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# Kinetics and Mechanism of Oxidation of Xylitol and Galactitol by Hexacyanoferrate(III) Ion in Aqueous Alkaline Medium

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Kinetics of oxidation of xylitol and galactitol by hexacyanoferrate(III) ion in aqueous alkaline medium is reported. The reaction rate is of first order with respect to hexacyanoferrate(III) in each substrate. The reaction is first order at lower concentrations of xylitol and galactitol and tends towards zero order as the concentration increases. Similarly first order kinetics was obtained with respect to hydroxide ion at lower concentrations and tends to lower order at higher concentration in the oxidation of xylitol; in the oxidation of galactitol the reaction is first order with respect to hydroxide ion even up to manyfold variation. The course of reaction has been considered to proceed through the formation of an activated complex between $[\mathrm{K\,Fe(CN)_6}]^{2-}$ and substrate anion which decomposes slowly into radical and $[\mathrm{K\,Fe(CN)_6}]^{3-}$. A probable reaction mechanism is proposed.

*(Keywords: Galactitol; Kinetics; Mechanism; Oxidation; Reduction; Xylitol)*

## *Kinetik und Mechanismus der Oxidation von Xylit und Galaktit mit Hexacyanoferrat(III) in wäßriger, alkalischer Lösung*

Das Geschwindigkeitsgesetz der Titelreaktion ist in beiden Fällen erster Ordnung bezüglich Hexacyanoferrat(III). Die Oxidation ist erster Ordnung bei niedrigen Konzentrationen von Xylit und Galaktit und geht bei Erhöhung der Konzentration gegen null. In gleicher Weise wurde eine Kinetik erster Ordnung bezüglich Hydroxyl bei niedrigen Konzentrationen und eine erniedrigte Ordnung bei höheren Konzentrationen für die Oxidation von Xylit beobachtet; bei Galaktit bleibt die Oxidation auch bei höheren Hydroxyl-Konzentrationen erster Ordnung. Es wird angenommen, daß die Reaktion über einen aktivierten Komplex zwischen $[\mathrm{KFe(CN)_6}]^{2-}$ und dem Substrat-Anion verläuft; dieser Komplex zerfällt in $[\mathrm{KFe(CN)_6}]^{3-}$ und ein Substrat-Radikal. Ein möglicher Reaktionsmechanismus wird vorgeschlagen.

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## Introduction

Mechanistic studies of reactions in solution have achieved commendable importance during the last few decades. As far as the kinetics of oxidation of polyhydroxy alcohols is concerned, it was less studied in alkaline medium. A limited account of data dealing with alkaline permanganate[1] oxidation of diols is available. Recently a large amount of data has been collected for the oxidation of diols[2,3] during the course of their oxidation by alkaline hexacyanoferrate(III) ion in aqueous alkaline medium. The kinetic data suggest that the oxidation involves the formation of anions of substrate which undergoes oxidation with hexacyanoferrate(III) via the formation of a complex between the anion and the hexacyanoferrate(III) ion. The complex disproportionates into the free radical and $[KFe(CN)_6]^{3-}$ ion[4]. For further information concerning the oxidation kinetics of polyhydroxy alcohols in aqueous alkaline medium, the authors now wish to report the results on the kinetics of oxidation of xylitol and galactitol with hexacyanoferrate(III) in aqueous alkaline medium.

## Results and Discussion

The kinetic measurements for the rate of oxidation of xylitol and galactitol were carried out by alkaline hexacyanoferrate(III) ion. It has been observed that the order of the reaction is unity with respect to hexacyanoferrate(III) even up to ten-fold variation (Fig. 2) which is obvious on plotting ($-\mathrm{d}c/\mathrm{d}t$) against hexacyanoferrate(III) concentration. The values of $-\mathrm{d}c/\mathrm{d}t$ have been calculated from the initial slope of the curve obtained on plotting the remaining hexacyanoferrate(III) concentration against time in order to avoid the possible errors involved due to intervention of the products (Fig. 1). It is clear from Fig. 3 that the reaction rate follows first order kinetics in lower concentration range and tending towards zero order at higher concentration with respect to both substrates. Similar is the result of hydroxide ion variation in the oxidation of xylitol as stated above (Fig. 4). But in the oxidation of galactitol the hydroxide ion concentration shows direct proportionality even up to many-fold variation (Fig. 4). Thus, taking the above observation in view, the general rate expression might be suggested for the oxidation at lower concentrations of reactants as,

$$-\frac{\mathrm{d}[Fey]}{\mathrm{d}t} = k\,[\mathrm{Alditol}]\,[\mathrm{OH}^-]\,\{[\mathrm{Fe(CN)_6}]^{3-}\} \qquad (1)$$

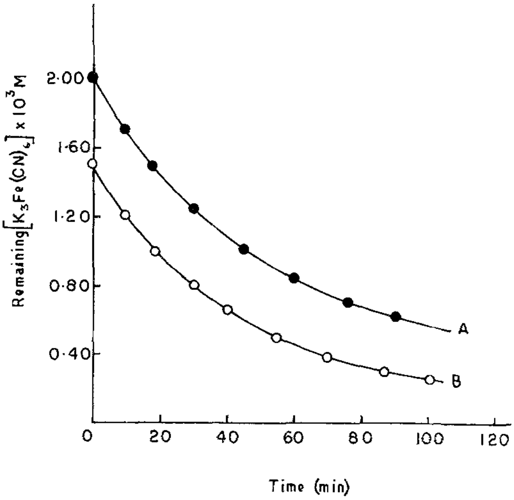

Fig. 1. Effect of hexacyanoferrate(III) in particular runs. *A* Temp. 35 °C, $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$, $[NaOH] = 8.00 \times 10^{-1} M$, $[Xylitol] = 5.00 \times 10^{-1} M$, $\mu = 2.00 M$; *B* Temp. 35 °C, $[K_3Fe(CN)_6] = 1.60 \times 10^{-3} M$, $[NaOH] = 2.00 \times 10^{-1} M$, $[Galactitol] = 4.00 \times 10^{-1} M$, $\mu = 2.00 M$

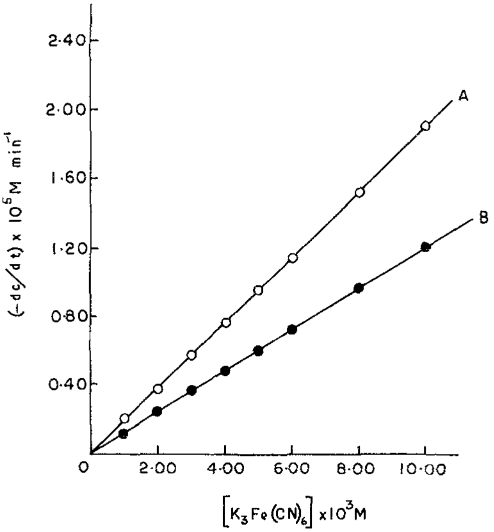

Fig. 2. Effect of hexacyanoferrate(III) variation. *A*: Xylitol: Temp. 35 °C, $[Xylitol] = 5.00 \times 10^{-1} M$, $[NaOH] = 8.00 \times 10^{-1} M$, $\mu = 2.00 M$; *B*: Galactitol: Temp. 35 °C, $[Galactitol] = 4.00 \times 10^{-1} M$, $[NaOH] = 3.00 \times 10^{-1} M$, $\mu = 2.00 M$

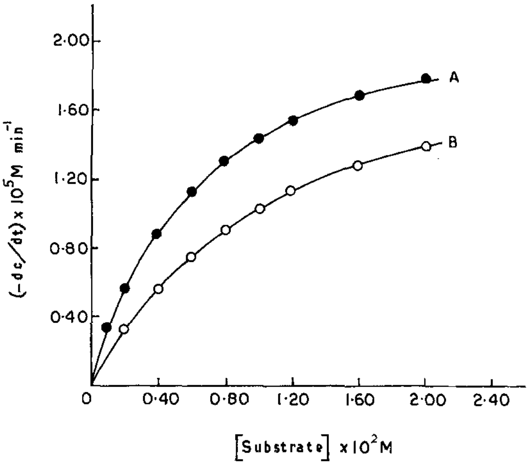

Fig. 3. Effect of substrate variation. *A*: Xylitol: Temp. 35 °C, $[K_3Fe(CN)_6] = 3.00 \times 10^{-3} M$, $[NaOH] = 1.00 M$, $\mu = 2.00 M$; *B*: Galactitol: Temp. 35 °C, $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$, $[NaOH] = 1.00 M$, $\mu = 2.00 M$

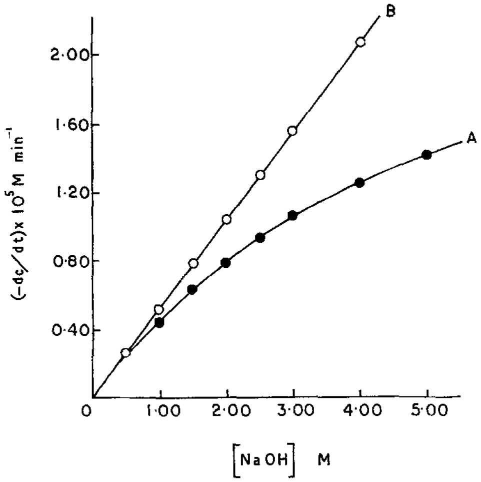

Fig. 4. Effect of hydroxide ion variation. *A*: Xylitol: Temp. 35 °C, $[K_3Fe(CN)_6] = 3.00 \times 10^{-3} M$, $[Xylitol] = 5.00 \times 10^{-1} M$, $\mu = 2.00 M$; *B*: Galactitol: Temp. 35 °C, $[K_3Fe(CN)_6] = 2.00 \times 10^{-3} M$, $[Galactitol] = 4.00 \times 10^{-1} M$, $\mu = 2.00 M$

where $k$ is the rate constant and $Fey$ is hexacyanoferrate(III). The observed "$k$" values were found to be $1.28 \times 10^{-2}\,\mathrm{mol^{-2}\,lit^{2}\,s^{-1}}$ and $1.70 \times 10^{-2}\,\mathrm{mol^{-2}\,lit^{2}\,s^{-1}}$ at 30 °C for xylitol and galactitol respectively.

In order to explain the mechanistic path of alcohol permanganate reaction in alkaline medium it is reported by previous workers[5] that an alkoxide ion is formed due to ionisation of alcohols in presence of alkali.

$$R\mathrm{CH_2OH} + \mathrm{OH^-} \rightarrow R\mathrm{CH_2O^-} + \mathrm{H_2O}$$

In the present case the dependence of the reaction rate on hydroxide ion concentration clearly indicates that it may be involved in the formation of active alkoxide ion. On the basis of above experimental findings, the mechanism proposed for the oxidation of xylitol and galactitol will be as follows

$$\mathrm{K^+} + [\mathrm{Fe(CN)_6}]^{3-} \overset{K}{\rightleftharpoons} [\mathrm{KFe(CN)_6}]^{2-} \tag{I}$$

$$S + \mathrm{OH^-} \overset{K_1}{\rightleftharpoons} S^- + \mathrm{H_2O} \tag{II}$$

$$S^- + [\mathrm{KFe(CN)_6}]^{2-} \underset{\mu_2}{\overset{k_1}{\rightleftharpoons}} C \tag{III}$$

$$C \underset{\text{slow}}{\overset{k}{\rightarrow}} S\cdot + [\mathrm{KFe(CN)_6}]^{3-} \tag{IV}$$

$$S + \mathrm{KFe(CN)_6}^{2-} \underset{\text{fast}}{\overset{k_2}{\rightarrow}} \textit{intermediate products} + \mathrm{KFe(CN)_6}^{3-}$$

where $S$ represents the substrates and $C$ the complex between the substrate anion and the $[\mathrm{KFe(CN)_6}]^{2-}$ ion. It has already been reported by several[4,6] workers that step (1) of the proposed reaction scheme will be mainly towards right.

Now considering steady state condition and the total hexacyanoferrate(III) ion as concentration $[Fey]_T = [\mathrm{Fe(CN)_6}^{3}] + [\mathrm{KFe(CN)_6}^{2-}] + C$. The rate law in terms of decreasing hexacyanoferrate(III) ion concentration would be

$$-\frac{\mathrm{d}[Fey]}{\mathrm{d}t} = \frac{2\,kk_1KK_1[\mathrm{K^+}][S][\mathrm{OH^-}][Fey]_T}{(k + k_{-1})(1 + K_1[\mathrm{K^+}]) + k_1KK_1[\mathrm{K^+}][S][\mathrm{OH^-}]} \tag{2}$$

Equation (2) is apparently consistent with the observed kinetics. It shows the first order kinetics with respect to hexacyanoferrate(III) and also explains the observed complex kinetic feature of the reaction rate with respect to substrate and hydroxide ion concentrations.

Now considering the views of previous workers[7,8], the inequality $K_1[\mathrm{K}^+] \gg 1$ would manifest and the rate law (2) reduces to (3)

$$-\frac{\mathrm{d}[Fey]}{\mathrm{d}t} = \frac{2kk_1K[S][\mathrm{OH}^-][Fey]_T}{(k+k_{-1}) + k_1K[S][\mathrm{OH}^-]} \tag{3}$$

At very low $[\mathrm{OH}^-]$ and $[S]$ the inequality $(k+k_{-1}) \gg k_1K[S][\mathrm{OH}^-]$ will hold well and under this condition the rate law (3) reduces to (4)

$$-\frac{\mathrm{d}[Fey]}{\mathrm{d}t} = \frac{2kk_1K[S][\mathrm{OH}^-][Fey]_T}{k+k_{-1}} \tag{4}$$

Equation (4) clearly shows the first order kinetics with respect to $[\mathrm{OH}^-]$ and substrate at very low concentrations of hydroxide ion and the substrate which is in agreement with our experimental data. The value of $k + k_1/kk_1K$ were calculated from linear plots of Fig. 2 and 3 and the values are quite close to each other. At higher concentrations of hydroxide ion and organic substrate the values of $k_1K[S][\mathrm{OH}^-]$ will be quite large and thus the retarding trend of hydroxide ion and organic substrate becomes noticeable as the inequality $(k+k_{-1}) \gg \mathrm{k}_1K[S][\mathrm{OH}^-]$ will no longer be valid at higher hydroxide ion and organic substrate concentrations. Further verification of the rate expression can be made by rewriting as

$$\frac{1}{-\frac{\mathrm{d}[Fey]}{\mathrm{d}t}} = \frac{k+k_{-1}}{2kk_1K[S][\mathrm{OH}^-][\mathrm{Fe(CN)_6}^{3-}]} + \frac{1}{2k[\mathrm{Fe(CN)_6}^{3-}]} \tag{5}$$

Equation (5) clearly indicates that if a plot is made between 1/rate vs. $1/\mathrm{OH}^-$ or 1/(substrate) certainly a straight line with positive intercept of the $y$-axis will be obtained. From the slope and intercept of these plots (Fig. 5) the values of $(k + k_{-1})\, kk_1K$ and $k$ are calculated. The results indicate a close similarity between the values of $(k + k_{-1})/(kk_1K)$ which are obtained from two different methods (i.e. by organic substrate and $\mathrm{OH}^-$ variation). It also supports the validity of rate law (3) on comparing the values of $(k + k_{-1})/kk_1K$ calculated from different figures. It again substantiates that the values are quite similar to each other. So the proposed reaction mechanism appears to be quite probable.

On the basis of product study from thin layer chromatography it was possible to conclude that the finally dicarboxylic acids are produced from the oxidation of xylitol and galactitol respectively.

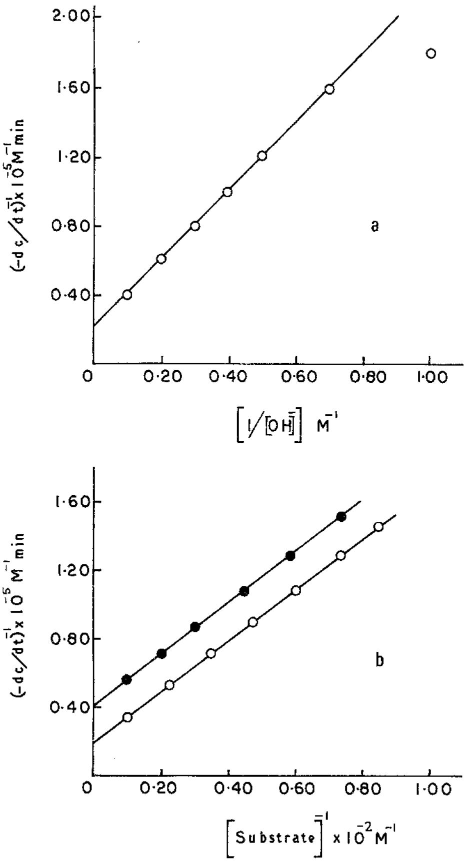

Fig. 5. Plots 1/rate vs. *a* $1/[OH^-]$, *b* 1/substrate concentration

## Materials and Methods

The solutions of xylitol (Sigma Chemical Company, U.S.A.) and galactitol (E. Merck), potassium hexacyanoferrate(III), potassium chloride and sodium hydroxide (AR. BDH. grade) were prepared in doubly distilled water.

Cerium(IV) sulphate being an oxidizing agent could also oxidize the organic substrates but it was observed that the estimation of hexacyanoferrate(II) ion by cerium(IV) was not affected in the presence of organic substrate.

The actual experimental procedure has already been reported elsewhere[7].

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