

# Study of Mechanism of Maltose Oxidation by Keggin type 12-tungstocobaltate (III) in acid medium

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## Abstract:

Kinetics and Mechanism of Oxidation of Maltose by keggin type 12-tungstocobaltate (III) in acidic medium has been investigated at 25°C for the first time. The value of pseudo-first-order rate constant remains constant with variation of Keggin type 12-tungstocobaltate (III) clearly indicating the order of reaction with respect to  $[\text{Co}^{\text{III}}]$  is unity. First-order rate constant values were found to be increased with increase in  $[\text{Maltose}]$  and  $[\text{H}^+]$ . The order with respect to maltose concentration was found to be one each. Variations in ionic strength ( $\mu$ ) and dielectric constant ( $D$ ) of the medium have not influenced the oxidation rates. The proposed mechanism, involving most reactive activated complex formed as a result of interaction between the Keggin type 12-tungstocobaltate (III) and maltose is supported by kinetic orders, Michaelis-Menten plot and the main oxidation products of the reaction was identified as formic acid.

## Introduction:

The study of the carbohydrates and their derivatives has greatly enriched chemistry, particularly with respect to the role of molecular shape and conformation in chemical reactions [1]. These biological and economic importances of the carbohydrates and especially the monosaccharides and disaccharides have been largely responsible for the interest in the study of their biological and physiochemical properties along with reactivities [2]. The kinetics of oxidation of sugars by a variety of oxidants has been reported [3-4] in both acidic and alkaline media. Several different mechanisms showing the importance of enediols, cyclic forms of sugars, etc. have been established. The oxidations of different substrates by  $\text{KMnO}_4$  in acidic medium are reported [5, 6]. N-Bromosuccinamide is reported for oxidation of [7-11] sugar (a biologically important substrate). These reports and recent publications concerning the oxidation of sugars by organic halo amines have prompted us to use the heteropolyoxometalate for the oxidation of maltose in perchloric acid medium. The oxidation

kinetics of maltose in alkaline[12] and ammoniacal[13] media have been described, but few studies in acidic media have been reported. The kinetics of oxidation of maltose by thallium (III), in the presence of sulphuric acid, in aqueous acetic acid was reported [14]. Studies involving the oxidation of the sugars by polyoxometalates are scarce, therefore we have undertaken the study of oxidation of maltose sugar by showing the importance of enediols, cyclic forms of sugars, etc. have been established. The oxidation of different substrates by  $\text{KMnO}_4$  in acidic medium are reported[5, 6]. N-Bromosuccinamide is reported for oxidation of [7-11] sugar (a biologically important substrate). These reports and recent publications concerning the oxidation of sugars by organic halo amines have prompted us to use the heteropolyoxometalate for the oxidation of maltose in perchloric acid medium. The oxidation kinetics of maltose in alkaline[12] and ammoniacal[13] media have been described, but few studies in acidic media have been reported. The kinetics of oxidation of maltose by thallium (III), in the presence of sulphuric acid, in aqueous acetic acid was reported [14]. The first direct measurements of self exchange rates for electron transfer between POM anions in water using  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$  and its one electron oxidized derivative  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  first synthesized and characterized by Baker and co-workers [4] has been extensively used as an oxidant both for organic and inorganic substrates [5]. The potential utility of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  as a well defined probe for determining the nature of outer-sphere oxidations of alkyl aromatic hydrocarbons [6]. When it is complexed with polytungstate ions  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}/[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$  which is attributed to the distribution of the charge density of the cobalt ion over a large area. The complex of transition metal ions with polyoxoanions like polytungstates are well known outer- sphere electron transfer reagent [7]. The redox reaction of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  have been recently revived [4,5]. Among various heteropolyacids structural classes the keggin type heteropolyacids have been widely used as homogeneous and heterogeneous catalysts for acid-base and oxidation reactions[8].The studies involving the oxidation of the sugars by polyoxometalates are scarce, therefore we have undertaken the study of oxidation of maltose sugar by 12-tungstocobaltate (III) in perchloric acid medium.

### Materials and methods:

All the solutions were prepared in doubly distilled water. The solution of Maltose was prepared by dissolving D-maltose (SD Fine) in water. 12-tungstocobaltate (III) was prepared, by reported method. The solution of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  was standardized iodimetrically with excess of  $\text{As}^{\text{III}}$ , and spectrophotometrically at 624 nm.

**Kinetic Measurements:**

The reaction between  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  and maltose was studied under pseudo-first-order conditions at a constant temperature of  $25.0 \pm 0.1^\circ\text{C}$ . The reaction was initiated by mixing the previously thermostated solutions of maltose and  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  which also contained the requisite amount of perchloric acid, and doubly distilled water. The reaction was followed by determining the concentration of remaining  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  spectrophotometrically at 624 nm. The sample run is given in Table 1 and the graph of  $\log(a/a-x)$  versus 't' is shown in Fig 1. Ionic strength was maintained using  $\text{NaClO}_4$  and to vary hydrogen ion concentrations  $\text{HClO}_4$  (BDH) was used. The pseudo-first-order rate constants were determined from the plots of  $\log [[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}]$  against time and the rate constants were reproducible within  $\pm 4\%$ .

**Test for free radicals:**

The reaction was also studied in presence of added acrylonitrile to understand the intervention of free radicals [15,16] in the reaction. There was no effect of added acrylonitrile on the reaction and also no precipitate due to the polymerization of the added acrylonitrile was observed thus confirming the absence of any free radical formation in the reaction.

**Results and discussion:****Stoichiometry and product analysis:**

The stoichiometry was studied by keeping concentration of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  constant at  $3 \times 10^{-3} \text{ mol dm}^{-3}$  and varying concentration of maltose from  $0.2 \times 10^{-3}$  to  $3.0 \times 10^{-3} \text{ mol dm}^{-3}$ . Different reaction mixtures containing varying concentration of maltose were prepared, which also contained required amount of perchloric acid. The concentration of unreacted  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  was determined spectrophotometrically at 624 nm after 24 hours. The stoichiometry was found to be one mole of maltose per two mole of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ . The main oxidation product, formic acid was detected [17] by TLC and spot test methods [18,19].

**Reaction order:**

The reaction was carried out under pseudo-first-order conditions, keeping the concentration of perchloric acid constant at  $0.3 \text{ mol dm}^{-3}$  and varying either maltose from 0.01 to  $0.1 \text{ mol dm}^{-3}$  at constant [one mole of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) or [one mole of  $[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$  from  $2.2 \times 10^{-4}$  to  $1.8 \times 10^{-3} \text{ mol dm}^{-3}$  at constant methionine ( $3.0 \times 10^{-2} \text{ mol dm}^{-3}$ ). The pseudo-first-order rate constants were found to be increased with increase in the concentration of the maltose and the order was found to be 0.88 as determined by plot of  $\log (k_{\text{obs}})$  against  $\log [\text{maltose}]$ . The order in oxidant concentration was found to be unity

as the pseudo-first-order plots were found to be linear and the pseudo-first-order rate constants were fairly constant as the concentration of oxidant is varied (Table 2).

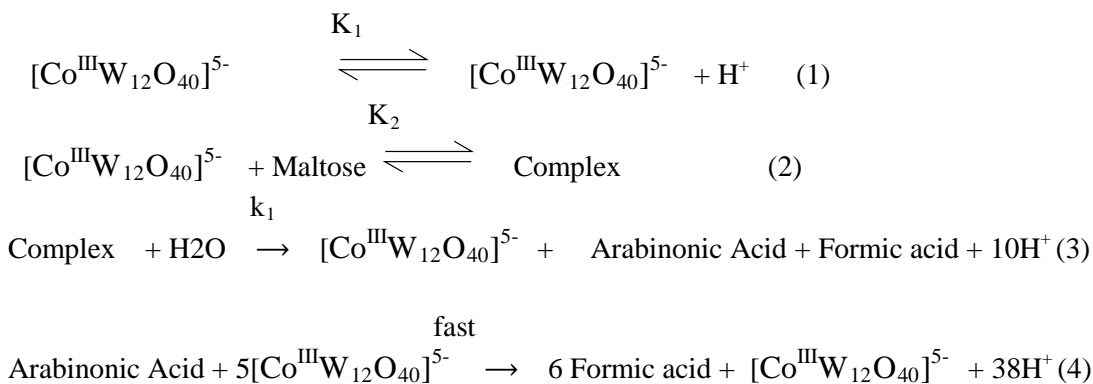
The effect of hydrogen ion concentration on the reaction was studied to know probable prior protonation equilibria of either the oxidant or the substrate and to identify the active reactant species. The concentration of H<sup>+</sup> ion was varied from 0.1 to 0.5 mol dm<sup>-3</sup> keeping all other concentrations constant. It was found that the reaction rate increases with the concentration of H<sup>+</sup> ions (Table 2) and the order in [H<sup>+</sup>] was determined from the plot of log k<sub>obs</sub> against log [H<sup>+</sup>] and was found to be 0.91.

**Effect of solvent polarity and ionic strength:**

The effects of ionic strength and solvent polarity were studied keeping concentration of [Co<sup>III</sup>W<sub>12</sub>O<sub>40</sub>]<sup>5-</sup>, methionine and perchloric acid constant at 1.0x 10<sup>-3</sup> mol dm<sup>-3</sup>, 0.03 mol dm<sup>-3</sup> and 0.35 mol dm<sup>-3</sup> respectively at 25°C. Sodium perchlorate and acetonitrile were used to vary the ionic strength and solvent polarity, respectively. The rate of the reaction was unaffected by increasing ionic strength from 0.40 to 0.90 mol dm<sup>-3</sup>.

**Mechanism and rate law:**

The mechanism according to Scheme 3 proceeds with the formation of a complex between the maltose and [Co<sup>III</sup>W<sub>12</sub>O<sub>40</sub>]<sup>5-</sup> in a prior equilibrium which then decomposes to give Arabinonic Acid, Formic acid and [Co<sup>III</sup>W<sub>12</sub>O<sub>40</sub>]<sup>8-</sup> in a rate determining step. Arabinonic Acid reacts with five molecules of oxidants in fast step to give the product formic acid.



**Scheme 3**

$  \text{Rate} = \frac{k_1 K_2 [\text{H}^+] [\text{maltose}] [\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}}{([\text{H}^+] + K_1)(1 + K_2 [\text{maltose}])} \quad (5)  $
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$$k_1 K_2 [H^+] [\text{maltose}]$$

$$k_{\text{obs}} = \frac{\text{-----}}{([H^+] + K_1)(1 + K_2 [\text{maltose}])} \quad (6)$$

**Conclusions:**

Kinetics of oxidation of maltose by protonated 12-tungstocobaltate (III) has been investigated at 25°C. Almost constant values of pseudo-first-order rate constant obtained during the variation of oxidant, 12-tungstocobaltate (III) clearly reveal that order of reaction with respect to [Co<sup>III</sup>] is unity. First-order kinetics with respect to [Maltose] and [H<sup>+</sup>] is evident from the observed values of rate constants. Variations in ionic strength ( $\mu$ ) and dielectric constant ( $D$ ) do not affect the rate of reaction. Protonated 12-tungstocobaltate (III) and unprotonated maltose have been postulated as the reactive species during the reaction. The main oxidation product of the reaction was identified as formic acid.

**Table 1: Sample run for oxidation of maltose by 12-tungstocobaltate (III) in perchloric acid**

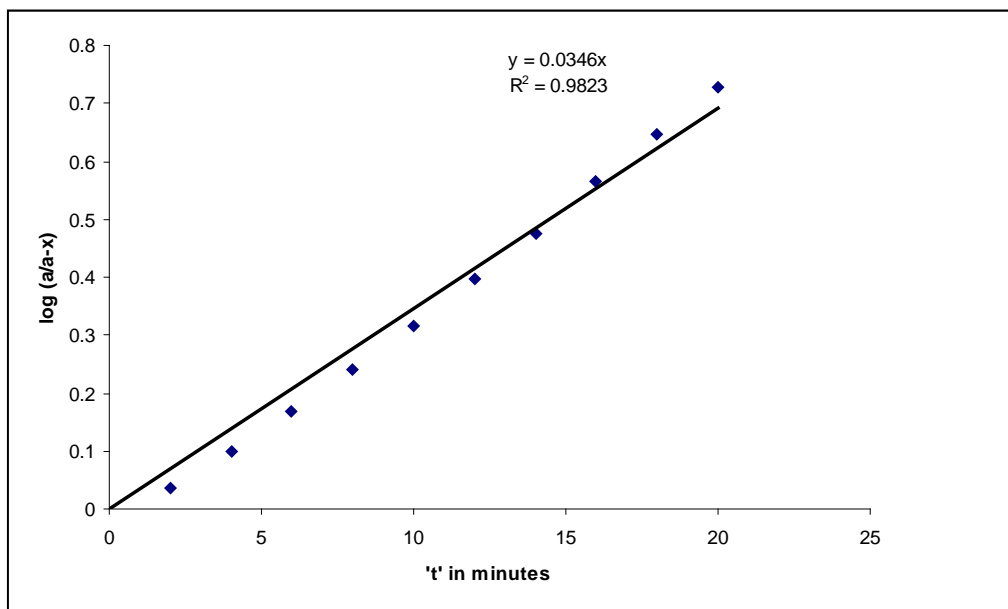
**medium at 25<sup>0</sup>C .**  
**[HClO<sub>4</sub>]= 0.3 mol dm<sup>-3</sup>, [Co<sup>III</sup>] = 1x10<sup>-3</sup> mol dm<sup>-3</sup>, [Maltose] =0.1 mol dm<sup>-3</sup>, I=0.4.**

Time in min	Absorbance at 624 nm	Log(a/a-x)
0	0.284	-
2	0.261	0.036678
4	0.226	0.09921
6	0.193	0.167761
8	0.163	0.241131
10	0.137	0.316598
12	0.114	0.396413
14	0.095	0.475595
16	0.077	0.566828
18	0.064	0.647138
20	0.053	0.729042

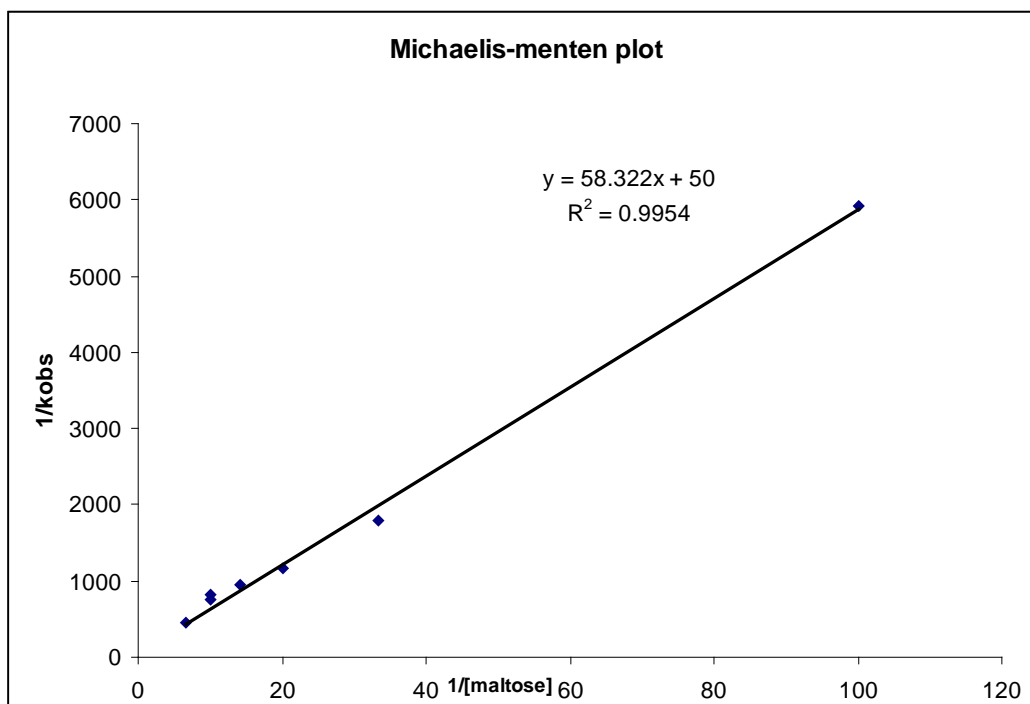
**Table 2: Effect of concentration of maltose, perchloric acid and 12-tungstocobaltate (III) ion, on the reaction between maltose and 12-tungstocobaltate (III) at 25°C**

$10^3[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ mol dm <sup>-3</sup>	$10[\text{HClO}_4]$ mol dm <sup>-3</sup>	$10[\text{Maltose}]$ mol dm <sup>-3</sup>	$10^3 k_{\text{obs}}$ s <sup>-1</sup>
0.2	3.0	1.0	1.20
0.4	3.0	1.0	1.10
0.6	3.0	1.0	1.12
0.8	3.0	1.0	0.99
1.0	3.0	1.0	1.23
1.0	1.0	1.0	0.43
1.0	2.0	1.0	0.90
1.0	3.0	1.0	1.23
1.0	4.0	1.0	1.86
1.0	5.0	1.0	2.30
1.0	3.0	0.1	0.16
1.0	3.0	0.3	0.56
1.0	3.0	0.5	0.85
1.0	3.0	0.7	1.05
1.0	3.0	1.0	1.23

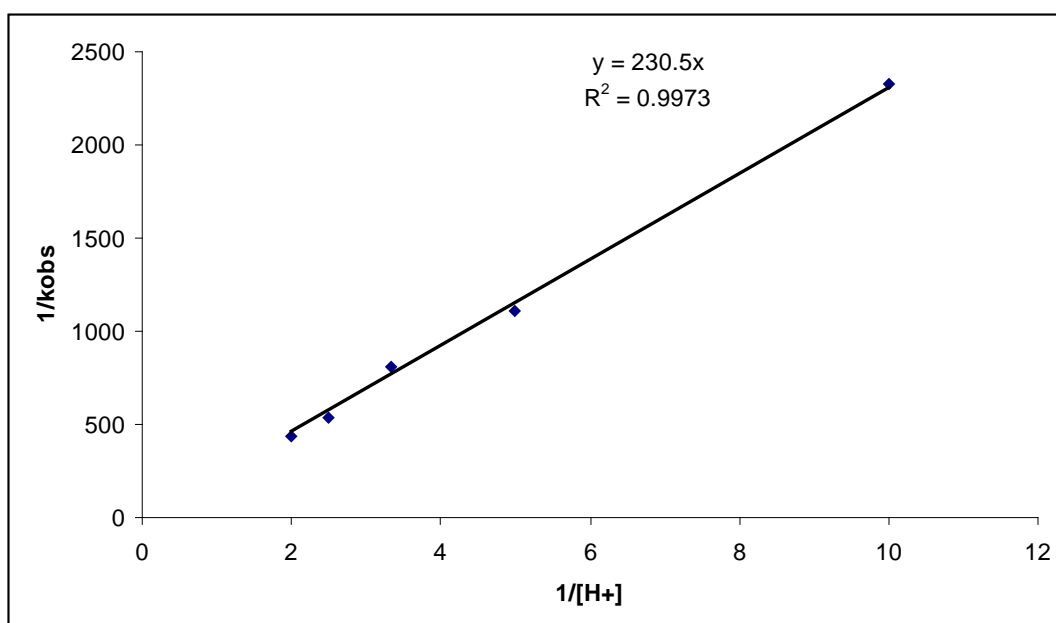
**Fig:1 Pseudo first order plot for oxidation of maltose by 12-tungstocobaltate (III) in perchloric acid. (Conditions as in table 1)**



**Fig: 2 Michaelis-Menten plot for oxidation of maltose by 12-tungstocobaltate (III) in perchloric acid. (Conditions as in table 2)**



**Fig. 3 Verification of rate law (Plot of  $1/k_{obs}$  versus  $1/[H^+]$ )**



## References

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