

Oxidation of Xylitol, Gullitol and Tallitol in aqueous alkaline medium by Hexacyanoferrate(III) ion: A kinetic and mechanistic study.

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Abstract: The rate of oxidation of xylitol, gullitol and tallitol were studied. It appears that the rates were found to be directly proportional to the substrate and hydroxide ion concentrations. The dependance of the rate of reaction on oxidant concentration were nearly seems to be first order of lower concentration and tends towards zero order at higher concentration. The results corroborates the previous observation. A probable mechanism has been suggested for the overall reaction.

A very little study has been made on the mechanism of oxidation of polyhydroxy alcohols in alkaline medium. A limited work on alkaline permanganate¹⁻³ is available. The kinetic data suggests that the oxidation involves the formation of a complex between the amount of substrate and $[KFe(CN)_6]^{2-}$. The complex gets disproportionate into the free radical and $[KFe(CN)_6]^{3-}$ ion²⁻⁴. Extending the information concerning the oxidation kinetics of polyhydroxyalcohol in aqueous alkaline medium. It is here by reported the kinetics of oxidation of xylitol, gullitol and tallitol with hexacyanoferrate(III)ion in aqueous alkaline medium.

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I. Results and Discussion:

Oxidation of xylitol, gullitol and tallitol were carried out in aqueous alkaline medium of constant ionic strength of the medium & temperature.

The reaction follows nearly first order kinetics at lower concentration of hexacyanoferrate(III) ion approaching towards zero order at its higher concentration(Fig.1). The concentration of hexacyanoferrate ion variations for xylitol, gullitol & tallitol was 2.0×10^{-3} to 10.0×10^{-3} M, 1.0×10^{-3} to 8.0×10^{-3} M and 1.0×10^{-3} to 10.0×10^{-3} M.

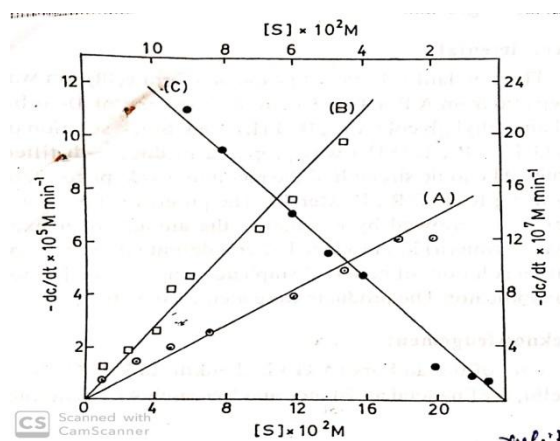


Fig. I Effect of $K_3 [Fe(CN)_6]$ on the reacton rate (A) xylitol 8.0×10^{-2} M $[NaOH]=0.6$ M, $\mu=0.8$ M at $30^\circ C$ (B) [gullitol] = $8. \times 10^{-2}$ M, $[NaOH]$ = 0.5 M, $\mu=0.8$ M at $30^\circ C$ and (C) [tallitol] = 5.0×10^{-2} N, $[NaOH]$ 0.3 M, $\mu=1.0$ M.

The graphical representation in Fig.2 and 3 confirms the 1st order kinetics with respect to substrate as well as hydroxide ion concentration respectively the substrate concentration was 0.4×10^{-2} to 8.5×10^{-2} M for xylitol, Similarly 1.5×10^{-2} to 18×10^{-2} M for zullitol and 1.5×10^{-2} to 16×10^{-2} M for tallitol. The

hydroxide ion concentration was varied from 0.5×10^{-1} to 7.5×10^{-1} M for xyllitol, 1×10^{-1} to 8.5×10^{-1} M for gullitol and 0.8×10^{-1} to 10.5×10^{-1} M for tallitol.

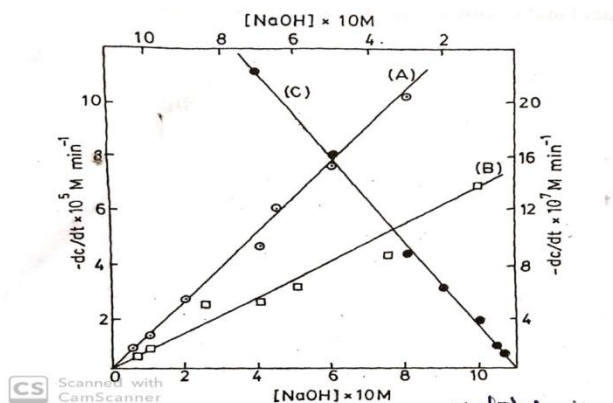


Fig. II Effect of substrate concentration on reaction rate; (xyllitol) $K_3 [Fe(CN)_6] = 2.5 \times 10^{-3}$ M $[NaOH] = 0.5$ M, $\mu = 0.915$ M at $30^\circ C$ (B) [gullitol] $K_3 [Fe(CN)_6] = 3 \times 10^{-3}$ M, $[NaOH] = 0.5$ M, $\mu = 0.8$ M at $30^\circ C$ and (C) [tallitol] $K_3 [Fe(CN)_6] = 3.0 \times 10^{-3}$ M, $[NaOH] = 0.5$ M, $\mu = 1.0$ M at $25^\circ C$

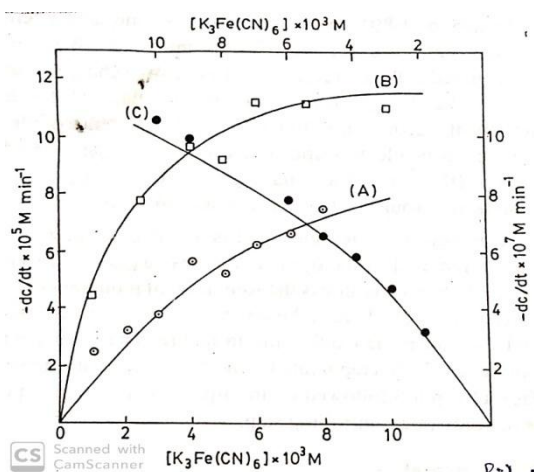


Fig. III Effect of OH^- concentration on reaction rate; A (xyllitol) $= 1.0 \times 10^{-3}$ M $K_3 [Fe(CN)_6] = 5.0 \times 10^{-3}$ M, $\mu = 1.05$ M at $30^\circ C$ (B) [gullitol] $K_3 [Fe(CN)_6] = 3.0 \times 10^{-3}$ M, $\mu = 1.02$ M at $30^\circ C$ and (C) [tallitol] $K_3 [Fe(CN)_6] = 3.0 \times 10^{-2}$ M, $\mu = 1.0$ M at $25^\circ C$

II. Mechanism:

Keeping in view all the observation at low of reactants, the following rate expression may hold good.

$$-\frac{d[HCF(III)]}{dt} = k[Fe(CN)_6^{3-}][OH][S] \quad \text{-----(1)}$$

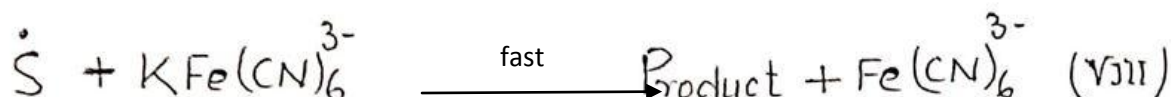
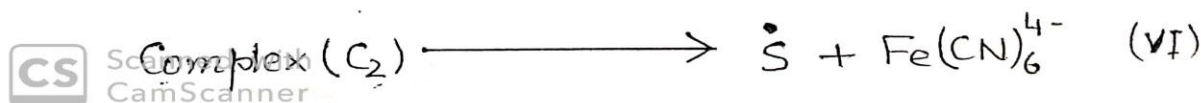
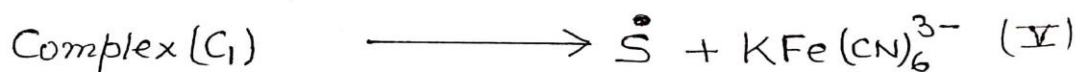
Where k is the rate constant. The k value as observed were found to be 1.2×10^{-2} , 2.05×10^{-2} and $1.95 \times 10^{-2} \text{ mol}^{-2} \text{ dm}^{-6} \text{ s}^{-1}$ for xyllitol, D-zullitol and D-tallitol respectively.

$Fe(CN)_6^{3-}$ ion is used as an oxidant at aqueous alkaline medium at presence of KCl. The equilibrium set up is



The equilibrium lies towards right as reported³

Therefore considering $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{2-}$ ion as oxidants, the following mechanism may hold good.



Scheme-I

In this scheme complex (C₁) and (C₂) stands for labile complex between substrate anion and $KFe(CN)_6^{2-}$ ion as well as substrate anion and $Fe(CN)_6^{3-}$ ion respectively. The oxidation rate were found to be dependent upon the concentration of the species hexacyanoferrate(III)ion. From equation 3 and 4 the rate of disappearance of hexacyanoferrate(III)ion given by following equation.

$$-\frac{d[HCF]}{dt} = k_2 [\bar{S}] [KFe(CN)_6^{2-}] + k_2 [\bar{S}] [Fe(CN)_6^{3-}] \quad (2)$$

By assuming total hexacyanoferrate(III)ion concentration as-

$$[Fe(CN)_6^{3-}]_T = [Fe(CN)_6^{3-}] + [KFe(CN)_6^{2-}] \quad (3)$$

Considering the steady state condition in equation (3) the final rate law becomes as in equation (4)

$$-\frac{d[HCF]}{dt} = \frac{2k_1[S][OH^-][HCF]_T\{k_3 + k_2(KK^+)\}}{K_{-1}[1+(KK^+)] + [HCF]_T\{k_3 + k_2(KK^+)\}} \quad (4)$$

The equation (4) so derived were found to be almost consistent with the observed kinetics results. At higher concentration of hexacyanoferrate(III), the value of

$$\frac{1}{R} = \frac{K_{-1}[1+(KK^+)]}{2k_1[S][OH^-][HCF]_T\{k_3 + k_2(KK^+)\}} + \frac{1}{2k_1[S][OH^-]} \quad (5)$$

Where $R = -\frac{d[HCF]}{dt}$

$[HCF]_T k_3 + k_2(KK^+)$ becomes larger than $K_{-1}(1+KK^+)$, therefore the equation becomes

The linear plot of $1/R$ Vs $1/[HCF]_T$ conforms the validity of the rate law equation (5) and it also substantiate the proposed reaction mechanism. The value of K_1 calculated from the intercept of the plot $R \times 10^{-5}$ for xyllitol, 1.5×10^{-3} for D-Gullitol and $2.5 \times 10^{-3} \text{ min}^{-1}$ for D-Tallitol. The final oxidation product were there corresponding acids.



SCHEME-I

$$-\frac{d[HCF]}{dt} = k_2[\dot{S}][KFe(CN)_6^{2-}] + k_2[\dot{S}][Fe(CN)_6^{3-}] \quad (2)$$

$$[Fe(CN)_6^{3-}]_T = [Fe(CN)_6^{3-}] + [KFe(CN)_6^{2-}] \quad (3)$$

$$-\frac{d[HCF]}{dt} = \frac{2k_1[S][OH^-][HCF]_T\{k_3 + k_2(KK^+)\}}{K_{-1}[1+(KK^+)] + [HCF]_T\{k_3 + k_2(KK^+)\}} \quad (4)$$

$$\frac{1}{R} = \frac{K_{-1}[1+(KK^+)]}{2k_1[S][OH^-][HCF]_T\{k_3 + k_2(KK^+)\}} + \frac{1}{2k_1[S][OH^-]} \quad (5)$$

Where $R = -\frac{d[HCF]}{dt}$

The linear plot of $1/R$ vs $1/[HCF]_T$ conforms of validity of rate equation.

III. Experimental:

Standard solution of hexacyanoferrate(III) ion was prepared from A.R (BDH) quality sample xylitol, gullitol and tallitol (A.R.BDH) used. NaOH solution was prepared in double distilled water. Ionic strength maintained by using KCl solution. Reaction progress was followed the estimation of the amount of hexacyanoferrate(IV) ion produced after a definite time interval with a solution of Ce(IV) sulphate using ferroin as a redox indicator. The products were identified by thin layer chromatography.

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