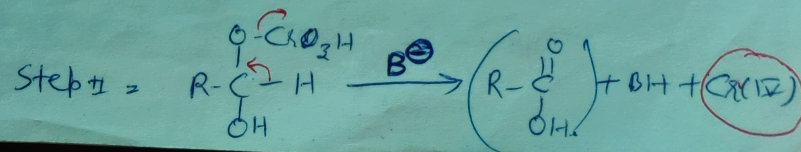
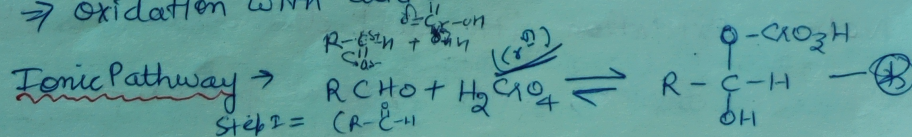
Mechanism: mechanism of aldehyde oxidation is not firmly established.

⇒ but it seems to be ~~by~~ at least two types.

① a free-radical mechanism

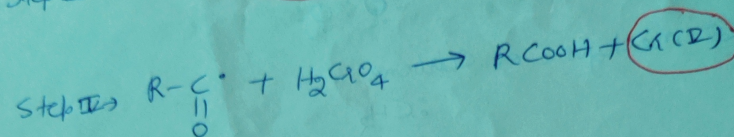
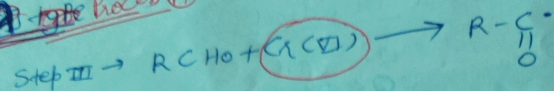
② an ionic mechanism

⇒ oxidation with acid dichromate -

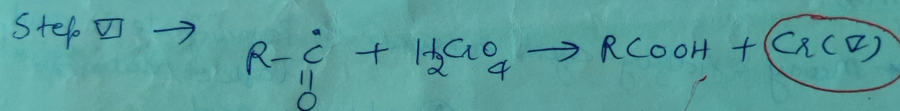
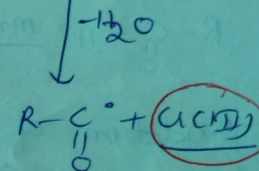
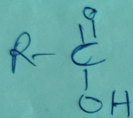
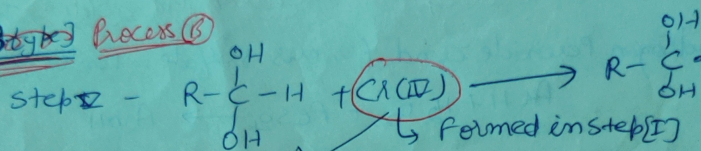


Free radical pathway -

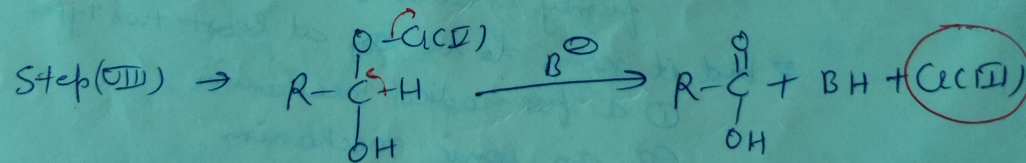
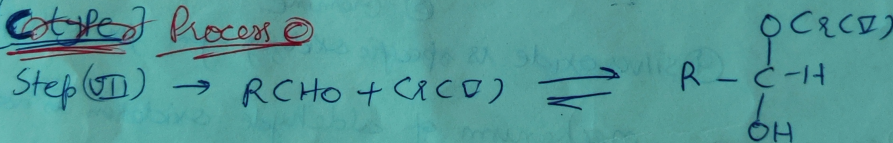
[A] type process (I)



[B] type process (II)



[C] type process (III)

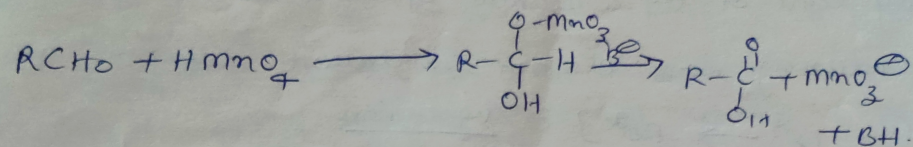


Note → Oxidation with acid dichromate is quite complex, with several processes of both types going on.

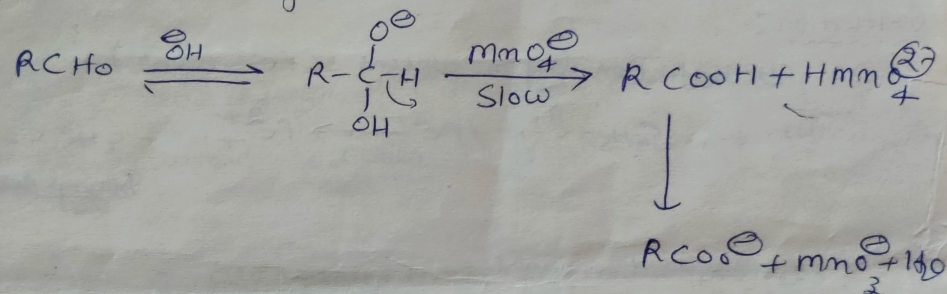
Mechanism with Permanganate →

→ less well known

⇒ Ionic mechanism has been proposed for neutral and acid Permanganate



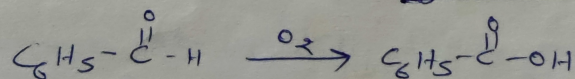
⇒ For alkaline Permanganate



⑥ autooxidation :- O.P. aglawall Page 396

definition :- Slow oxidation of organic substances by atmospheric oxygen is termed as autooxidation. [C-H to C-O-O-H]

Example of autooxidation → Conversion of benzaldehyde to benzoic acid. Ⓟ

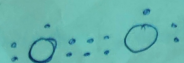


Note :- ① Benzylic, allylic and tertiary position are, most susceptible to oxidation.

② The oxidation of isopropylbenzene (Cumene) is carried out on an industrial scale and the end product are acetone and Phenol.

③ .

Mechanism of Autooxidation of benzaldehyde is catalyzed by H_2O_2



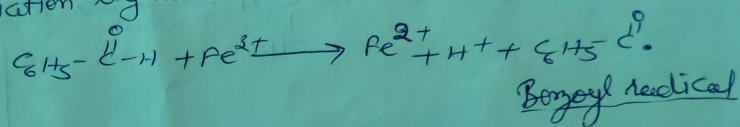
$$\begin{array}{r} 0-1s^2 \quad 2s^2 \quad 2p^6 \\ \hline 6e^- \\ \text{total} = 12e^- \end{array}$$

* Last oxidation

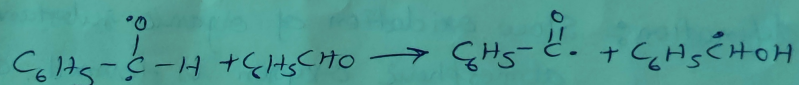
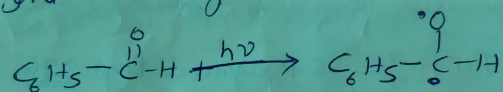
by light or by a number of metal ions capable of undergoing one electron oxidation-reduction transition (e.g. $Fe^{3+} \rightarrow Fe^{2+}$) or by radical.

Initiation:-

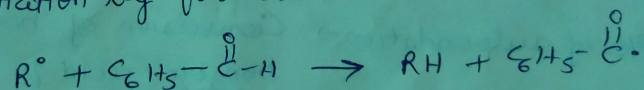
(1) Initiation by metal ions (Fe^{3+} or Co^{3+}) -



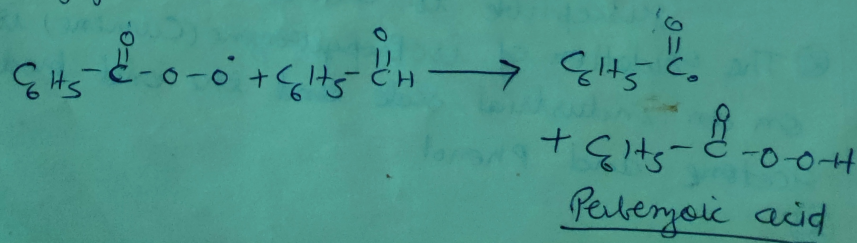
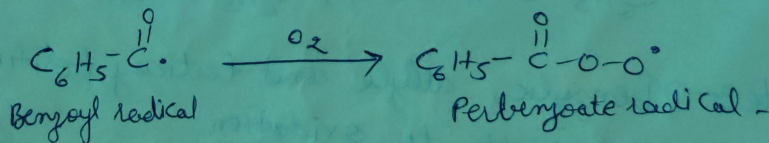
(2) Initiation light -



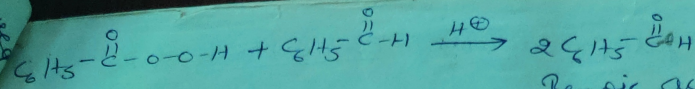
(3) Initiation by free-radicals $\rightarrow$



Propagation:-



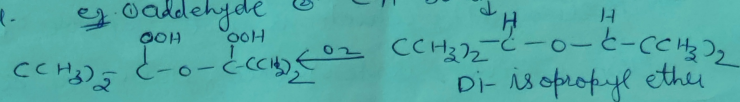
52
62
128



Benzoic acid

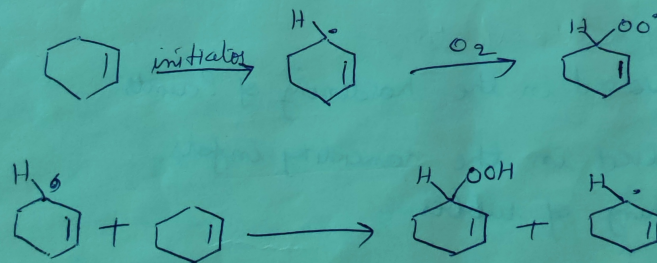
* Last rxn is ~~acc~~ catalysed by hydrogen ions, the oxidation is accelerated as the amount of benzoic acid formed increases.

* autooxidation at ordinary temp only facilitated with reactive C-H bond. eg. aldehyde @ C-H bond next to ether oxygen

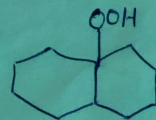


* Allylic, and benzylic C-H bonds are slightly weak. and the resultant radicals are stabilized by delocalization.

Mechanism of autooxidation of cyclohexene:-



* On simple alkanes, only tertiary C-H bond undergoes autooxidation eg. decalin forms hydroperoxide.



* The rate of autooxidation of organic substances is