

OSMIUM TETROXIDE CATALYSED OXIDATION OF SORBITOL AND MANNITOL WITH HEXACYANOFERRATE(III) IN AQUEOUS ALKALINE MEDIUM

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Kinetics of oxidation of sorbitol and mannitol with alkaline hexacyanoferrate (III) in presence of osmium tetroxide as a homogeneous catalyst is reported. Kinetic data demonstrate that the rates of oxidation are independent of hexacyanoferrate(III) and are directly catalysed by osmium tetroxide. The reaction rate shows nearly first order kinetics at lower hydroxide concentration and tends to zero at higher hydroxide concentrations. The dependence of the reaction rate on the organic substrate concentration is also complicated. The reaction rate which follows first-order kinetics at lower concentration and retards the reaction velocity at higher concentration of sorbitol. The reaction velocity shows nearly first order kinetics with respect to lower mannitol concentrations, reaches to maximum beyond which it falls at still higher concentration. In the present conditions, these substrates are also oxidized with hexacyanoferrate(III) itself. The empirical rate law in terms of disappearance of hexacyanoferrate(III) might be proposed as follows :

$$\frac{-d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = k_a[\text{Fe}(\text{CN})_6]^{3-} + k_b[\text{OsO}_4]$$

where k_a is observed first order rate constant in hexacyanoferrate (III) and k_b is the constant depending upon the concentration of the substrates and hydroxide ion.

INTRODUCTION

Hexacyanoferrate(III) oxidations of organic compounds in alkaline medium have recently received much attention presumably due to its less complexity involved in the mechanistic elucidation. Many reviews presenting very interesting information have also been written by many authors (Thyagarajan 1956; Stewart 1964; Waters 1964; and Wilson 1966). Solymosi (1957) has reported osmium tetroxide as a universal catalyst in the oxidation reaction with hexacyanoferrate(III) in alkaline medium, but his findings were from analytical view points. The first kinetic attempt was made by Krishna and Singh (1966) in the oxidation study of methanol and ethanol with alkaline Hexacyanoferrate(III). Recently osmium(VIII) catalysis is reported in alkaline Hexacyanoferrate(III) oxidation of Ketones (Singh, V. N. *et al.* 1969), Hydroxy acid (Singh, N. P. *et al.* 1970), Glycollic and Lactic acids (Lal *et al.* 1972). The mechanism proposed for the oxidation of organic substrates involves the formation of a 1 : 1 complex of osmium(VIII) and the anion of the organic substrate as the first step followed by its decomposition to intermediate products and the

osmium(VI) species. Osmium(VI) thus formed was rapidly oxidized to osmium(VIII) with hexacyanoferrate(III). Our interest in this field has led us to investigate the way by which osmium tetroxide participates in the oxidation of Sorbitol and Mannitol by alkaline hexacyanoferrate(III) ion.

EXPERIMENTAL

The samples of the sorbitol and mannitol used in this investigation were of S. Merk (India). G. R. (S. Merk) samples of sodium hydroxide, sodium carbonate and sodium bicarbonate were used by dissolving in distilled water. The standard solution of sodium perchlorate was made by dissolving pure sample of Riedel (Germany) in distilled water to keep the ionic strength of the medium constant. The osmium tetroxide was from Johnson Metthey & Co., and the solution was prepared by dissolving a known amount of the sample in aqueous potassium hydroxide. The final strength of KOH was kept at $5 \times 10^{-2} M$ and that of the OsO_4 was $3.92 \times 10^{-2} M$.

The kinetic procedure is reported elsewhere (Singh, V. N. *et al.* 1969; Singh, N. P. *et al.* 1970; and Lal *et al.* 1972). The identification of the oxidation products was made by the paper chromatography study.

RESULTS AND DISCUSSION

The kinetic measurements for the rate of the oxidation of sorbitol and mannitol were carried out with a wide range of reactant concentrations. It is worth mentioning here that hexacyanoferrate(III) ion oxidation of these substrates has also been studied by us in aqueous alkaline medium in the absence of osmium tetroxide catalyst and it was noticed that uncatalysed route of the reaction takes place upto very low alkali concentrations. Thus, the kinetic study has been made in such a condition where catalysed as well as uncatalysed reaction is occurring simultaneously.

The exact nature of the reaction is presented in Fig. 1, which shows a typical zero order plot for the rate of oxidation of sorbitol. In order to avoid the possible error involved due to interference of the reaction products on the reaction rate, the initial $\left(\frac{-dc}{dt}\right)$ has been calculated.

The values of $\left(\frac{-dc}{dt}\right)$, obtained at varying concentrations of hexacyanoferrate (III) are presented in Fig. 2, where $\left(\frac{-dc}{dt}\right)$ is plotted against corresponding concentration of hexacyanoferrate (III). This deviation from the straight line clearly demonstrates that deactivation of the osmium tetroxide is playing the measure role in the reaction. The straight line intercepting the rate axis leads to use, the idea that a part of the reaction is independent of the hexacyanoferrate(III) concentration while the other part is dependent on it. In the oxidation of sorbitol by hexacyanoferrate (III), the reaction obeyed perfect first order Kinetics with respect to it (Singh, M. P. *et al.* 1970). Thus this confirms that the order with respect to hexacyanoferrate(III) is zero even upto wide range of concentrations. Similarly the kinetic data collected for mannitol are presented in Fig. 3. From this data it is again obvious that the reaction is taking place in two part, one in which osmium tetroxide catalysed oxidation

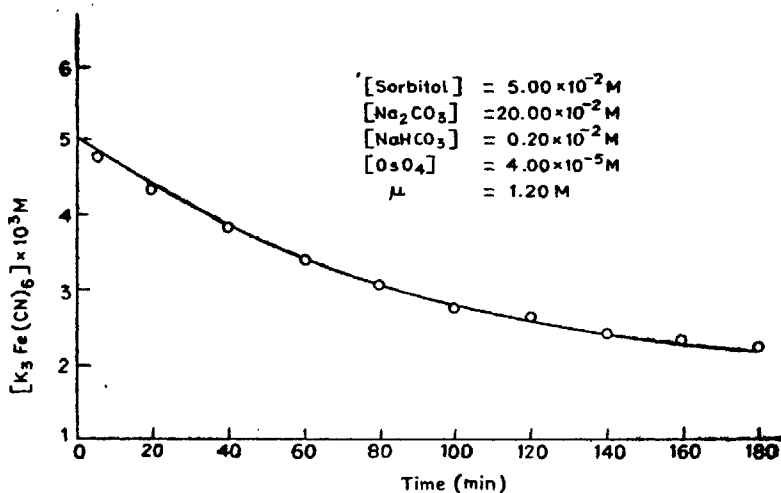
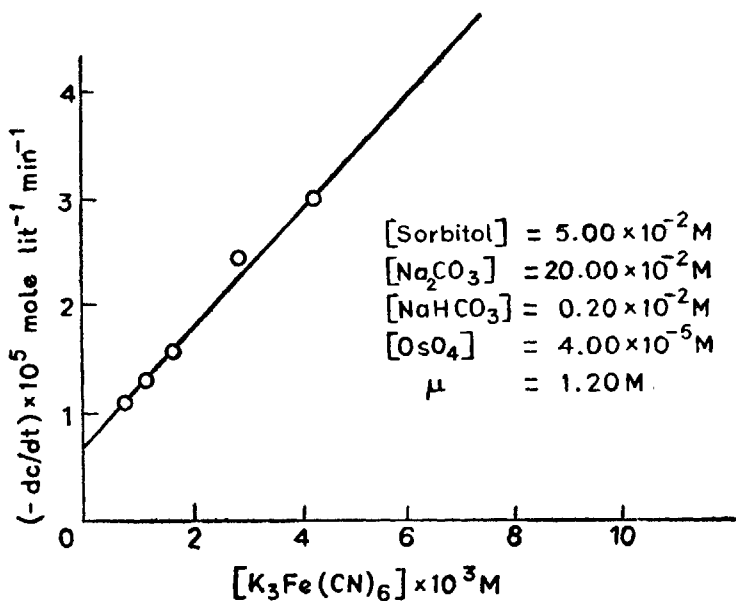


FIG. 1. Rate of Oxidation of Sorbitol.

FIG. 2. Reaction rate (dc/dt) obtained at varying concentrations of hexacyanoferrate(III)

shows zero order dependence of the reaction rate and other in which uncatalysed oxidation indicates direct proportionately of the reaction rate with respect to hexacyanoferrate(III) in each case. Fig. 4 demonstrates that the reaction rate, which follows nearly first order kinetics at low sorbitol concentration tends to decrease at higher concentration.

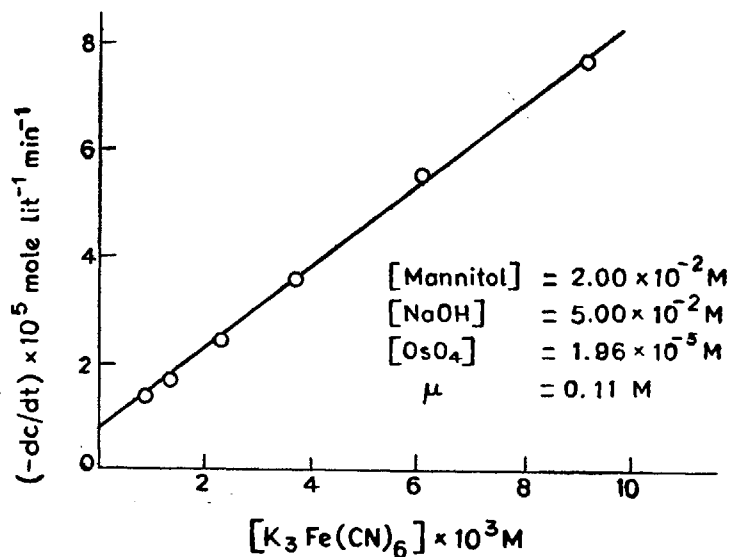


FIG. 3. The kinetic data for Mannitol.

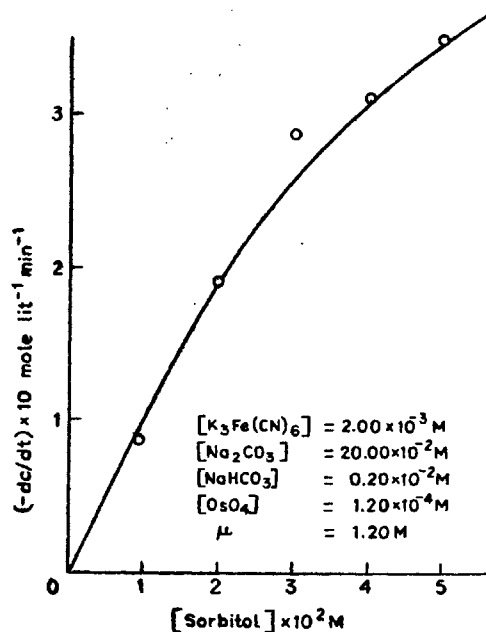


FIG. 4. Reaction rate following nearly first order kinetics at low Sorbitol concentration.

The results presented in Fig. 5, again indicates that the reaction rate, which follows nearly first order kinetics with respect to low mannitol concentration, reaches a maximum beyond which it falls at still higher concentration. The kinetic study of

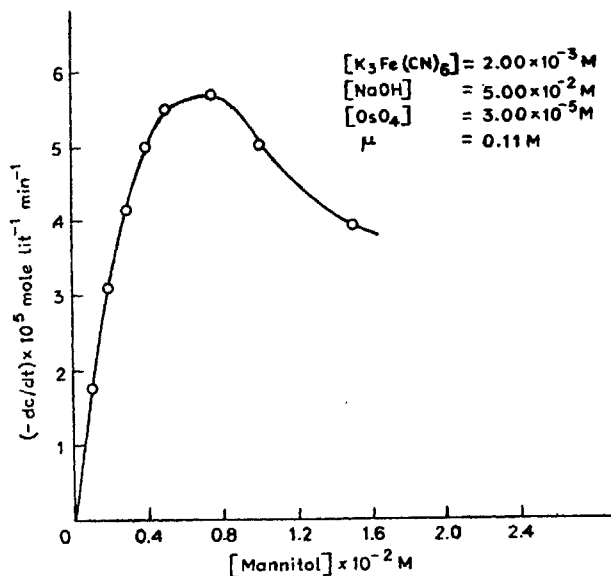


FIG. 5. Reaction rate following nearly first order kinetics at low mannitol concentration.

TABLE I

The kinetics of Sorbitol

$[Na_2CO_3]$	$= 20.00 \times 10^{-2} M$
$[Sorbitol]$	$= 5.00 \times 10^{-2} M$
$[K_3Fe(CN)_6]$	$= 2.00 \times 10^{-3} M$
$[OsO_4]$	$= 4.00 \times 10^{-3} M$
μ	$= 1.20 M$

pH	$\left[\frac{-dc}{dt} \right] \times 10^5$	$\frac{\left[\frac{-dc}{dt} \right] \times 10^5}{[OH^-]}$
10.60	1.51	3.73
10.65	1.57	3.52
10.70	1.63	3.25
10.75	1.67	2.97
10.80	1.76	2.79
10.85	1.84	2.60

sorbitol carried out in alkaline buffer containing sodium carbonate and bi-carbonate, indicates that reaction rate follows nearly first order kinetics of low hydroxyl ion concentration and shows retarding effect at its higher concentration (Table I). Similarly, hydroxyl ion variation in the oxidation kinetics of mannitol indicates the same nature as observed in case of sorbitol (Fig. 6). Fig. 7 indicates the effect of osmium

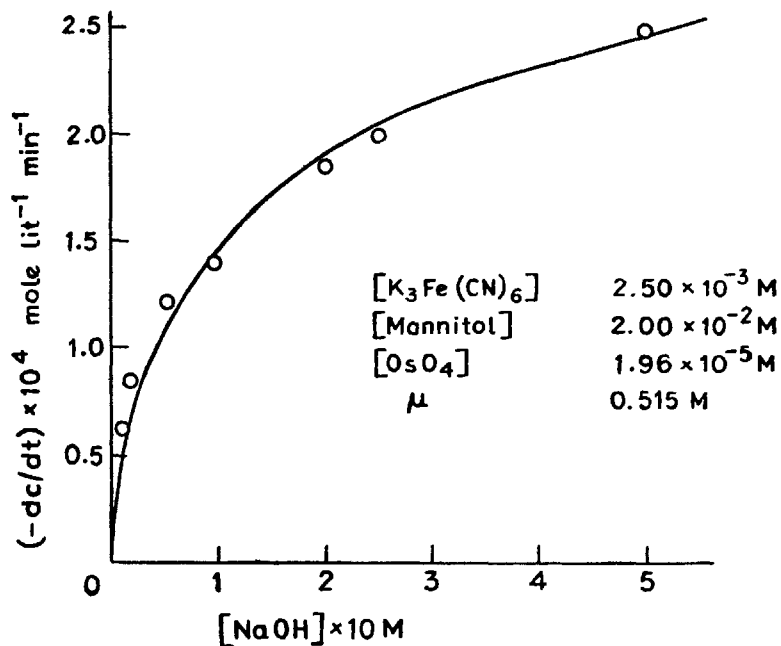


FIG. 6. Hydroxyl ion variation in the oxidation kinetics of mannitol.

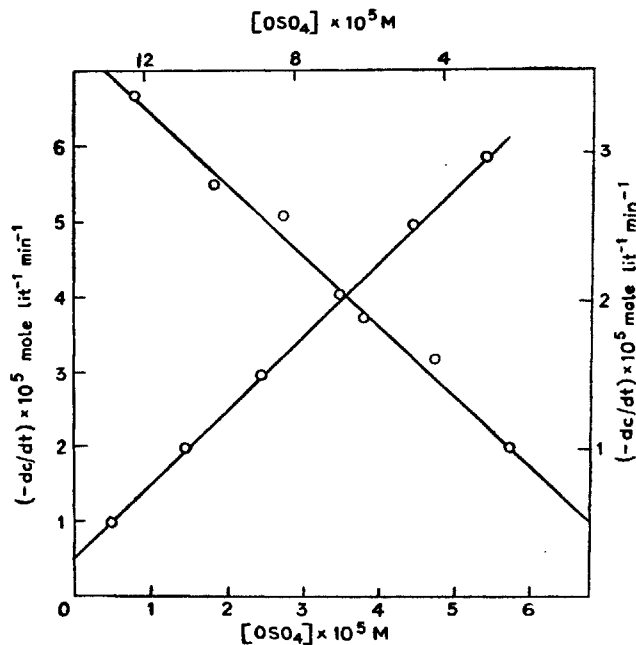


FIG. 7. Effect of Osmium Tetroxide on the oxidation velocity of sorbitol and mannitol.

tetroxide on the oxidation velocity of sorbitol and mannitol. The straight line suggests the direct proportionality of the reaction rate with respect to the catalyst concentration and the intercept is for uncatalysed path of the reaction.

Now on the basis of the experimental results it is worth to assume the first order dependence of the reaction rate on catalyst, alcohol and hydroxyl ion at their lower concentrations and zero order on hexacyanoferrate(III) ion. Thus under these conditions a probable rate law might be given as :

$$-\frac{d[\text{Fey}]}{dt} = k_a [\text{Fey}] + k_b [\text{OsO}_4] \quad \dots \quad \dots \quad (1)$$

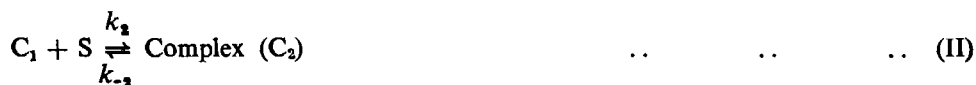
Where $\text{Fey} = [\text{Fe}(\text{CN})_6]^{-3}$ and k_a is the observed first order rate constant in hexacyanoferrate(III) and k_b is the constant depending upon the concentration of the substrates and hydroxyl ion. The first term of the right hand side of the eq. (1) is due to the part of the oxidation going on without catalyst osmium tetroxide while the second is due to the oxidation taking place with catalyst osmium tetroxide. The values of k_a and k_b calculated from the slope and the intercept of the plot of hexacyanoferrate(III) and osmium tetroxide concentration are given in Table II.

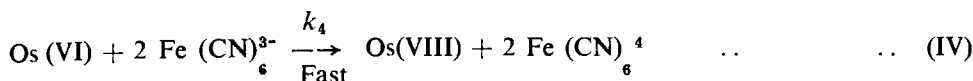
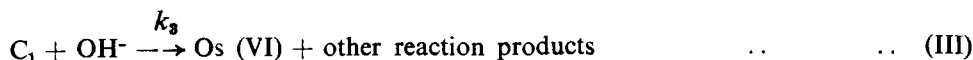
TABLE II

Mannitol		Sorbitol	
k_{a-1} (min)	k_b	k_{a-1} (min)	k_b
0.78×10^{-2}	0.41	0.46×10^{-2}	0.18 ($\text{K}_3\text{Fe}(\text{CN})_6$ plot)
0.31×10^{-2}	0.90	0.27×10^{-2}	0.24 (OsO_4 plot)

The values for mannitol are not much convincing but those for sorbitol are nearly the same in both the conditions. From that the values of former is negligible as compared to the latter. For an approximation the total velocity of oxidation in present conditions might be assumed as only due to the catalyst osmium tetroxide.

In the previous publications, i.e., of Singh *et al.* (1969, 1970) and Lal *et al.* (1972), it has been pointed out that the decrease in the zero order velocity constant, after a certain percentage of the reaction, is due to the complex formed between Os(VI) and the organic substrate. Thus, it might not be possible for hexacyanoferrate(III) to oxidize Os(VI) to Os(VIII) species in alkaline medium. Because, it has been confirmed that Os(VI) formed during the course of reaction is again oxidized to Os(VIII) species by hexacyanoferrate(III). On such evidences, the scheme of oxidation of polyhydric alcohols might be set out as follows :





Where [S] represents the respective polyhydric alcohols. The formation of the Complex C_2 is only evidenced in case of mannitol.

Assuming the steady state conditions for the concentration of C_1 and C_2 the above scheme results

$$[C_1] = \frac{k_1 [Os(VIII)] [S] + k_{-2} [C_2]}{k_{-1} + k_2 [S] + k_3 [OH^-]} \quad \dots \quad \dots \quad (2)$$

$$[C_2] = \frac{k_2 [C_1] [S]}{k_{-2}} = K [C_1] [S] \quad \dots \quad \dots \quad (3)$$

$$\left(K = \frac{k_2}{k_{-2}} \right)$$

Eliminating C_2 from eq. (2), the concentration of C_1 would be

$$[C_1] = \frac{k_1 [Os(VIII)] [S]}{k_{-1} + k_3 [OH^-]} \quad \dots \quad \dots \quad (4)$$

From the present study it is quite apparent that the rate of oxidation can appreciably be retarded with further addition of substrates when the concentration of latter is high. Similar effects have been observed with ceric sulphate oxidation of the alcohols (cf. Litler & Waters 1960). Under such conditions it is better to express the final rate law in terms of the total osmium(VIII) as [Os(VIII)].

The total Os(VIII) concentration might be obtained from eq. (5).

$$[Os(VIII)]_0 = [Os(VIII)] + [C_1] + [C_2] \quad \dots \quad \dots \quad (5)$$

Substituting the value of Os(VIII) in (3) and eliminating C_2 , the value of C_1 comes out to be

$$[C_1] = \frac{k_1 [S] [Os(VIII)]_0}{k_{-1} + k_3 [OH^-] + k_1 [S] [1 + k(S)]} \quad \dots \quad \dots \quad (6)$$

Now the rate law in terms of decreasing concentration of hexacyanoferrate (III) would be

$$\frac{-d[Fe(CN)_6]^{3-}}{dt} = \frac{2 d[Os(VI)]}{dt} = 2 k_3 [C_1] [OH^-] \quad \dots \quad \dots \quad (7)$$

From eqs. (6) and (7) the rate law comes out to be

$$\frac{-d[Fe(CN)_6]^{3-}}{dt} = \frac{2 k_1 k_3 [S] [Os(VIII)]_0 [OH^-]}{k_{-1} + k_3 [OH^-] + k_1 [S] \{1 + R[S]\}} \quad \dots \quad \dots \quad (8)$$

The rate law (8) is valid only upto first stage of oxidation of the substrate.

The actual rate law in terms of hexacyanoferrate(III), should be multiplied by the equivalence of hexacyanoferrate(III) as obtained for the respective organic substrates.

The validity of the rate law (8) could be verified under different conditions. When no complex C_2 is formed ($K=0$), equation (8) reduces to

$$\frac{-d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = \frac{2 k_1 k_3 [\text{S}] [\text{Os}(\text{VIII})]_0 [\text{OH}^-]}{k_{-1} + k_3 [\text{OH}^-] + k_1 [\text{S}]} \quad \dots \quad (9)$$

The same form is obtained if both K and $[\text{S}]$ are small, so that $K_1 K [\text{S}]^2$ is negligible as comparison to $k_1 [\text{S}]$. With the help of the equation (9), the specific feature of the curve obtained for the effect of mannitol variation on the reaction rate might be explained as follows.

When the concentration of (S) (mannitol) is increased so that

$$[k_{-1} + k_3(\text{OH}^-)] \ll k_1(\text{S}) [1 + k(\text{S})]$$

$$\frac{-d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = V = \frac{2k_3 [\text{Os}(\text{VIII})]_0 [\text{OH}^-]}{1 + k [\text{S}]} \quad \dots \quad (10)$$

Equation (10) evidently accounts for the decrease of velocity with increasing concentration of $[\text{S}]$ as in the descending portion of the curve shown in Fig. 5. Differentiation of Eqn (8) gives for the concentration of $[\text{S}]$ producing the maximum rate

$$[\text{S}] = \left\{ \frac{k_{-1} + k_3 [\text{OH}^-]}{K k_1} \right\}^{\frac{1}{2}} \quad \dots \quad (11)$$

a quantity independent of catalyst concentration.

In a separate set of experiments with the catalyst at double the concentration used for Fig. 5 it was observed that the concentration of mannitol producing a maximum rate was practically unchanged. Similarly the retarding effect of sorbitol also falls under the conditions assumed for the eqn (9). If $k_1 [\text{S}] \ll \{k_{-1} + k_3 [\text{OH}^-]\}$, the rate law (9) reduces to the equation (12).

$$\frac{-d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = \frac{2k_1 k_3 [\text{S}] [\text{Os}(\text{VIII})]_0 [\text{OH}^-]}{k_{-1} + k_3 [\text{OH}^-]} \quad \dots \quad (12)$$

The retarding effect obtained on the variation of hydroxyl ion in mannitol is very well explained from eq. (12). The oxidation products of sorbitol and mannitol could not be determined significantly. The formation of only oxalic acid was confirmed chromatographically.

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