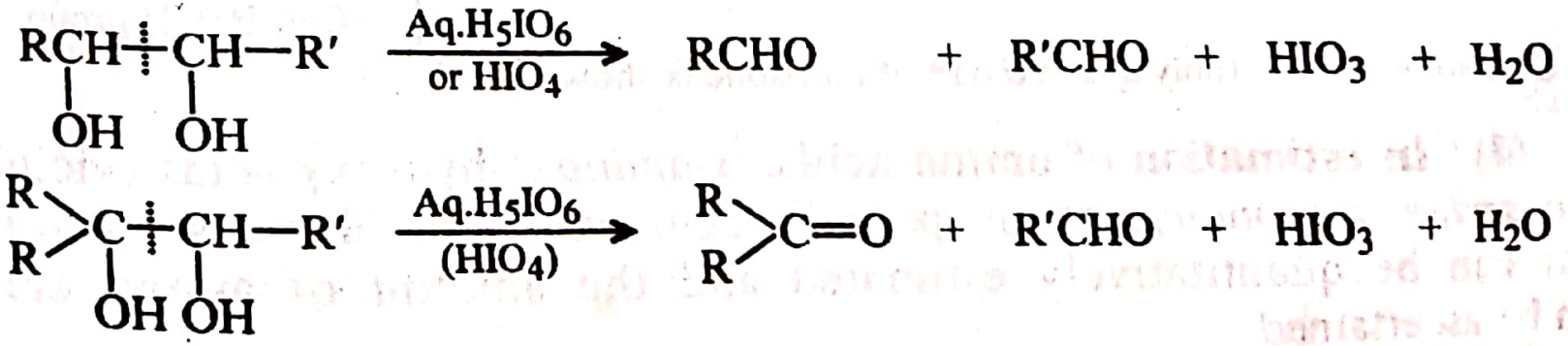
11. PERIODIC ACID, H_5IO_6 or $HIO_4.2H_2O$.

Preparation. It is prepared by treating an aqueous solution of perchloric acid with *iodine*.

$$2HClO_4 + I_2 \longrightarrow 2HIO_4 + Cl_2$$

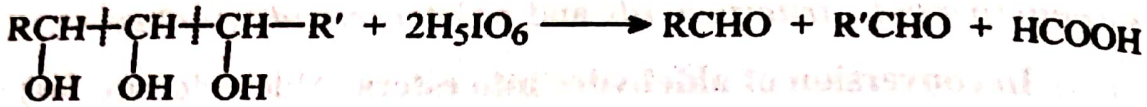
Applications. It finds use in organic chemistry because of its selective oxidative cleavage of *vic*-diols, α-amino alcohols, α-hydroxy carbonyl and 1,2-dicarbonyl compounds. Some of its main applications are described below.

(1) In oxidation of *vic*-diols to carbonyl compounds. For example,

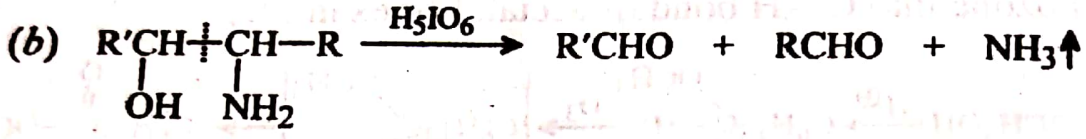


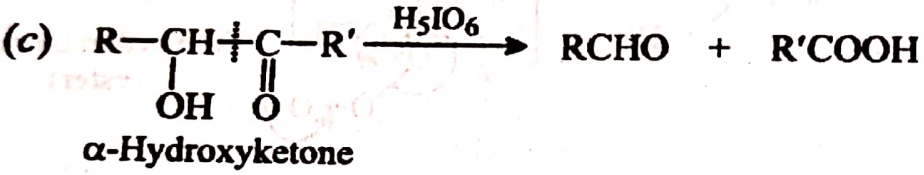
(2) Oxidation of *vic*-triols, α-hydroxyamines, α-hydroxy ketones and 1,2–dicarbonyl compounds.

(a) If *three adjacent —OH groups are present,* the *middle –OH group containing carbon always gets oxidised to formic acid.* For example,

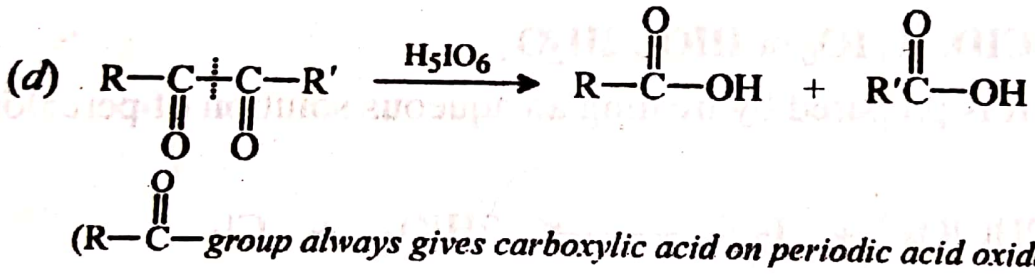


(If, the terminal R=H, it will always give formaldehyde)



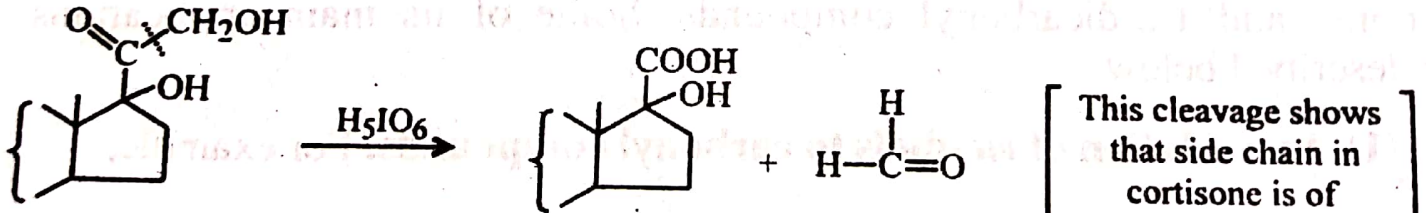


α-Hydroxyketone



(R—C(=O)—*group always gives carboxylic acid on periodic acid oxidation*)

(3) For ascertaining the side chains of steroids. Reichstein used periodic acid for ascertaining the side chain of *adrenal* cortical, steroid, *cortisone.*



Cortisone (only *affected* part of cortisone is shown here)

This cleavage shows that side chain in cortisone is of $-COCH_2OH$ group

(4) In estimation of amino acids. α-*amino*-β-hydroxy acids (vicinal) like *serine, threonine, etc.* on periodic acid oxidation liberates ammonia that can be quantitatively estimated and the amount of amino acids can be ascertained.

$$RCH(OH)CH(NH_2)COOH \xrightarrow{H_5IO_6} RCHO + NH_3 + OHC{-}COOH$$

If **R** = H (*serine*), **R** = CH_3 (*Threonine*)

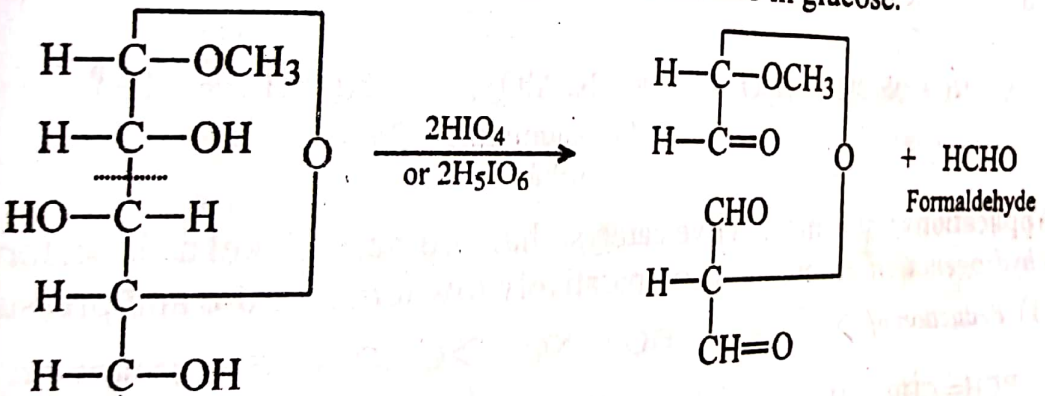
(5) In Carbohydrate Chemistry. Periodic acid is mainly used in carbohydrate chemistry for the following purposes.

(*a*) In indentification of aldoses and ketoses. For example, *D-Glucose* (an *aldohexose*) is cleaved by 5 moles of H_5IO_6 to give *5 moles* of formic acid whereas fructose (a ketohexose) uses *4 moles* of H_5IO_6 to give 3 moles of formic acid on *oxidation*. From this we can ascertain their structure as :

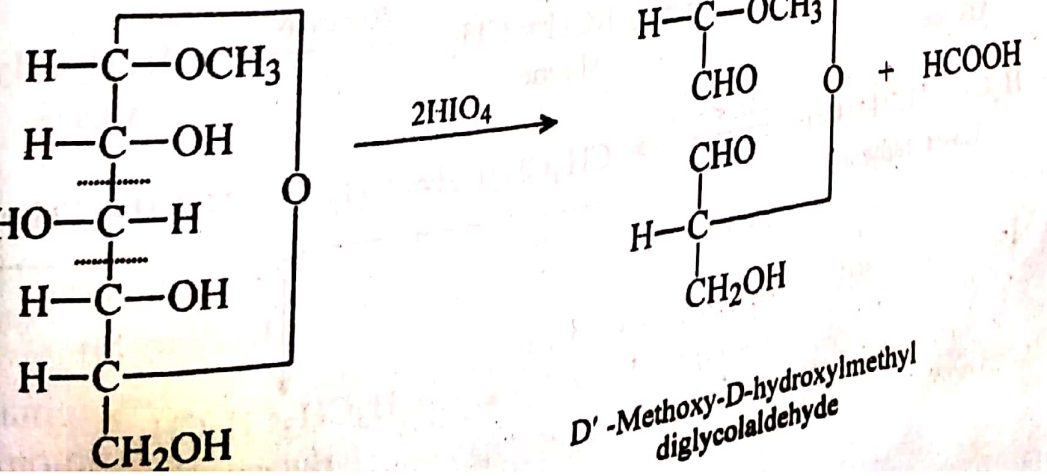
$$\underset{\text{D-Glucose}}{OHC(CHOH)_4CH_2OH} + 5H_5IO_6 \xrightarrow{\text{Periodic acid}} \underset{\text{Formic acid}}{5HCOOH} + HCHO$$

$$\underset{\text{Fructose}}{HOCH_2CO(CHOH)_3{-}CH_2OH} + 4H_5IO_6 \longrightarrow \underset{\text{Formic acid}}{3HCOOH} + \underset{\text{Glycollic acid}}{HOCH_2COOH} + HCHO$$

(*b*) In determination of the size to the ring in hexoses. For example, when methyl α-*D-glucofuranoside* is oxidised by two molecule of H_5IO_6 one molecule of formaldehyde is formed. These results suggest the presence of *five membered ring in* α-*D-gluco furanoside* (as shown below). Whereas a normal methyl α-*D-glucoside* consumes two molecules of HIO_4 and forms 1 molecule of *formic acid* and *D'- methoxy-D-hydroxymethyl diglycolaldehyde*, as the oxide ring is stable to resist opening by this reagent. This confirms the presence of **six membered** pyranose structure in glucose.



Methyl α-D-Glucofuranoside



D' -Methoxy-D-hydroxylmethyl diglycolaldehyde

(c) This oxidation method can also be used for strcutural elucidation of cane sugar in the same manner.

***(6)* In structural determination of Chloromycetin.** Chloromycetin on hydrolysis gives a base which when oxidised with periodic acid give one molecule of each NH_3, HCHO and *p*-nitrobenzaldehyde.

These results establish the structure of chloromycetin as