Br- catalysed oxidation of D-Arabinose by one electron oxidant in aqueous sulphuric acid medium. –A kinetic study

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Abstract: *Kinetic study of oxidation of D-Arabinose has been investigated in presence of bromide catalyst in aq. Sulphuric acid medium at constant ionic strength. The reaction is of first order each in D-Arabinose and [Ce(4)]. The rate of reaction decreases on increasing the concentration of H+ ion. The sulphate and bisulphate ions show retarding effects on the reaction rate at constant ionic strength. The bromide ion exihibits the +ve catalytic effects on the reaction rate. The value of activation energy has been calculated and a suitable mechanism conforming to the kinetic data proposed.*

I.   Introduction :-

CERIC SULPHATE, FERRICYANIDE DICHROMATE& VANADIUM-*V* etc. have been used as oxiding agents in acid medium. Ceric oxidation of oxalic acid, dextrose, fructose and L- sorbose have been studied earlier. The present study deals with the kinetics and mechanism of bromide catalysed oxidation of D-arabinose by Ce4 in aq sulphuric acid solution.

II.   Experimental:-

All the chemicals used in this work were of analytical reagent grade. A stock of standard solution of sodium thiosulphate solution prepared in 2N H_2SO_4 and the prepared solution was standardised iodometrically against standard using starch as indicator. The kinetics was being followed by removing 5ml aliquot from the reaction mixture at different intervals and the reaction was arrested by adding 10 ml of 5% KI solution; the liberated iodine which is equivalent to the concentration of unreacted ce(iv) was determined by the titration with standard solution of sodium thiosulphate. The stoichiometry of the reaction was determined by estimating the ce^4 disappearance by titiometry and substrate disappearance by measuring the volume of carbondioxide formed, which was confirmed by lime water test. The stoichiometry thus determined was found to be 2 mols of ce^4 to one mole of D-Arabinose, thus the overall stoichiometric equation could be written as

$C_5 H_{10} O_5 + 20Ce^{4+} + Br^- + H_2O ---- 6co_2 + 20\ ce^{3+} + Br^- + 20\ H^+$
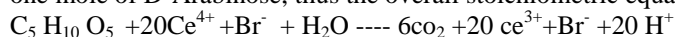
III.   Results & Discussion :-

Under the discussion [D-Arabinose]$<<$[ce^4] when –dc/dt values are plotted against ce^4 a straight line is obtained which passes through the origin showing that the reaction is of first order with respect to ce^4 fig 1(A) The reaction was observed to so linear relationship between –dc/dt and [d- Arabinose] indicating thus first order with respect to the substrate. Fig1(B)

Fig1(A) (B)

Fig1(A) Plot of(–dc/dt)vs(ce^4) at 37^0 [D-Arabinose]=12.5X10^{-3}M   [Br^-]=5.0X10^{-3}M H_2SO_4=5.0x10^{-1}M;μ =1.685

Fig 1(B) Plot of (-dc/dt) vs[D-Arabinose] at 37^0 c [Ce^{4+}]=2.5x10^{-3}M μ=1.55 [Br^-]= 5.0x10^{-3}M H_2SO_4= 5.0x10^{-1} M

EFFECT OF HYDROGEN AND BROMIDE ION:-

The rate of reaction decreases on increasing the increasing the concentration of sulphuric acid (Fig2A)due to the conversion of unreactive species $Ce(SO_4)^{2+}$ as described in the equation.

$Ce(SO_4)_2 + H^+ = Ce(SO_4)^{2+} + HSO_4^-$ ----------- (1)
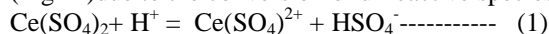
The addition of potassium bromide shows +ve catalytic effect of bromide ions on reaction rate. The rate of reaction on increasing the concentration of [Br^-]. Fig 3A.

EFFECT OF BISULPHATE AND SULPHATE ION :-

Sulphate being used as a better ligand can combine with Ce^4 to a varying degree forming various species. Several   investigations reported that in H_2SO_4 medium. Ceric sulphate exists mainly as $Ce(SO_4)^{2+}$ $Ce(SO_4)_3^{2-}$ &$Ce(SO_4)^4_4$ depending upon the concentration of sulphate from the [SO_4^{2-}] on the rate it was

concluded that neutral $Ce(SO_4)_2$ is the reactive species. The inhibitory action of HSO_4^- (Fig 2B) and $[SO_4^{2-}]$ Fig 3B is due to conversion of reactive form of $(CeSO_4)^{2-}$ and $(CeSO_4)^{4-}$

EFFECT OF TEMPERATURE:-

The reaction has been studied at different temperature and the activation parameters has been evaluated in the temperature range 35^0-50^0c. The values of δ E & δ S ^{0} were found to be 105.75 kJmol^{-1} And -111.85 JK^{-1} mol^{-1} respectively. The fairly high –ve values of δ s* suggests the formation of more ordered activated complex.

MECHANISM:-

On the basis of the results following mechanism may be proposed in order to explain the mechanistic path of oxidation of D- Arabinose.
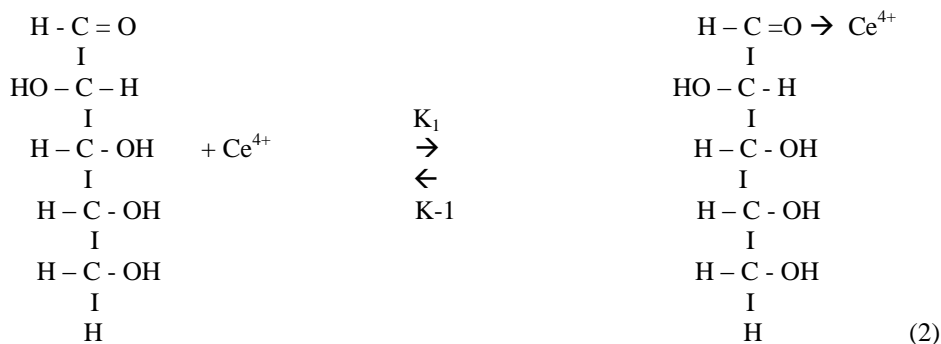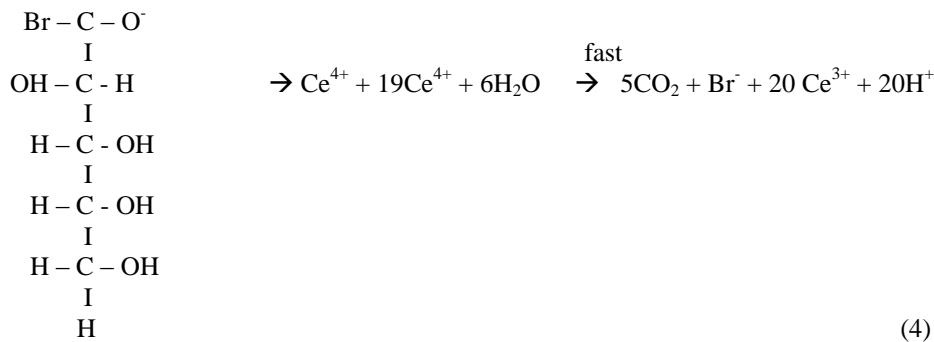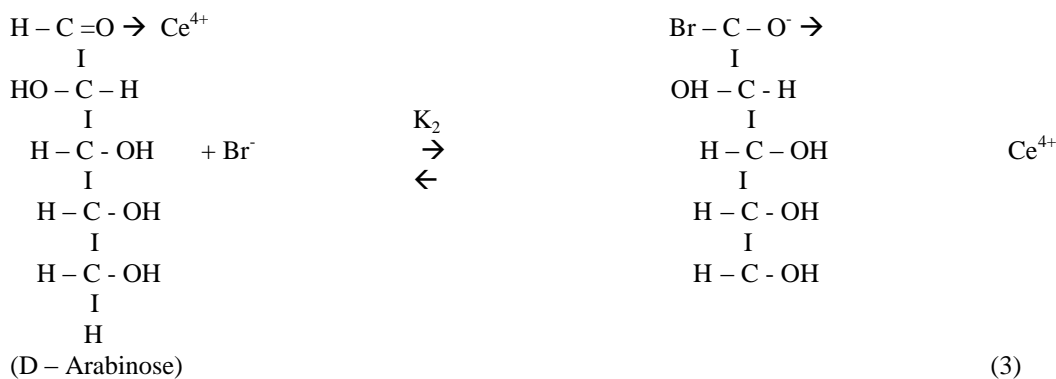
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  H - C = O                                    H – C =O → Ce⁴⁺
      I                                            I
  HO – C – H                                   HO – C - H
      I                    K₁                      I
   H – C - OH    + Ce⁴⁺     →                   H – C - OH
      I                     ←                      I
   H – C - OH              K-1                  H – C - OH
      I                                            I
   H – C - OH                                   H – C - OH
      I                                            I
      H                                            H           (2)
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Fig3(A) Plot of(–dc/dt) vs [KBr] at 37^0c [D- Arabinose] = 3.125×10^{-3}M [Ce^{4+}]=2.50×10^{-3}M [H$_2$SO$_4$]= 5.1×10^{-1}M μ =1.56
Fig 3(B) Plot of(-dc/dt) vs [K$_2$SO$_4$] at 37^0C [KBr]= 5.0×10^{-3}M; [D-Arabinose]=12.5×10^{-3} M [H$_2$SO$_4$]= 5.0×10^{-1}M μ =2.225

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  H – C =O → Ce⁴⁺                              Br – C – O⁻ →
      I                                            I
  HO – C – H                                   OH – C - H
      I                    K₂                      I
   H – C - OH    + Br⁻      →                    H – C – OH              Ce⁴⁺
      I                     ←                      I
   H – C - OH                                   H – C - OH
      I                                            I
   H – C - OH                                   H – C - OH
      I
      H
(D – Arabinose)                                                          (3)
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  Br – C – O⁻
      I                                    fast
 OH – C - H          → Ce⁴⁺ + 19Ce⁴⁺ + 6H₂O  →   5CO₂ + Br⁻ + 20 Ce³⁺ + 20H⁺
      I
   H – C - OH
      I
   H – C - OH
      I
   H – C – OH
      I
      H                                                              (4)
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The rate law is derived on the basis of above mechanism which is as follows.
d [R]/dt =K$_1$ [S] [Ce^{4+}]------------- k$_{-1}$[R] - k$_2$[Br$^-$]----------(5)
Now at steady state
K$_1$ [S] [Ce^{4+}] =[R] [K$_{-1}$+ K$_2$(Br$^-$)]
[R] = K$_1$[S][Ce^{4+}]/k$_{-1}$+k$_2$[Br$^-$]------------------------------ (6)

Now at steady conditions the rate of disappearance of Ce^{4+} may be given by

$-d[Ce^{4+}]/dt = k_2[R][Br^-]$--------------------------------------(7)

Substituting the value of (6) into (7)

$-d[Ce^{4+}]/dt = k_1k_2[S][Br^-][Ce^{4+}]/K-1 +K_2[Br^-]$

Or $-d[Ce^{4+}]/dt = (k_1[S][Br^-][Ce^{4+}])/(k-1/k2) +[Br^-]$------------(8)

Since $k_2 >> k_{-1}$ and hence k_{-1}/k_2 can be neglected.

Thus equation (8) assumes the form.

$-(d[Ce^{4+}]/dt) = k_1[S][Ce^{4+}]$--(9)

Where S & R represents the D- Arabinose & radicals respectively.

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