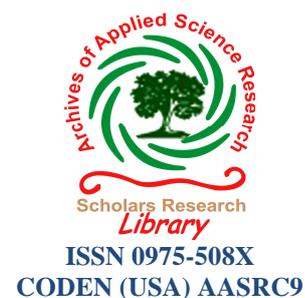




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Kinetics and Mechanism of Oxidation of Allyl Alcohol in Perchloric Acid Medium by Waugh-Type Enneamolybdomanganate(IV)

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ABSTRACT

Two-electron transfer complimentary reaction between Waugh type enneamolybdomanganate(IV) and allyl alcohol is investigated in perchloric acid medium. The reaction is first order with respect to both the reactant and the order with respect to H^+ ion is 1.45. The activation parameters were also determined and a possible complimentary two electron transfer mechanism is suggested for the reaction between allyl alcohol and Waugh-Type Enneamolybdomanganate(IV)

Key Words: Allyl Alcohol, Oxidation, Waugh-Type Enneamolybdomanganate(IV).

INTRODUCTION

Most versatile and environmental friendly oxidizing agent comes under the group of polyoxometalates(POMs) like polytungstates, molybdates, silicotungstates and phosphotungstates. In recent years these POMs are used in medicines for AIDS treatment[1], radioactive waste treatment, oxidant for polymers, thin film electro-chromic devices[2], transformation of wood-pulp into papers, radioactive waste treatment and many other applications. Hence necessity of understanding the reaction mechanism of POM mediated reactions, motivates this work. Transition metal substituted heteropolymetalates exhibit different chemical and electrochemical properties, which makes them attractive for catalytic and electro-catalytic applications[3]. These attractive features include stability under highly oxidizing conditions, availability of a variety of transition metal ions, which can be incorporated into the heteropolymetalate structure with variable oxidation states, reversible oxidation and reduction of the incorporated metal ion and ability to modify the formal redox potentials[4]. Modification of the properties of a metal ion by complexation with other ions is required for their utility in many applications like electro-optics, corrosion protection, dopant in non-conducting polymers, radioactive waste treatment, photochemical cells[5-7], redox flow cells[8,9], electrochemical reaction initiators[10,11], electron acceptors for hydrogen reduction[12] and electro-catalysis[13,14]. The complexed ions may be simple anions or oxoanions such as tungstate or molybdate. The redox potential of 1.82V[15] for the Co^{3+}/Co^{2+} couple decreases to 1.0 V[16] 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 larger area. In isopoly and heteropolymetalates charge density is considerably lower than those observed in traditional anions like ClO_4^- and NO_3^- , due to which complexes of transition metal ions with polyoxoanions like polytungstates are well known outer-sphere electron transfer reagents[17a] that trivial oxidizing agents[17b] and the properties of the metal ions will be altered, increasing their stability considerably in aqueous solutions.

In the present study a two-electron transfer complimentary reaction between Waugh type enneamolybdomanganate(IV) and allyl alcohol is investigated. Ammonium enneamolybdomanganate(IV) is a Waugh-type heteropolyacid salt in which manganese is coordinated to six oxygen atoms in a slightly distorted octahedral arrangement. Each of these oxygen atoms is coordinated to three molybdenum atoms and each molybdenum is also surrounded by six atoms in a much distorted octahedral geometry. It can oxidize organic as well as inorganic substrates[18] but there are very few reports on the study of kinetics and mechanism[19] involving this heteropolyacid salt. Oxidation of Mn(II) as a hetero-atom, by various oxidants in presence of oxometalate anions like MoO_4^{2-} and its mechanism have been studied recently. The work was carried out to develop a method for generating manganic heteropolyoxometalate in its higher oxidation state, Mn(IV).[20] Under ordinary reaction conditions and in absence of oxometalate anions, the oxidation of mn(II) generally leads to a solid manganese dioxide. This solid form of Mn(IV) also used as a heterogeneous catalyst and oxidant in many organic reactions. Therefore, it is necessary to understand the path followed by the oxidation reactions of Mn(IV), and in the present study a soluble complex, $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ was used as an oxidant. Herein we report the oxidation of allyl alcohol with Waugh-Type Enneamolybdomanganate(IV).

MATERIALS AND METHODS

2.1 Materials

The solution of oxidant was prepared in doubly distilled water. The ammonium salt of Mn(IV) complex, $(\text{NH}_4)_6[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]$ was prepared by reported method[21] and recrystallized thrice from hot (80°C) water. The 0.01 mol dm^{-3} solution of $(\text{NH}_4)_6[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]$ was standardized by iodometric method. AAS analysis of Mn and Mo using Perkin-Elmer AAnalyst-300 shows Mn- 3.501 % (3.4493 %) and Mo- 54.217 % (54.2125 %). IR-spectrum of Mn(IV) complex shows the peaks 3521 cm^{-1} , 933 cm^{-1} , 918 cm^{-1} and 900 cm^{-1} corresponds to lattice water molecules (as noted in TGA of the Mn(IV) complex at about 90 to 100°C), Mo-O stretching, Mn^{IV} -O stretching and tetrahedral MoO_4^{2-} groups, respectively.[22]

The Mn(II) complex, $(\text{NH}_4)_8[\text{Mn}^{\text{II}}\text{Mo}_9\text{O}_{32}]$, was prepared by reported method crystals were recrystallized thrice from hot (80°C) water. AAS analysis shows Mn- 3.378% (3.3729%) and Mo- 52.924% (53.0117%). In IR of Mn(II) complex metal oxygen stretching frequency is observed at 887 cm^{-1} . [22]

2.2 Kinetic Study

The reaction between $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ and allyl alcohol was carried out under pseudo-first-order conditions in Perchloric acid medium at a constant temperature of $30.0 \pm 0.1^\circ\text{C}$. The reaction was initiated by mixing the previously thermostated solutions of allyl alcohol and $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ containing required amount of perchloric acid. The ionic strength was maintained by using sodium perchlorate. The reaction is followed by decrease in concentration of $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ iodometrically and the rate constants were determined from the pseudo-first-order plots of

log[oxidant] against time. The pseudo-first-order plots were linear for more than 80% completion of the reaction and the rate constants were reproducible within $\pm 4\%$.

RESULTS

3.1 Stoichiometry

The stoichiometry was studied by keeping concentration of $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ constant at $8 \times 10^{-3} \text{ mol dm}^{-3}$ and varying concentration of allyl alcohol from 0.5×10^{-3} to $6 \times 10^{-3} \text{ mol dm}^{-3}$. The number of reaction mixtures containing varying concentration of allyl alcohol was prepared in 0.1 mol dm^{-3} of perchloric acid solution. The concentration of un-reacted $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ was determined after 24 hours. The stoichiometry was found to be one mole of $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ per mole of allyl alcohol. The product acraldehyde was also confirmed by 2-4-DNP derivative.

3.2 Reaction order

The reaction was carried out under pseudo-first-order conditions in 0.1 mol dm^{-3} of perchloric acid solution and varying either [allyl alcohol] from 1×10^{-2} to $4 \times 10^{-2} \text{ mol dm}^{-3}$ at constant $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ ($2 \times 10^{-3} \text{ mol dm}^{-3}$) or varying $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ from 0.5×10^{-3} to $5 \times 10^{-3} \text{ mol dm}^{-3}$ at constant concentration of allyl alcohol ($2.5 \times 10^{-2} \text{ mol dm}^{-3}$). The pseudo-first-order plots were found to be linear. When allyl alcohol was kept constant by varying the concentration of $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ then the pseudo-first-order rate constants were fairly constant (Table 1) indicating the order in oxidant to be unity. Since the pseudo-first-order rate constant increases linearly with increase in concentration of allyl alcohol, the order in substrate concentration is also unity confirmed by plot of $\log k_{\text{obs}}$ against $\log[\text{Allyl alcohol}]$ whose slope is unity. Free radical during the reaction was not detected by studying the reaction in presence of acrylonitrile.

3.3 Effect of H^+ ion concentration, ionic strength, temperature and solvent polarity

The effect of hydrogen ions concentration was carried out, in order to understand the nature of reactant species present in the solution. The concentration of $[\text{H}^+]$ was varied between 0.01 to 0.1 mol dm^{-3} keeping all other reactant constant. To vary the concentration of $[\text{H}^+]$ sodium perchlorate was used. The increase in rate was observed on increase in concentration of hydrogen ion. The order in $[\text{H}^+]$ ion was found to be 1.45 as determined from the plot of $\log(k_{\text{obs}})$ versus $\log[\text{H}^+]$. The effect of ionic strength and solvent polarity was studied keeping all other reactants constant. Sodium perchlorate and acetonitrile were used to vary the ionic strength and the solvent polarity respectively. The rate of the reaction increases as percentage of acetonitrile (from 0 to 50 % vol.) and increase in ionic strength (from 0.2 to 1.2 mol dm^{-3}). The relative permittivities of the reaction mixtures were computed from the values of the pure solvents and the plot of $\log k_{\text{obs}}$ against $1/D$ was found to be linear with positive slope. The reaction was studied at 25, 30, 35, and 40°C and the kinetic data and the activation parameters $\Delta H^\ddagger = 32.8 \text{ kJ mol}^{-1}$, $\Delta G^\ddagger = 42.6 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -115 \text{ J mol}^{-1}$ for the reaction.

DISCUSSION

pH-metric titration shows that the anion, $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ undergoes successive protonation in acidic solution as given in equations 1 to 6, with pK_1 at 3.3 and pK_2 at 2.75 corresponding to mono and di-protonated species of $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ respectively.[22] Further protonation constants are very close to each other.

In another experiment, $[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]^{6-}$ complex was treated with 10 mol dm^{-3} of HClO_4 , it gives a deep brown colored precipitate of hexa-protonated species, $\text{H}_6[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]$. This $\text{H}_6[\text{Mn}^{\text{IV}}\text{Mo}_9\text{O}_{32}]$ is unstable and undergoes deprotonation in aqueous solution containing less

amount of H^+ ions. In present experimental conditions only mono and di-protonated species were formed, which are the active species of the reaction. Further the order with respect to H^+ ion concentration was found to be greater than one, which supports the above conclusion. The heteropolyoxometalate, $[Mn^{IV}Mo_9O_{32}]^{6-}$, may oxidize allyl alcohol either by transfer of one electron to produce $[Mn^{III}Mo_9O_{32}]^{7-}$ and a free radical or by transfer of two electrons to form $[Mn^{II}Mo_9O_{32}]^{8-}$. In the present study, since free radical was not detected and there is no effect of ionic strength variation on the reaction, direct two-electron transfer is the more probable path forming acrylaldehyde as the product. Therefore, the mechanism of reaction considering the di-protonated $[Mn^{IV}Mo_9O_{32}]^{6-}$ species, which is formed in a prior equilibrium, as an active species is given in scheme-1 and the corresponding rate law by equation 1 and 2.



Scheme -1

$$\text{Rate} = \frac{k K_1 K_2 [H^+]^2 [Mn^{IV}Mo_9O_{32}]^{6-} [\text{Allyl Alc.}]}{1 + K_1 [H^+] + K_1 K_2 [H^+]^2} \quad (1)$$

$$k_{\text{obs}} = \frac{k K_1 K_2 [H^+]^2}{1 + K_1 [H^+] + K_1 K_2 [H^+]^2} \quad (2)$$

The effect of ionic strength on the rate qualitatively explains the reaction between the charged ion and neutral molecule as shown in Scheme-1. Increase in the acetonitrile content in the reaction medium leads to the increase in the rate of the reaction and the plot of $\log k_s$ against $1/D$, where D is the relative permittivity, was linear with a positive slope. Formation of an inner-sphere complex between central Mn(IV) ion and the reductant species is unlikely because Mn(IV) is completely shielded by a shells of MoO_4^{2-} tetrahedra.[20] Therefore, formation of an outer-sphere complex by the replacement of one of the water molecules of hydration is more probable transition state. Since, the probable transition state is less solvated and also is larger in size it will be more stabilized[16] in the medium of higher relative permittivity as observed. Decrease in the value of entropy of activation also supports formation of such a transition state.

Table 1 : Effect of oxidant and substrate on the rate of the reaction at 30°C.

$10^2[\text{Allyl alcohol}]$ mol dm ⁻³	$10^3[\text{Oxidant}]$ mol dm ⁻³	$10^2 k_{\text{obs}} \text{ s}^{-1}$
1.0	2.0	0.78
2.0	2.0	2.45
2.5	2.0	7.06
3.0	2.0	11.0
4.0	2.0	2.45
2.5	0.5	7.04
2.5	2.0	7.06
2.5	3.0	7.06
2.5	5.0	7.05

Table 2 : Effect of H⁺ on the rate of the reaction.
 $10^3 [\text{Allyl alcohol}] = 2.5 \text{ mol dm}^{-3}$ $10^3 [\text{Oxidant}] = 2.0 \text{ mol dm}^{-3}$

H ⁺ Mol dm ⁻³	10 ² k _{obs} s ⁻¹
0.01	0.09
0.03	0.44
0.05	1.01
0.07	1.51
0.08	1.88
0.1	2.45

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