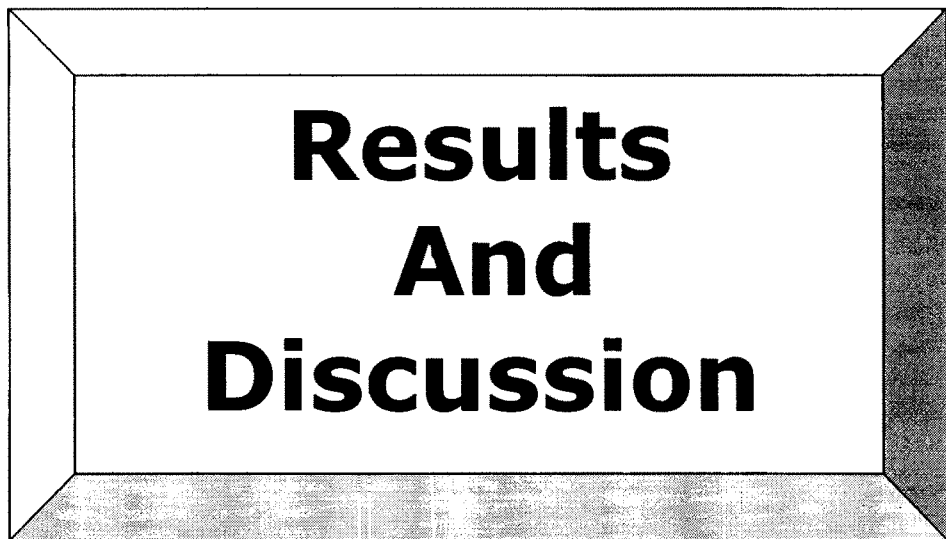


CHAPTER -III



Introduction

Heteropolyoxometalates[1] are very good candidates for homogeneous outer-sphere electron transfer processes. These are also used extensively as model systems for fundamental research providing a unique opportunities for mechanistic studies on molecular level. One such complex, the 12-tungstocobaltate(III) is also known[1] as soluble anode as it acts as a one-electron outer-sphere oxidant. Transition metal substituted heteropolyoxometalates exhibit different chemical and electrochemical properties, which makes them attractive for catalytic[1-3] and electrocatalytic[4] applications.

The hexamolybdo compounds of trivalent ions like aluminium, chromium, iron and cobalt are quite stable[5,6] and are easily prepared. The isomorphism between Cr^{III} , Co^{III} and Fe^{III} hexamolybdates has been established chemically[6] and crystallographically[7]. Amongst the polyoxometalates Keggin type 12-tungstocobaltate(III) ion has received considerable attention as an oxidant for the oxidation of various inorganic and organic substrates. Hexamolydocobaltate(III) ion resembles that of 12-tungstocobaltate(III) ions in its inertness for the substitution but has received comparatively less attention. Therefore, in continuation of our earlier work[8,9] on the oxidations by polyoxometalates herein we report the 6-molybdocobaltate(III) oxidation of ethanediol and propanediol in acidic medium.

Results

The stoichiometry for the reaction between ethanediol and $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ was studied by performing the product analysis as follows. Ethanediol(2mmol, 0.12 ml) and $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ (0.2 mmol, 2.2gm) were dissolved in 20 ml of 0.2 mol dm^{-3} HClO_4 . The reaction mixture was allowed to stand for 10 hr and it was treated with saturated solution of 2,4-dinitrophenylhydrazine. The solid formed was filtered and recrystallized from ethanol. The mp of the product was found to be 165°C which matches with the 2,4-DNP derivative of formaldehyde. Therefore, the stoichiometry was found to be 2 moles of $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ per mole of ethanediol.

The stoichiometry for the reaction between propanediol and $[\text{H}_5\text{CoMo}_6\text{O}_{24}]^{3-}$ was studied by performing the product analysis as follows. Propanediol and $[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-}$ (0.2 mmol, 2.2 gm) were dissolved in 20 ml of 0.2 mol dm⁻³ HClO₄. The reaction mixture was allowed to stand for 10 hours to ensure completion of the reaction. It was then treated overnight with an excess of saturated solution of 2,4-dinitrophenylhydrazine (DNP) was filtered off, dried, recrystallized from ethanol and weighed. In these cases the mixture of product will be obtained. The identity of products was confirmed by using mixed melting points. Therefore stoichiometry was found to be 2 moles of $[\text{H}_6\text{Co(III)Mo}_6\text{O}_{24}]^{3-}$ per mol of propanediol.

Reaction Order

The reaction was studied under pseudo-first-order condition keeping large excess of diols to that of $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$. The pseudo-first-order rate constants, k_{obs} , of the reaction (Table 3.1) remain unchanged as the concentration of diols increases from 0.2 to 1.2 mol dm⁻³ indicating first-order dependence of the reaction on their concentration. Whereas the pseudo-first-order rate constants decrease with increase in concentration of the oxidant, $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ (Table 3.2). The order in oxidant concentration was found to be -0.3 as determined (Figure 3.1 and 3.2) from the log k_{obs} against log $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$. The increasing $[\text{H}^+]$ increases the values of pseudo-first-order rate constants (Table 3.3) with an order of 1.4 in $[\text{H}^+]$ (Figure 3.3 and 3.4) as determined from the plots of log k_{obs} against log $[\text{H}^+]$. The added molybdate between the concentration of 1.0×10^{-3} to 1.0×10^{-2} mol dm⁻³ decreases the values of k_{obs} (Table 3.4). The effect of ionic strength and solvent polarity on the reaction was studied by varying the concentration of sodium perchlorate (0.5 to 1.0 mol dm⁻³) and acetonitrile (0-50% v/v). The data of effect of ionic strength and solvent polarity are given in Table 3.5 and 3.6 respectively. There was no effect of ionic strength and change in solvent polarity on the reaction as the k_{obs} values remain unaffected. The effect of temperature was studied at 15, 20, 25, 30 and 35 °C (Table 3.7) and the activation parameters for $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ oxidation of ethanediol and propanediol were calculated from

the plots of $\log k_{\text{obs}}$ and $\log k_{\text{obs}}/T$ against $1/T$ (Figures 3.5 to 3.8). The activation parameters thus calculated are tabulated in Table 3.8.

Table 3.1

Effect of diols on the oxidation of Ethanediol and Propanediol by 6-molybdocobaltate(III) at 25 °c.

$$10^3[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-} = 5.0 \text{ mol dm}^{-3}, [\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}, I = 0.6 \text{ mol dm}^{-3}$$

[Diol] mol dm ⁻³	10 ⁴ k _{obs} s ⁻¹	
	Ethanediol	Propanediol
0.2	3.8	5.2
0.5	3.8	5.2
0.8	3.8	5.3
1.0	3.8	5.2
1.8	3.8	5.2

Table 3.2

Effect of oxidant on the oxidation of Ethanediol and Propanediol by 6-molybdocobaltate(III) at 25 °c.

[Diol] = 0.5 mol dm⁻³ , [HClO₄] = 0.5 mol dm⁻³ , I = 0.6 mol dm⁻³

10 ³ [H ₆ CoMo ₆ O ₂₄] ³ mol dm ⁻³	10 ⁴ k _{obs} s ⁻¹	
	Ethenediol	Propanediol
2.0	5.5	7.4
5.0	3.8	5.2
10.0	3.3	4.4
15.0	3.1	3.9
20.0	2.6	3.2

Figure 3.1

Order in [Oxidant] ; Plot of $\log[\text{Oxidant}]$ against $\log k_{\text{obs}}$ for ethanediol.

(Conditions as in Table 3.2)

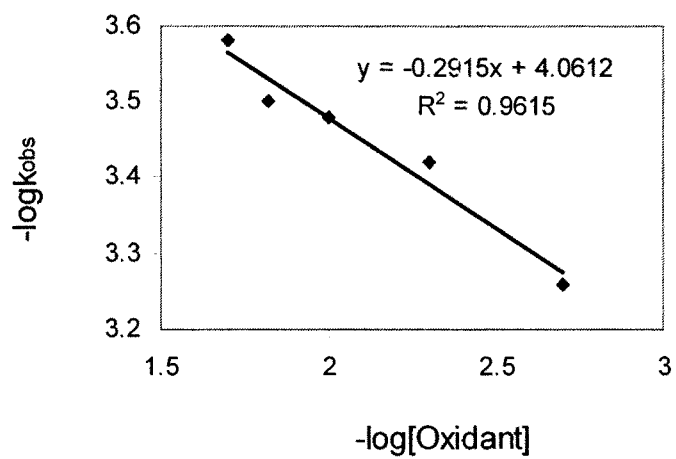


Figure 3.2

Order in [Oxidant] ; Plot of $\log[\text{Oxidant}]$ against $\log k_{\text{obs}}$ for propanediol.

(Conditions as in Table 3.2)

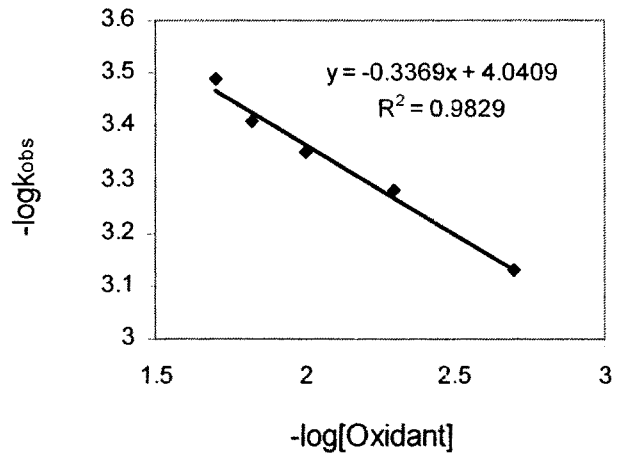


Table 3.3

Effect of $[H^+]$ on the oxidation of Ethanediol and Propanediol by 6-molybdocobaltate(III) at 25 °c.

$$10^3 [H_6CoMo_6O_{24}]^{3-} = 5.0 \text{ mol dm}^{-3}, [\text{Diol}] = 0.5 \text{ mol dm}^{-3}, I = 0.6 \text{ mol dm}^{-3}$$

$[HClO_4] \text{ mol dm}^{-3}$	$10^4 k_{\text{obs}} \text{ s}^{-1}$	
	Ethanediol	Propanediol
0.05	0.1	0.2
0.1	0.3	0.7
0.3	0.7	1.5
0.4	1.6	3.0
0.5	3.8	5.2

Figure 3.3

Order in $[H^+]$; Plot of $\log[H^+]$ against $\log k_{obs}$ for ethanediol.

(Conditions as in Table 3.3)

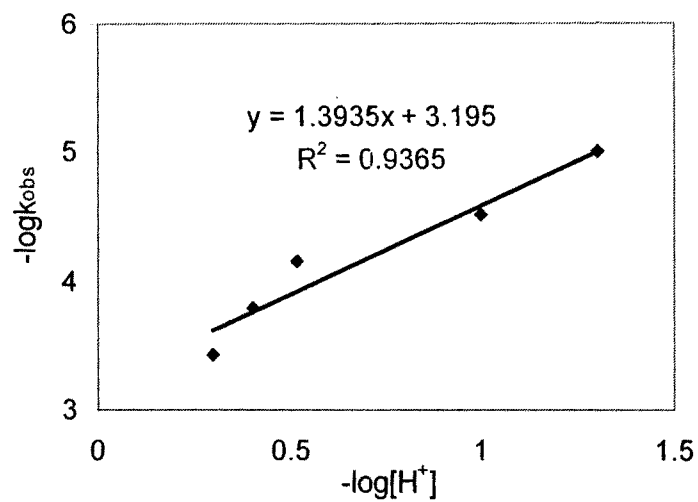


Figure 3.4

Order in $[H^+]$; Plot of $\log[H^+]$ against $\log k_{obs}$ for propanediol.
(Conditions as in Table 3.3)

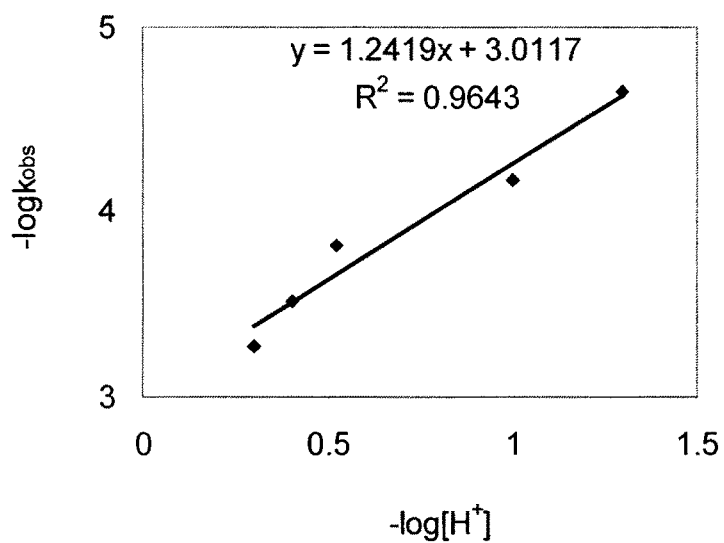


Table 3.4

Effect of [Molybdate] on the oxidation of Ethanediol and Propanediol by 6-molybdocobaltate(III) at 25 °c.

$$10^3 [\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-} = 5.0 \text{ mol dm}^{-3}, [\text{Diol}] = 0.5 \text{ mol dm}^{-3}, [\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}$$
$$I = 0.6 \text{ mol dm}^{-3}$$

$10^3 [\text{Molybdate}]$ mol dm^{-3}	$10^4 k_{\text{obs}} \text{ s}^{-1}$	
	Ethanediol	Propanediol
0.0	3.8	5.2
1.0	2.3	3.4
5.0	0.52	2.0
7.0	0.38	1.0
10.0	0.22	0.5

Table 3.5

Effect of Ionic strength on the oxidation of Ethanediol and Propanediol by 6-molybdocobaltate(III) at 25 °c.

$$10^3[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-} = 5.0 \text{ mol dm}^{-3}, [\text{Diol}] = 0.5 \text{ mol dm}^{-3}, [\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}$$

Ionic strength mol dm ⁻³	10 ⁴ k _{obs} s ⁻¹	
	Ethanediol	Propanediol
0.52	3.5	5.2
0.55	3.6	5.1
0.51	3.7	5.2
0.52	3.8	5.2
0.6	3.8	5.1
1.0	3.8	5.2

Table 3.6

Effect of Dielectric constant on the oxidation of Ethanediol and Propanediol by
6-molybdocobaltate(III) at 25 °c.

$10^3[\text{H}_3\text{CoMo}_6\text{O}_{24}]^{3-} = 5.0 \text{ mol dm}^{-3}$, $[\text{Diol}] = 0.5 \text{ mol dm}^{-3}$, $[\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}$
 $I = 0.6 \text{ mol dm}^{-3}$

% Acetonitrile	$10^4 k_{\text{obs}} \text{ s}^{-1}$	
	Ethanediol	Propanediol
0.0	3.8	5.2
20	3.8	5.2
30	3.8	5.2
40	3.9	5.1
50	3.8	5.2

Discussion

The electron transfer reactions involving polyoxometalates (PMO) generally proceed with an outer-sphere path and amongst these PMO's the Keggin type 12-tungstocobaltate has received considerable attention as an oxidant for several organic as well as inorganic reductants. Comparatively less attention has been given in the literature to other PMO's like Anderson type 6-molybdocobaltate(III), $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$. The cobalt ion in the structure of $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ is surrounded by six octahedral molybdenum ions and the associated 24 oxide ions. Six protons attached to the oxide ions in the $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ are non ionisable [12] and other three are strongly ionisable. Since the ion $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ is a strong acid, in solution it exists as free ion with three negative charge without any protonation even in acidic medium. The $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ ion has the Anderson-Evans Structure with six non-ionisable protons. Therefore, the formula of the 6-molybdocobaltate(III) is written as $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ incorporating the six non-ionisable protons within the bracket representing the ion. It is also observed that the $[\text{H}_6\text{Co}^{\text{III}}\text{Mo}_6\text{O}_{24}]^{3-}$ loses molybdate [10] units as a result of dissociation and dimerises in solution to give $[\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]^{6-}$. The dimerization has inverse dependence on the hydrogen ion concentration in the solution. In the present study the k_{obs} values were found to be constant as concentration of diol increases (Table 3.1) indicating an order of unity in its concentration where as the values decrease as the concentration of oxidant increases (Table 3.2). The order in oxidant concentration was found to be negative. The added molybdate between the concentration range of 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3} decreases the values of k_{obs} showing an inverse dependence on the molybdate ion concentration (Table 3.4).

Table 3.7

Effect of temperature on the oxidation of Ethanediol and Propanediol by 6-molybdocobaltate(III).

$$10^3 [\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-} = 5.0 \text{ mol dm}^{-3}, [\text{Diol}] = 0.5 \text{ mol dm}^{-3}, [\text{HClO}_4] = 0.5 \text{ mol dm}^{-3}$$

$$I = 0.6 \text{ mol dm}^{-3}$$

T K	$10^3(1/T)$	$10^4 k_{\text{obs}} \text{ s}^{-1}$		-log k_{obs}		-log (k_{obs}/T)	
		Ethane diol	Propane diol	Ethane diol	Propane diol	Ethane diol	Propane diol
288	3.47	2.1	2.3	3.67	3.59	6.13	6.09
293	3.42	2.6	3.8	3.58	3.42	6.05	5.89
298	3.35	3.8	5.2	3.42	3.27	5.89	5.74
303	3.30	6.1	6.9	3.22	3.16	5.69	5.64
313	3.25	11.0	9.6	2.96	3.01	5.45	5.5

Figure 3.5

Plot of $\log[k_{\text{obs}}]$ against $(1/T)$ for ethanediol.
(Conditions as in Table 3.7)

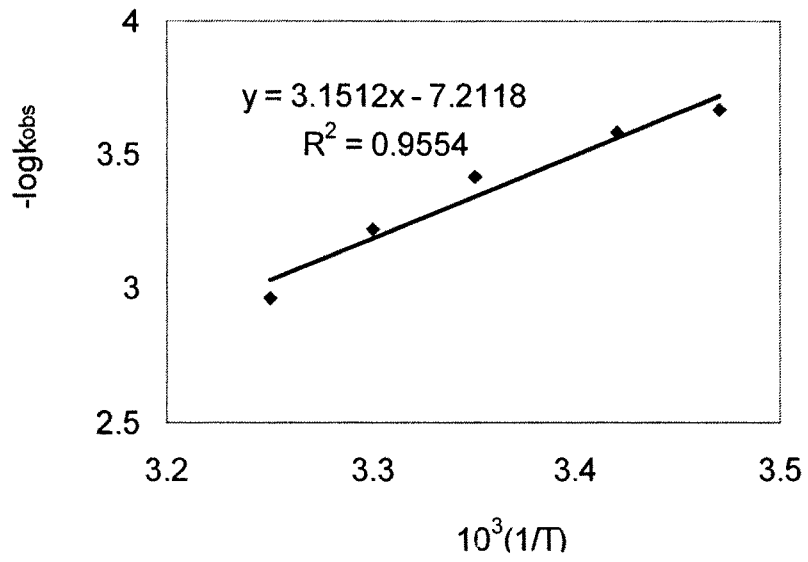


Figure 3.6

Plot of $\log[k_{\text{obs}}]$ against $(1/T)$ for propanediol.

(Conditions as in Table 3.7)

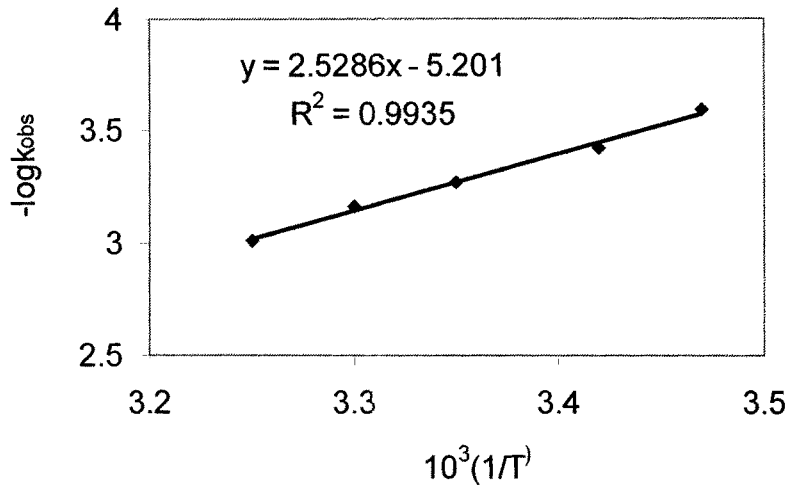


Figure 3.7

Plot of $\log(k_{\text{obs}}/T)$ against $(1/T)$ for ethanediol.

(Conditions as in Table 3.7)

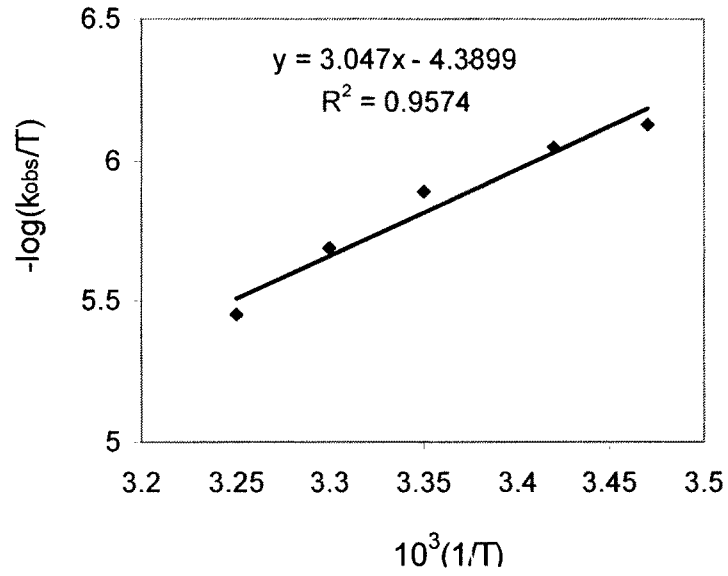


Figure 3.8

Plot of $\log(k_{\text{obs}}/T)$ against $(1/T)$ for propanediol.
(Conditions as in Table 3.7)

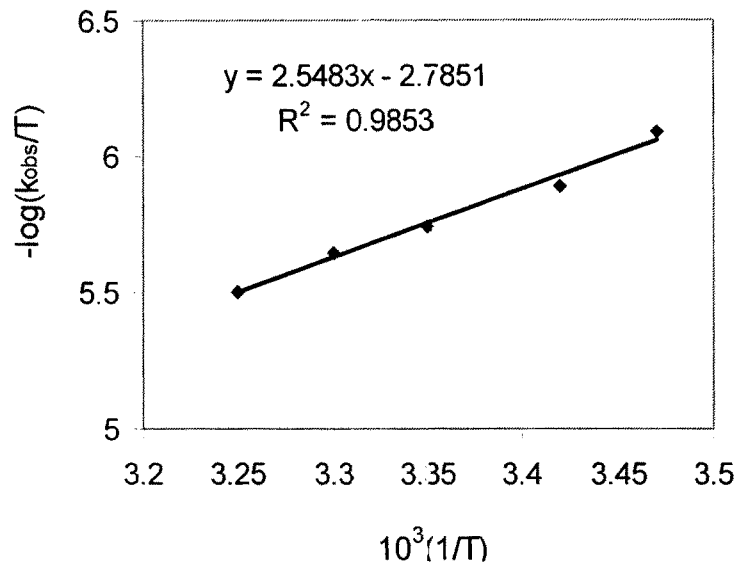
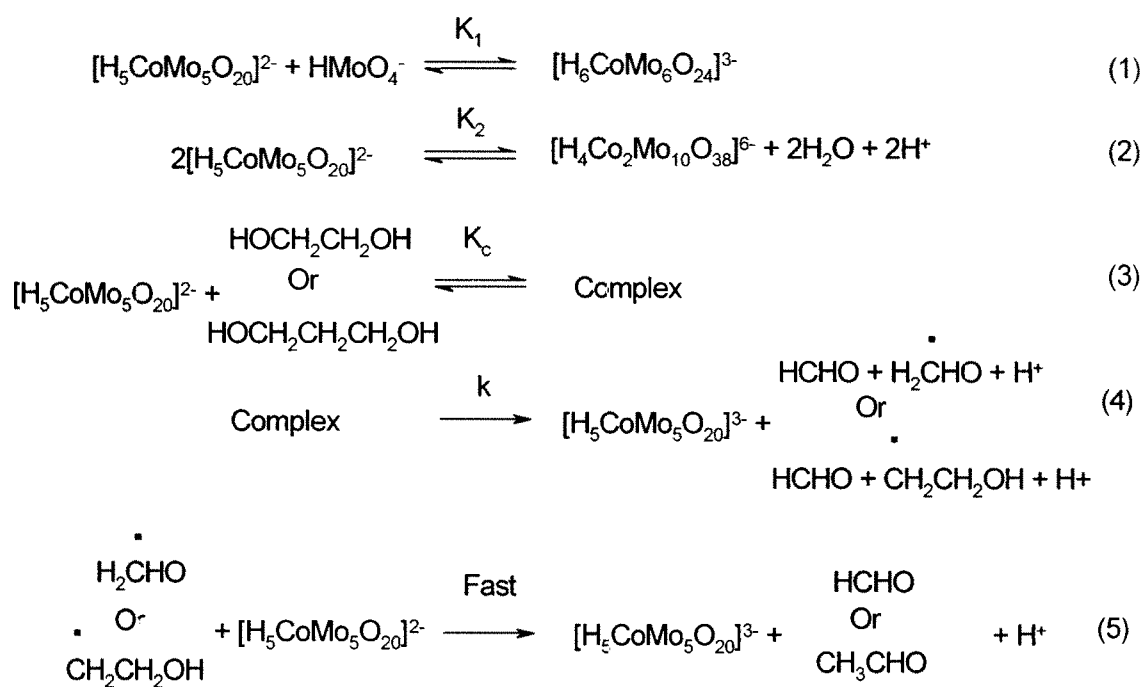


Table 3.8

Activation parameters of the oxidation of Ethanediol and Propanediol by 6-molybdocobaltate(III).

	Ethanediol	Propanediol
E_a kJmol ⁻¹	60.7 ± 3	48.7 ± 3
ΔH^\ddagger kJmol ⁻¹	58.7 ± 6	49.1 ± 6
ΔG^\ddagger kJmol ⁻¹	92.8 ± 6	94.76 ± 6
$-\Delta S^\ddagger$ JK ⁻¹ mol ⁻¹	114.6 ± 6	153.3 ± 5

The kinetic data of the present study suggest that the active oxidant species will be consumed in a prior equilibria involving its interaction with molybdate ion and another prior equilibria in which it is formed at the expense of hydrogen ions. As mentioned earlier (the) it has been reported that the 6-molybdocobaltate(II) ion dissociates with the loss of molybdate units. Since, the oxidant, 6-molybdocobaltate(III) ($[H_6CoMo_6O_{20}]^{3-}$) is isost^ystructural with 6-molybdocobaltate(II) it will be losing a molybdate unit in the form of $HMoO_4^-$, and produces the active oxidant species $[H_5CoMo_5O_{20}]^{2-}$. Further this active oxidant species undergo dimerization to form $[H_4Co_2Mo_{10}O_{38}]^{6-}$. Therefore on the basis of kinetic data the active oxidant species is $[H_5CoMo_5O_{20}]^{2-}$ which interact with $HMoO_4^-$ ion to form an inactive $[H_6CoMo_6O_{20}]^{3-}$ thus explaining the inverse dependence on the molybdate ion concentration. The catalytic effect of hydrogen ion concentration on the reaction is due to the dimerization of the $[H_5CoMo_5O_{20}]^{2-}$ which is inhibited by the hydrogen ions. The active oxidant $[H_5CoMo_5O_{20}]^{2-}$ will form a complex with the substrate, diol, which decomposes in the rate determining step to give the free radical and aldehyde molecule. The free radical produced in the rate determining step reacts in a fast step with another oxidant molecule to produce aldehyde. The detailed mechanism of the reaction involving all these considerations can be represented in Scheme 1 and the corresponding rate law is given by equation 1. The rate law derived on the basis of Scheme 1 explains the inverse dependence of the k_{obs} value on molybdate ion and accelerating effect of hydrogen ion concentration on the reaction. The decrease in the rate of reaction as the concentration increases is due to the formation of dimerization of the active oxidant, $[H_5CoMo_5O_{20}]^{2-}$, thus reducing its concentration.



Scheme 1

According to Scheme 1 the rate law can be derived as follows

$$\text{Rate} = k[\text{Complex}] \quad (6)$$

$$= kK_c [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-} [\text{Diol}] \quad (7)$$

But from equilibrium 1 and 2 of Scheme 1 we have

$$K_1 = \frac{[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-}}{[\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-} [\text{HMoO}_4]^-}$$

$$[\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-} = K_1 [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-} [\text{HMoO}_4]^- \quad (8)$$

$$\text{and } K_2 = \frac{[\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]^{6-} [\text{H}^+]^2}{([\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-})^2}$$

$$[\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]^{6-} = \frac{K_2([\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-})^2}{[\text{H}^+]^2} \quad (9)$$

Therefore total $[\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}$ is given by

$$[\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_T = [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}} + [\text{H}_6\text{CoMo}_6\text{O}_{24}]^{3-} + [\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]^{6-} \quad (10)$$

From equations (8) and (9)

$$\begin{aligned} [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_T &= [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}} + K_1 [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}} [\text{HMoO}_4]^- \\ &\quad + \frac{K_2 ([\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}})^2}{[\text{H}^+]^2} \end{aligned}$$

$$[\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_T = [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}} (1 + K_1 [\text{HMoO}_4]^-) + \frac{K_2 ([\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}})^2}{[\text{H}^+]^2}$$

$$[\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_T = [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}} \frac{([\text{H}^+]^2 + K_1 [\text{H}^+]^2 [\text{HMoO}_4]^- + K_2 ([\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}})^2)}{[\text{H}^+]^2}$$

$$[\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}} = \frac{[\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_T [\text{H}^+]^2}{([\text{H}^+]^2 + K_1 [\text{H}^+]^2 [\text{HMoO}_4]^- + K_2 [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}})} \quad (10)$$

Substituting equation (10) in rate equation (7) we get

$$\text{Rate} = \frac{kK_c [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_T [\text{H}^+]^2 [\text{Diol}]}{([\text{H}^+]^2 + K_1[\text{H}^+]^2[\text{HMoO}_4]^- + K_2 [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}})}$$

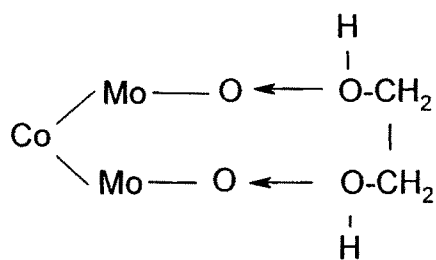
and the pseudo-first-order constant will be given by equation (11)

$$k_{\text{obs}} = \frac{kK_c [\text{H}^+]^2}{([\text{H}^+]^2 + K_1[\text{H}^+]^2[\text{HMoO}_4]^- + K_2 [\text{H}_5\text{CoMo}_5\text{O}_{20}]^{2-}_{\text{Free}})} \quad (11)$$

The oxidation of diols by various oxidants [11-13] has been studied and the reactions proceed either by the cleavage of C-C or C-H bonds. The former path produces formaldehyde [11] as the product where as the later leads to formation of acetaldehyde alcohol¹⁴. The reported values of entropies for the C-C cleavage[11,13] is of the order of 160 JK⁻¹mol⁻¹ while that of C-H cleavage[12] is about 80 JK⁻¹ mol⁻¹. The entropy of activation during the C-C cleavage involve a cyclic transition state resulting in large decrease in entropy in comparison with the C-H cleavage path. In the present study the entropy of activation obtained is 152.5 JK⁻¹mol⁻¹ and the product obtained is formaldehyde which indicates the C-C cleavage as the probable path involving a cyclic transition state as shown in Figure 3.9. A decrease in entropy of the reaction may be attributed to the transition state formed between the substrate and the oxidant. The oxidant is an outer-sphere reagent and the transition state is probably replacement of one of its hydrated water molecule by the oxidant. The transition state is less solvated and is more stabilized in a medium of low relative permittivity.

Figure 3.9

Structure of the probable transition state.



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