Kinetics and Mechanism of oxidation of D-Glucose by Hexamolybdocobaltate(III) in acidic medium

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Abstract : The oxidation of D-glucose by Anderson-Evans type Hexamolybdocobaltate(III) anion was studied under pseudo-first order condition in aqueous perchloric acid medium. The reaction is accelerated by hydrogen ion concentration. Inhibition of the reaction by the oxidant $[H_6CoMo_6O_{24}]^{3-}$ anion and added molybdate ion kinetically indicates existence of prior equillibria between various forms of the oxidant. In present study, the oxidant exist in the monomers $[H_6CoMo_6O_{24}]^{3-}$ anion, $[H_5CoMo_5O_{20}]^{2-}$ anion and dimer $[H_4Co_2Mo_{10}O_{38}]^{6-}$ forms between the pH 2 and 1. The active oxidant species is $[H_5CoMo_5O_{20}]^{2-}$ anion. Under experimental conditions, D-glucose exists in unprotonated form. The reaction involves direct electron transfer from D-glucose center to the oxidant anion generating free radicals in a rate determining step. The reaction rate is independent of the ionic strength. The thermodynamic parameters are evaluated by temperature variation kinetic data. The possible mechanism and rate equation is proposed for the reaction.

IndexTerms - Anderson-Evans type, pseudo-first-order, kinetic, monomer, dimer.

I. INTRODUCTION

Carbohydrates are polyhydroxy aldehydes or polyhydroxy ketones and are well known privilege core in natural products exhibiting chemical properties associated with both alcohols and carbonyl compounds. D-Glucose is an important monosaccharide that plays an active role in biological systems, in mammalian food supply and metabolism. It is a simple sugar pharmaceutically important to manage hypoglycemia and intervenous feeding. Its carbohydrate unit is a constituent of nucleic acid. Liquid glucose prepared by controlled hydrolysis of starch exhibit property as tablet binder, tablet coating agent. D-Glucose refined from corn-starch is commonly used as a sweetener. It is a source of rapidly absorbed energy and a carrier in water-soluble medications. The cell uses D-glucose as a source of energy in most organisms from bacteria to humans and metabolic intermediate because it is one of the main products of photosynthesis and starts cellular respiration in both prokaryotes and eukaryotes. In recent applications, glucose has been successfully employed as a renewable feed for fuel cells.

Carbohydrate oxidation has some industrial applications [1]. Recent reviews reveals that oxidation of carbohydrates is complex because of their multifunctional nature [2, 3]. The kinetic investigations of oxidation of D-Glucose had been reported earlier by using various oxidants under different conditions[4-14]. The general mechanism of oxidation of D-Glucose in acidic medium involves a prior complex formation between the substrate and oxidant [1, 5-6] Oxidation of reducing sugar in acidic medium reports a direct attack on the free carbonyl and or cyclic forms of the reducing sugar[7]. Depending upon the nature of active oxidizing species in the chosen media, acceleration and inhibition by hydrogen ion concentration was reported [7, 8]. In some study, proposed mechanism involves free radical formation [9-12]. Successive C_1-C_2 bond cleavage was also reported[14].

POM represents a large class of co-ordination compounds used in various sectors of science and technology. Trivalent ions of aluminum, chromium, cobalt and iron of hexamolybdo compounds are well known, easily prepared and are quite stable. Many POM's exhibit fast reversible multi-electron redox transformations under mild conditions. They are most versatile and environmental friendly oxidizing agent[15]. It is reported that, hetero POM's have considerably lower charge density and has central hetero metal ion securely caged by polymetal ions, thus making them best candidates for the investigation of outer

sphere electron transfer reaction. Due to discrete structure POMs resemble enzymes in their activities specifically the oxidative transformations of some substrates[16-18]. A mixture of the blue-green monomer $[(H_6CoMoO_{24})_2]^{-3}$ species and the olive green dimeric $[(H_4CoMoO_{19})_2]^{-6}$ can be produced in the oxidation of Co^{II} in presence of Molybdate It is recently noted that the oxidation by peroxomonosulphate ion produces the dimeric product as dominant species and monomer percentage composition increased with the increase in $[H^+]$ ion [19]. Literature survey reveals that researchers working mainly on Keggin or Dawson species. In comparison with Keggin and Dawson-types of salts, 6-molybdocobaltate(III) salts are substitution inert and are compact. It belongs to Anderson-Evans structure and contains six non-ionisable proton. To the best of our knowledge, very limited study is available on kinetic and mechanistic study of oxidation by 6-molybdocobaltate(III) anion[20-24]. In present investigations the kinetics of Oxidation of D-Glucose by Hexamolybdocobaltate(III) ion in aqueous perchloric acid has been studied in order to understand the reaction mechanism.

Characterization of Hexamolybdocobaltate(III)

The FT-IR spectrum of 6-molybdocobaltate(III) was recorded on Bruker instrument in KBr. The stretching vibration frequency of metal-oxygen lies in the region 1100-400 cm⁻¹. The spectrum shows the peak at 940 cm⁻¹ is characteristic of Molybdate ion. The Mo-O-Co stretching vibration is found at 1422 cm⁻¹. The broad peak at 3181 cm⁻¹ and 1627 cm⁻¹ indicates water associated with Anderson structure.

The dimer $[H_4Co_2Mo_{10}O_{38}]^{6-}$ and the monomers $[H_6Co^{III}Mo_6O_{24}]^{3-}$ anion absorbs at 599 nm and active species absorbs at 618 nm instead of 599 nm indicating $[H_5Co^{III}Mo_5O_{20}]^{2-}$ as the prominent oxidant species under the reaction conditions. In present study, the oxidant exist in the monomer $[H_6CoMo_6O_{24}]^{3-}$, $[H_5CoMo_5O_{24}]^{2-}$ anion and dimer $[H_4Co_2Mo_{10}O_{38}]^{6-}$ forms between the pH 2 and 1. In present study, the active oxidant species is $[H_5Co^{III}Mo_5O_{24}]^{2-}$ anion (**Figure 1** Polyhedral representation of oxidant).



Figure 1 Polyhedral representation of: a) $[H_6CoMo_6O_{24}]^{3-}$ anion, b) $[H_5CoMo_5O_{24}]^{2-}$ anion, c) $[H_4Co_2Mo_{10}O_{38}]^{6-}$ anion. The central Co(III) atom is indicated by the blue (online) color

2. Experimental

Materials and methods:

Reagent grade chemicals and double distilled water were used throughout the work. D-Glucose (98%) was purchased from Loba Chemie pvt Ltd (Mumbai, Maharashtra, India) and used without further purification. The solution of D-Glucose was freshly prepared each time. The ionic strength was maintained by using sodium perchlorate and to vary hydrogen ion concentration perchloric acid was used. Perchloric acid, chloroform and ethyl alcohol were purchased from Thomas Baker and Acrylonitrile from S D fine.

The cobalt complex 6-molybdocobaltate(III) was prepared by reported method [15] by using Co(II) sulphate, ammonium heptamolybdate, potassium persulphate (all S D Fine) and sulphuric acid (Thomos Baker). Further it was standardized spectrometrically (at 602 nm $\varepsilon = 16.9$ dm³ mol⁻¹cm⁻¹)[19] by using Systronic 119 UV-Visible spectrophotometer. The pH of the reaction mixture was observed by using

Equip-Tronics EQ-602 pH meter. Product analysis was monitored at different time intervals by LCMS spectroscopy. IR determinations were performed using Bruker Model Alpha FTIR spectrophotometer.

3. Kinetic Measurements

D-Glucose oxidation was studied under pseudo-first-order condition in acid medium at constant temperature of 298 K by keeping a large excess of substrate over that of oxidant and following the decrease in absorbance of 6-molybdocobaltate(III) at 602 nm wavelength.

Product Analysis and Stoichiometry: The reaction mixture containing known excess of oxidant, 0.005 mole of D-Glucose in 0.1 mol dm⁻³ of HClO₄ was prepared and allowed to stand for 24 h. The decrease in concentration of 6-molybdocobaltate(III) anion was analyzed spectrometrically at 602 nm. The stoichiometry was found to be 10 moles of 6-molybdocobaltate(III) anion per mole substrate. Product analysis was done by using LCMS spectroscopy at different time interval(**Fig. 2**). Oxidation intermediates were found to be lower aldoses showing peaks at 149, 118 and 59. Further oxidation of formaldehyde was not observed under experimental conditions. The formation of formaldehyde under kinetic condition i.e. [oxidant] >> [substrate] was identified by spot test and by forming its 2,4-dinitrophenylhydrazone derivative as reported earlier [24,25]. The solid DNP–derivative formed was filtered, extracted with chloroform and recrystallized by ethanol. It shows M.P.166^oC which matches with the reported value [10] and also m/z at 210 support formation of formaldehyde. (**Fig. 3**)



Formaldehyde

2,4-dinitrophenylhydrazine (2,4-DNPH) For

Formaldehyde-2,4-dinitrophenylhydrazone



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The active oxidant 6-molybdocobaltate(II) anion will form a complex with substrate that decomposes in rate determination step to give free radicals such as $C_6H_{11}O_{\cdot 6}$, $C_5H_9O_{\cdot 5}$, $C_4H_7O_{\cdot 4}$, $C_3H_5O_{\cdot 3}$. The free radical reacts fast with another nine oxidant molecules to produce formaldehyde after C-C oxidative cleavage. The detailed mechanism of reaction involving all these considerations can be represented and the corresponding rate law is given by equation (5).



Figure 3 LCMS Spectrum of 2, 4-DNPH derivative of oxidation product

Scheme 1 Stoichiometric equation of oxidation of D-Glucose by 6-molybdocobaltate(III) $C_6H_{12}O_6 + 10 [H_5CoMo_5O_{20}]^{-2} \longrightarrow 6 HCHO + 10 [H_5CoMo_5O_{20}]^{-3}$ (1)

$$[H_5CoMo_5O_{20}]^{2-} + H_2MoO_4 \xrightarrow{K_1} [H_6CoMo_6O_{24}]^{3-} + H^+$$
(2)

$$2 [H_5 CoMo_5 O_{20}]^{2-} = [H_4 Co_2 Mo_{10} O_{38}]^{4-} + 2H_2 0 + 2H^+$$
(3)

Scheme 2 Probable Mechanism of oxidation of D-Glucose by Hexamolybdocobaltate(III):

$$[H_{5}CoMo_{5}O_{20}]^{2} + C_{6}H_{12}O_{6} \xrightarrow{slow} K_{1} \qquad C_{6}H_{11}O_{6} + [H_{5}CoMo_{5}O_{20}]^{3} + H^{+}$$

$$[H_{5}CoMo_{5}O_{20}]^{2} + C_{6}H_{11}O_{6} + H^{+} \xrightarrow{Fast} C_{5}H_{10}O_{5} + HCHO + [H_{5}CoMo_{5}O_{20}]^{3}$$

$$C_{5}H_{10}O_{5} + [H_{5}CoMo_{5}O_{20}]^{2} \xrightarrow{Fast} C_{5}H_{9}O_{5} + [H_{5}CoMo_{5}O_{20}]^{3} + H^{+}$$

$$C_{5}H_{9}O_{5} + [H_{5}CoMo_{5}O_{20}]^{2} + H^{+} \xrightarrow{Fast} C_{4}H_{8}O_{4} + HCHO + [H_{5}CoMo_{5}O_{20}]^{3}$$

$$C_{4}H_{8}O_{4} + [H_{5}CoMo_{5}O_{20}]^{2} \xrightarrow{Fast} C_{4}H_{7}O_{4} + [H_{5}CoMo_{5}O_{20}]^{3} + H^{+}$$

$$C_{4}H_{7}O_{4} + [H_{5}CoMo_{5}O_{20}]^{2} + H^{+} \xrightarrow{Fast} C_{3}H_{6}O_{3} + HCHO + [H_{5}CoMo_{5}O_{20}]^{3}$$

$$C_{3}H_{6}O_{3} + [H_{5}CoMo_{5}O_{20}]^{2} \xrightarrow{Fast} C_{3}H_{6}O_{3} + [H_{5}CoMo_{5}O_{20}]^{3} + H^{+}$$

$$C_{3}H_{6}O_{3} + [H_{5}CoMo_{5}O_{20}]^{2} \xrightarrow{Fast} C_{2}H_{4}O_{2} + HCHO + [H_{5}CoMo_{5}O_{20}]^{3}$$

$$C_{2}H_{4}O_{2} + 2 [H_{5}CoMo_{5}O_{20}]^{2} \xrightarrow{Fast} 2 HCHO + 2 [H_{5}CoMo_{5}O_{20}]^{3}$$

Test for free radical :-Free radical involvement in oxidation was studied by adding acrylonitrile that showed gel formation suggesting that free radicals may have been produced as intermediate in the reaction.

The rate law derived on the basis of mechanism explains the inverse dependence of the K_{obs} value on added molybdate ion and accelerating effect of [H⁺] on the D-Glucose oxidation. The stoichiometry of D-Glucose oxidation was found to be 10 moles of 6-molybdocobaltate(III) anion per mole of D-Glucose as represented by **scheme 1** after 24 h.

Rate =
$$\frac{k_1 [D-glucose] [H_5 CoMo_5 O_{20}]^2 [H^+]^2}{([H^+]^2 + K_1 [H_2 MoO_4] [H^+] + K_2 [H_5 CoMo_5 O_{20}]^2 -)}$$
(4)

$$\frac{\text{Rate}}{[\text{H}_{5}\text{CoMo}_{5}\text{O}_{20}]^{2^{-}}} = \text{k}_{\text{obs}} = \frac{\text{k1} [\text{D}-\text{glucose}] [\text{H}^{+}]^{2}}{([\text{H}^{+}]^{2} + \text{K}_{1}[\text{H}_{2}\text{MoO}_{4}] [\text{H}^{+}] + \text{K}_{2}[\text{H}_{5}\text{CoMo}_{5}\text{O}_{20}]^{2^{-}})}$$
(5)

Result and Discussion:

3.1 Effect of Oxidant and substrate concentration:

The effect of oxidant was studied by varying concentration of $[H_6CoMo_6O_{24}]^{-3}$ from 4.0 x 10⁻³ to 8.0 x 10⁻³ mol dm⁻³ at constant [D-Glucose], $[H^+]$, ionic strength and temperature. The pseudo-first-order rate constant was found to decrease with increase in the concentration of oxidant (Table 1). The order with respect to oxidant concentration was determined as ca.- 1.446 from the slopes of linear plots of log K_{obs} against log $[H_6CoMo_6O_{24}]^{-3}$ (**Fig. 4**). A plot of (1/ K_{obs}) against [oxidant] was found to be linear. The effect of D-Glucose was studied by varying its concentration at constant [oxidant] and $[H^+]$ ion together with constant ionic strength and temperature. The pseudo-first-order rate constant was found to remain constant with increasing D-Glucose concentration indicating the order in D-Glucose to be unity **Table 1.** Effect of loxidant] on the pseudo-first-order rate constant

	$(I = 0.2 \text{ mol } dm^{-3}, T = 298 \text{ K})$			
10 ² [D-glucose]	10 ³ [oxidant]	[HClO ₄]	$10^{5}k_{obs} s^{-1}$	
mol dm ⁻³	mol dm ⁻³	$mol dm^{-3}$ $mol dm^{-3}$		
6.0	4.0	0.1	10.25	
6.0	5.0	0.1	7.17	

		-	
Table 1. Effect of [o	xidant] on the pseudo-first-order	rate cons	51
	$(I = 0.2 \text{ mol } dm^{-3}, T = 298 \text{ K})$		
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Figure 4 Plot of Log kobs v/s Log [Hexamolybdocobaltate(III)] 10^{2} [D-Glucose] = 6 moldm⁻³, [HClO₄]= 0.1 moldm⁻³, I= 0.2 moldm⁻³

3.2 Effect of H⁺:-

The effect of $[H^+]$ on the reaction was investigated by varying $[HClO_4]$ from 0.01 to 0.2 mol dm⁻³ at constant [oxidant], [D-Glucose], $[H^+]$, ionic strength and temperature.. With increase in $[H^+]$, the values of the pseudo-first order rate constant were found to increase (Table1). A plot of K_{obs} against $[H^+]$ was linear, indicating first-order dependence on $[H^+]$. The reaction order with respect to H^+ was determined as 0.80 from the plot (**Figure 5**).

	Table 2. Effect of [H	IClO ₄] on the pseudo	-first-or <mark>der rate consta</mark> r	nt (I = 0.2 mol dm^{-3} , T= 298 K)
	10 ² [D-glucose]	10 ³ [oxidant]	[HClO ₄]	$10^5 k_{obs} s^{-1}$	
	mol dm ⁻³	mol dm ⁻³	mol dm ⁻³		
-	6.0	5.0	0.01	1.02	
	6.0	5.0	0.02	1.68	
	6.0	5.0	0.05	3.57	
	6.0	5.0	0.1	7.17	
	6.0	5.0	0.2	10.34	



Figure 5 Plot of Log kobs v/s Log [H⁺]

3.3 Effect of added molybdate:

The effect of added molybdate to reaction mixture was studied by keeping all other conditions constant. Increase in concentration of added molybdate decelerated the values of rate constant (Table 3). A plot of $(1/k_{obs})$ against [molybdate] was found to be linear as shown in **Figure 6**. The rate equation (5) was confirmed by plotting a graph of 1/k against [H₂MoO₄] concentration and 1/k against [oxidant] concentration.

Table 3. Effect of $[MoO_4^{2-}]$ on the pseudo-first-order rate constant. (I = 0.2 mol dm ⁻³ , T= 298 K)						
10 ² [D-glucose]] 10 ³ [oxidant]	[HClO ₄]	$10^{3}[MoO_{4}^{2}]$	$10^{5} k_{obs} s^{-1}$		
mol dm ⁻³	mol dm ⁻³	mol dm ⁻³	mol dm ⁻³			
6.0	5.0	0.1	1.0	5.40		
6.0	5.0	0.1	3.0	4.52		
6.0	5.0	0.1	5.0	3.83		
6.0	5.0	0.1	6.0	3.32		

3.4 Effect of ionic strength, solvent polarity and Temperature:

Sodium perchlorate and acetonitrile were used to vary the ionic strength and the solvent polarity respectively. The values of pseudo-first-order rate constants remains constant with increase in ionic strength and the solvent polarity under experimental conditions. The reaction rate was measured at variable temperature, keeping all other conditions constant. With increase in temperature, the rate of reaction accelerated. The rate constants for oxidation of D-Glucose at different temperatures were calculated (Table 4). Activation energy and other parameters were determined from graphs of log K_{obs} against (1/T) (**Fig. 6**).

Table 4. Effect of temperature on the pseudo-first-order rate constant

	$(10^3[\text{Oxidant}] = 5.0 \text{ mol})$	dm-3, 102[D-glu	cose] = 6.0 mol dr	m^{-3} , [HClO ₄] = 0.1 mol	$I dm^{-3}$, $I = 0.2 mol dm^{-3}$)
Т	$10^5 \rm \ k_{obs} \ s^{-1}$	Ea	$\Delta H^{\#}$	$\Delta S^{\#}$	$\Delta G^{\#}$
		kJ mol ⁻¹	kJ mol ⁻¹	J K ⁻¹ mol ⁻¹	kJ mol ⁻¹
288	5.22				
298	7.17				
303	9.42	43.14 ± 3	40.66 ± 3	-165.26 ± 5	89.90 ± 3
308	13.1				
313	16.6				



Figure 6 Arrhenius plot for D-Glucose oxidation

The Anderson-Evans structure of 6-molybdocobaltate(III), $[H_6CoMo_6O_{24}]^{3-}$ anion consisting six nonionisable protons is reported more compact than other Keggin-type 12-tungstocobaltate(III) [22]. The cobalt ion in the structure of $[H_6CoMo_6O_{24}]^{3-}$ is surrounded by six octahedral molybdenum ions and the associated 24 oxide ion. Six proton attached to the oxide ion in the $[H_6CoMo_6O_{24}]^{3-}$ are non-ionizable [19] and other three are strongly ionizable. The species $[H_6CoMo_6O_{24}]^{3-}$ is a strong acid, therefore in solution it exits as a free ion with three negative charges without any protonation even in acidic solution. The $[H_6CoMo_6O_{24}]$ group is made up of a compact package of six MoO₆ which are surrounding one XO₆ in a planar hexagonal configuration, with approximative overall D₃d symmetry [26].

Effect of Enolization on the Oxidation: In aqueous solution, an aldose molecule exists in acyclic (aldehyde and hydrated) and cyclic (pyranose and furanose) forms in dynamic equilibrium. Pyranose is thermodynamically stable and furanose is kinetically stable form [27]. In acidic solution various equillibria of D-Glucose are known [28].



At room temperature the distribution of these species is reported to be 36% of α -D- Glucopyranose, 64% β -D-Glucopyranose and the percentage of other forms are negligible. Conversion of D-Glucose into α - and β -D-Glucopyranose in aqueous acidic solution is so rapid that cannot be rate determining.

Conclusion:

The active oxidant species is $[H_5Co^{III}Mo_6O_{24}]^{2-}$ anion. Under experimental conditions, D-Glucose exists in unprotonated form. It has been reported that, $[H_5CoMo_5O_{20}]^{-3}$ anion dissociates with the loss of molybdate units in the form of $[HMoO_4]^{1-}$ and produces the active oxidant $[H_5CoMo_5O_{20}]^{-2}$ anion. Further, $[H_5CoMo_5O_{20}]^{-2}$ anion dimerises to produce $[H_4Co_2Mo_{10}O_{38}]^{-6}$. The deceleration in rate of reaction with increase in [oxidant] is due to dimerisation of active oxidant to $[H_4Co_2Mo_{10}O_{38}]^{-6}$ species, thus reducing its concentration.

The reaction involves direct electron transfer from D-Glucose center to the oxidant anion generating free radicals in a rate determining step. The free radical reacts fast with another five oxidant molecules to produce formaldehyde after successive C-C oxidative cleavage. The reaction is accelerated by hydrogen ion concentration. The catalytic effect of hydrogen ion concentration on the reaction is due to the dimerisation of active oxidant $[H_5Co^{III}Mo_6O_{24}]^{2-}$ anion. From the activation energy was calculated to be 43.14 KJmol⁻¹. And $\Delta G^{\#}$ was calculated to be 89.90 KJmol⁻¹, which is less than O-H bond dissociation energy (460 KJ/Mole) suggesting direct electron transfer during oxidation. The activation parameters determined supports the outer sphere nature of the reaction. The change in ionic strength and solvent polarity did not affect the rate of the reaction. A complex rate on the basis of probable mechanism was derived and verified.

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