

Kinetics and Mechanism of Oxidation of D-Galactose and D-Maltose with Potassium Permanganate in Acidic Medium by Spectrophotometry

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Oxidation of D-galactose and D-maltose with permanganate ion (MnO_4^-) as oxidant was observed in acidic medium by visible spectrophotometric method. The rate of reaction was followed by the change in absorbance of oxidant at λ_{max} 545 nm. The influence of different experimental parameters, such as change in concentration of D-galactose and D-maltose, MnO_4^- , H^+ and reaction temperature were investigated. The oxidation reaction was observed identical first order kinetics with respect to substrate and permanganate ion. A positive effect of H^+ was found whereas change in ionic strength (μ) has no effect on oxidation velocity. It was observed that rate of oxidation of maltose was much slower in absence of catalyst which was increased after the addition of mercuric acetate while in case of galactose reaction proceeds with out catalyst. The reaction were investigated at different temperatures to evaluate various activation parameters. A suitable mechanism consistent with experimental finding has been proposed.

Key Words: D-Galactose and D-Maltose, Permanganate ion, Absorbance, First order and Catalyst.

INTRODUCTION

The oxidation of carbohydrates was widely studied by many researchers¹⁻⁶. Sharma *et al.*⁷ reported oxidation of D-galactose, D-xylose and L-arabinose exhibited a uniform increase in pseudo first constant with increasing concentration of H_2SO_4 by chromium per oxy chromate. Kinetics of dextrose and serbose in sulphuric acid medium follows first order rate constant by Ce(IV) and zero order with glucose, fructose and galactose by ammonium metavanadate in sulphuric acid medium. Oxidation of some reducing sugars and nonreducing sugars by hexacyanoferrate(III) in alkaline medium were investigated by Nath and Singh⁵. They suggested

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that the rates of oxidation of aldo and ketosugars are their corresponding rates of enolization. Kinetics and spectrophotometric measurements of base catalyzed oxidation of carboxymethyl cellulose polymer by potassium permanganate revealed the base catalyzed formation of manganate(VI) transient species⁶. The influence of oxygen flow rate and of agitation on reaction follows first order kinetics. Kinetics of oxidation of reducing sugars D-galactose and D-ribose by N-bromoacetamide (NBA) in the presence of ruthenium(III) chloride as a homogenous catalyst and in perchloric acidic medium follows first order kinetics both with respect to sugar and NBA⁸. Change in ionic strength has no effect on rate of reaction⁹. The kinetics of oxidation of some reducing sugars *viz.*, glucose, galactose fructose, maltose and lactose by osmium(VIII) in presence of sodium *meta* periodate in alkaline medium have been investigated and showed zero order in periodate¹⁰. The kinetics of arabinose, galactose, xylose, fructose lactose, maltose by chloroamine T exhibit first order kinetics with respect to substrate, [Chloroamine T] and $[\text{OH}^-]$ ¹⁰.

The present investigation is concerned with the spectrophotometric studies of kinetics and oxidation of D-galactose and D-maltose by potassium permanganate in acidic medium and reaction will study at different concentration of substrate, oxidant, ionic strength, H^+ ion and temperature. An attempt will also be made to propose a mechanism of the reaction based on findings.

EXPERIMENTAL

The stock solutions for kinetics investigation were prepared in conductivity water. D-Galactose, D-maltose, potassium permanganate, sulphuric acid and potassium nitrate, used were of Merck and BDH, AR quality. The reaction was studied on thermostat ($\pm 1^\circ\text{C}$). The rate of reaction was followed by recording the optical density of KMnO_4 as a function of time on visible spectrophotometer (WBA UK). The rate constants were calculated from the slope of $\log [\text{concentration}]$ *vs.* time plots. The ionic strength was maintained throughout the experiments at 0.3 mol dm^{-3} by adding KNO_3 solution.

RESULTS AND DISCUSSION

Kinetics study of oxidation of D(+) galactose and D-maltose with KMnO_4 has been carried out spectrophotometrically in acidic medium at constant ionic strength of 0.3 mol dm^{-3} by KNO_3 . The reaction was followed by change in optical density of KMnO_4 in reaction mixture at λ_{max} 545 nm. The rate data of reaction was obtained in the form of pseudo first order rate constant (k_{obs}) under varying kinetics conditions. The order of reaction with respect to D-galactose and D-maltose, oxidant and H^+ has

been found identical (Table-1 and Fig. 1). The effect of ionic strength produced by KNO_3 does not alter the rate constant¹¹. This independence of rate on ionic strength leads to the conclusion that at least one of the reacting species is a neutral molecule. The plot of $\ln k$ vs. $\sqrt{\mu}$ as a straight line showed that rate of reaction was independent on ionic strength of the medium¹¹⁻¹⁵ (Fig. 2).

TABLE-1
VARIATION OF RATE CONSTANT (k s^{-1}) WITH KMnO_4 ,
D-GALACTOSE AND H_2SO_4 CONCENTRATION

$10^3 [\text{KMnO}_4]$ (mol dm^{-3})	$10^2 [\text{D-galactose}]$ (mol dm^{-3})	$10 [\text{H}_2\text{SO}_4]$ (mol dm^{-3})	$10^2 \text{ k (s}^{-1}\text{)}$
1.0	1.0	1.0	0.43
1.0	2.0	1.0	0.88
1.0	3.0	1.0	1.03
1.0	4.0	1.0	1.28
1.0	5.0	1.0	1.86
1.0	2.0	1.0	0.70
2.0	2.0	1.0	0.87
3.0	2.0	1.0	0.91
4.0	2.0	1.0	0.93
5.0	2.0	1.0	1.06
1.0	2.0	1.0	1.40
1.0	2.0	2.0	1.47
1.0	2.0	3.0	1.26
1.0	2.0	4.0	1.65
1.0	2.0	5.0	1.56

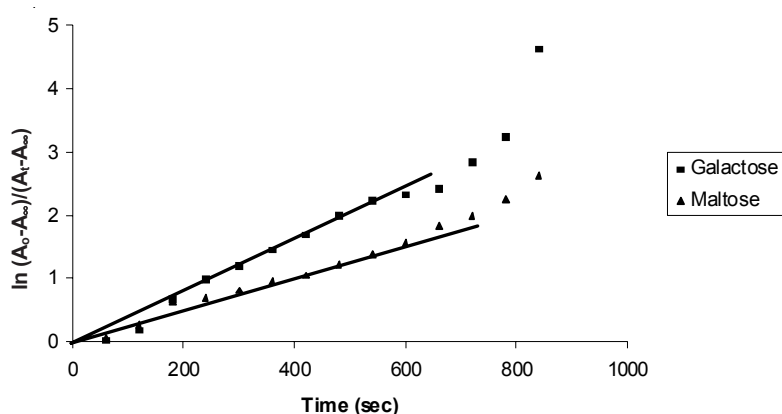


Fig. 1. Plot of $\ln (A_0 - A_\infty)/(A_0 - A_t)$ vs. time on rate of oxidation of galactose and maltose

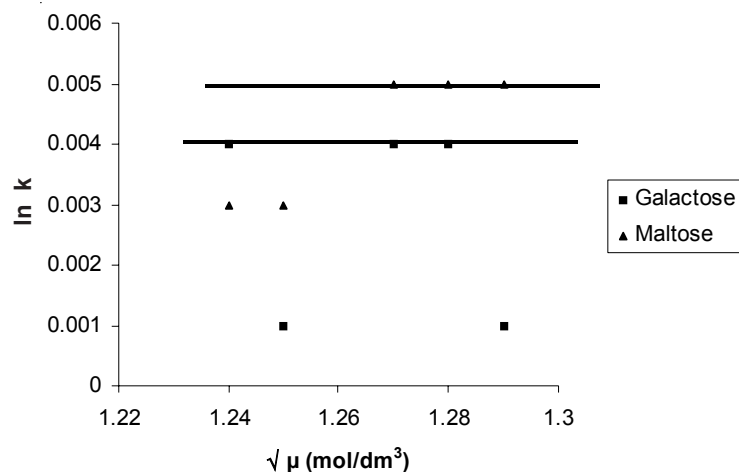


Fig. 2. Plot of $\sqrt{\mu}$ vs. $\ln k$ for the oxidation of maltose and KMnO_4 at different $\sqrt{\mu}$

The oxidation reaction of aldoses with potassium permanganate has been studied at various initial concentrations $(1, 2, 3, 4 \text{ and } 5) \times 10^{-2} \text{ mol dm}^{-3}$ of oxidant, keeping the substrate as well as sulphuric acid concentration and temperature constant at $2 \times 10^{-2} \text{ mol dm}^{-3}$ galactose and maltose $4 \times 10^{-2} \text{ mol dm}^{-3}$, $1 \times 10^{-1} \text{ mol dm}^{-3}$ and 308 k , respectively which is supported by earlier work^{11,12}. The pseudo first order rate constant is independent of the initial concentration of permanganate ion, indicating that reaction is first order with respect to oxidant (Table-1, Fig. 3). The rate of reaction with maltose was slower as compared with galactose, which get enhanced by the addition of catalyst (HgCl_2). It may be due to the hydrolysis of maltose in to simpler units of two monosaccharide.

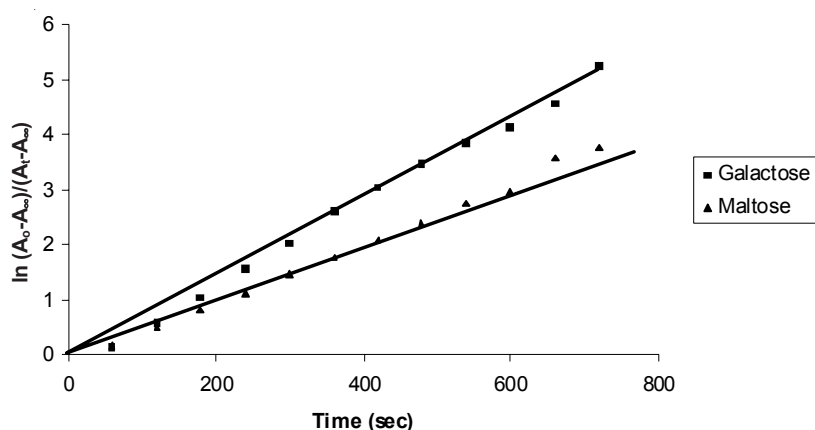


Fig. 3. Effect of concentration of oxidant KMnO_4 on rate of oxidation of galactose and maltose

The effect of changing substrate concentration has been investigated at constant oxidant and acid concentration at 308 K. An increase of substrate concentration enhances the rate of oxidation. A first order kinetics was observed with respect to concentration of substrate (Fig. 1). The plot of $1/k$ vs. $1/[\text{conc.}]$ (Fig. 4) has been found to be linear with positive intercept on Y axis and evidence of a complex formation between reducing sugars and permanganate ion $[\text{C}_6\text{H}_{12}\text{O}_6\text{---MnO}_4^-]$ ¹⁵⁻¹⁸. The following probable reaction may be observed in the oxidation of D-galactose and D-maltose in acidic medium by permanganate ion.

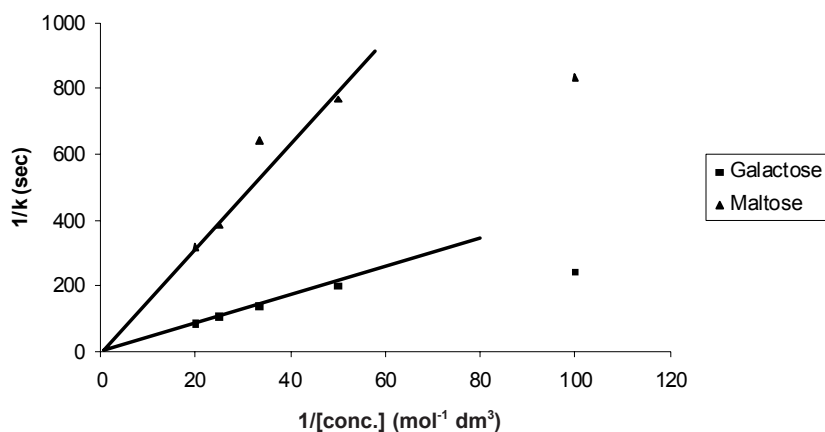
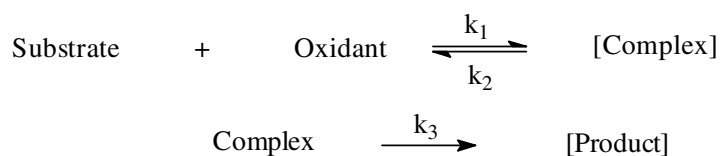
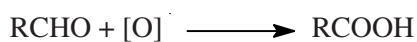


Fig. 4. Plot of $1/k$ vs. $1/[\text{conc.}]$ for galactose and maltose

The reaction has been studied at different hydrogen ion concentration varied by the addition of sulphuric acid but at constant ionic strength ($\mu = 0.3 \text{ mol dm}^{-3}$), oxidant and substrate concentration (Tables 1 and 2). The values of k_{obs} against $[\text{H}^+]$ are linear passing through the origin indicating that the order with respect to H^+ is unity (Fig. 5). The rate increases with increase in $[\text{H}^+]$, indicating that only one proton is involved in the reactions¹³.



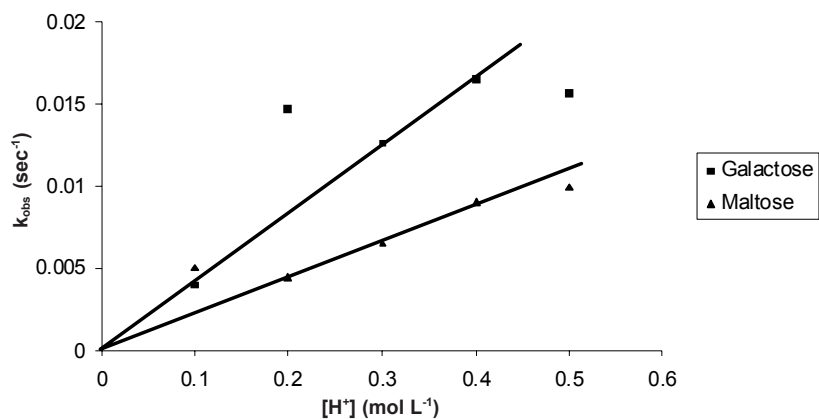


Fig. 5. Plot of k_{obs} vs. $[\text{H}^+]$ shows the effect of H^+ on oxidation of galactose and maltose

TABLE-2
VARIATION OF RATE CONSTANT (k s^{-1}) WITH KMnO_4 ,
D-MALTOSE AND H_2SO_4 CONCENTRATION

$10^3 [\text{KMnO}_4]$ (mol dm^{-3})	$10^2 [\text{D- maltose}]$ (mol dm^{-3})	$10 [\text{H}_2\text{SO}_4]$ (mol dm^{-3})	$10^2 \text{ k (s}^{-1}\text{)}$
1.0	1.0	1.0	0.12
1.0	2.0	1.0	0.13
1.0	3.0	1.0	0.14
1.0	4.0	1.0	0.24
1.0	5.0	1.0	0.25
1.0	4.0	1.0	0.15
2.0	4.0	1.0	0.59
3.0	4.0	1.0	0.54
4.0	4.0	1.0	0.44
5.0	4.0	1.0	0.53
2.0	4.0	1.0	0.59
2.0	4.0	2.0	0.28
2.0	4.0	3.0	0.86
2.0	4.0	4.0	0.94
2.0	4.0	5.0	0.16

The change in temperature on rate of reaction shows that rate of oxidation increases with the increase in temperature and yielded the values of activation parameters (Table-3 and Fig. 6). The value of activation parameters reflects that at least one of the reacting species in rate-determining step involve a neutral molecule.

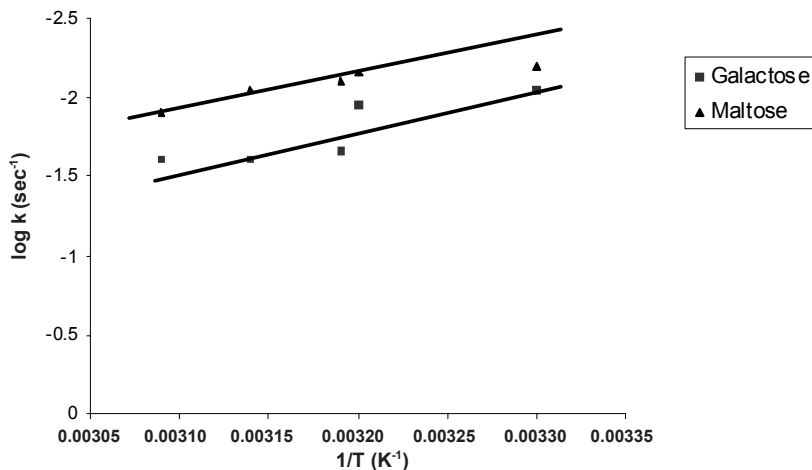


Fig. 6. Effect of temperature on rate of oxidation of galactose and maltose

TABLE-3

VALUES OF ACTIVATION PARAMETERS

Temp. = 32 °C, $[\text{KNO}_3] = 0.3 \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.2 \text{ mol dm}^{-3}$,
 Substrate = $2.0 \times 10^{-2} \text{ mol dm}^{-3}$ galactose and $4.0 \times 10^{-2} \text{ mol dm}^{-3}$ maltose

Substrate	$\sqrt{\mu}$ (mol/dm^3)	Ea (KJ/mol)	ΔH^* (KJ/mol)	ΔS^* (J/mol)	ΔG^* (KJ/mol)
Galactose	0.3	43.50	40.98	-199.6	101.4
Maltose	0.3	25.51	23.00	-227.0	91.8

Thus, based on above experimental facts the proposed reaction mechanism involves the formation [O] by the action of H_2SO_4 on KMnO_4 . The permanganate ion reacts with galactose to form complex $[\text{C}_6\text{H}_{11}\text{O}_6\text{---MnO}_4^-]$ ¹¹. This complex finally gives the aldonic acid in presence of nucleophile¹⁹⁻²¹.

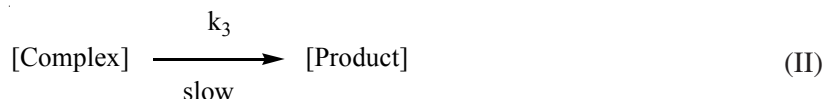
Reaction mechanism

On the basis of the results the following mechanism is proposed for the above reaction⁹:

$$\frac{-d[\text{MnO}_4^-]}{dt} = k[\text{RCHO}][\text{MnO}_4^-]$$

where RCHO represents the concentration of galactose and MnO_4^- is of Oxidant.





where k_1 and k_2 represent the rate constant in the forward and reverse direction and k_3 is the rate constant of the formation of product. Rate of formation of complex will be given as:

$$\frac{d[\text{Complex}]}{dt} = k_1[\text{RCHO}][\text{O}] - [k_2 + k_3][\text{Complex}] \quad (1)$$

$$\text{At steady state, } \frac{d[\text{Complex}]}{dt} = 0 \quad (2)$$

From eqn. 1 and 2 concentration of complex comes out to be:

$$[\text{Complex}] = \frac{k_1[\text{RCHO}][\text{O}]}{k_2 + k_3} \quad (3)$$

At steady state rate of disappearance of MnO_4^- may be:

$$\frac{d[\text{MnO}_4^-]}{dt} = k_3[\text{Complex}] \quad (4)$$

or

$$-\frac{d[\text{MnO}_4^-]}{dt} = \frac{k_1 k_3 [\text{RCHO}][\text{O}]}{(k_2 + k_3)} \quad (5)$$

Now the total $[\text{MnO}_4^-]$ may be considered as:

$$[\text{MnO}_4^-]_{\text{T}} = [\text{O}] + [\text{Complex}] \quad (6)$$

Now put the value of complex:

$$[\text{MnO}_4^-]_{\text{T}} = [\text{O}] + \frac{k_3[\text{RCHO}][\text{O}]}{(k_2 + k_3)} \quad (7)$$

from eqn. 7 the value of $[\text{MnO}_4^-]$ comes out:

$$[\text{MnO}_4^-] = \frac{(k_1 + k_3)[\text{MnO}_4^-]_{\text{T}}}{[k_2 + k_3] + k_3[\text{RCHO}]} \quad (8)$$

The final rate law from 5 to 8:

$$-\frac{d[\text{MnO}_4^-]}{dt} = \frac{k_1 k_3 [\text{RCHO}][k_2 + k_3][\text{MnO}_4^-]_{\text{T}}}{\{[k_2 + k_3 + k_1][\text{RCHO}]\}[k_2 + k_3]} \quad (9)$$

$$= \frac{k_1 k_3 [\text{RCHO}][\text{MnO}_4^-]_{\text{T}}}{[k_2 + k_3] + k_2[\text{RCHO}]} \quad (10)$$

In present experimental

$$(k_2 + k_3) > k_1[\text{RCHO}]$$

Hence above equation reduces to

$$\frac{d[\text{MnO}_4^-]}{dt} = \frac{k_1 k_3 [\text{RCHO}][\text{MnO}_4^-]_T}{k_2 + k_3} = k[\text{RCHO}][\text{MnO}_4^-]_T \quad (11)$$

where, $k = k_1 k_3 / k_2 + k_3$

The above equation indicates first order kinetics with respect to sugar and permanganate ion concentration.

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