“KINETICS AND MECHANISTIC STUDY OF OXIDATION OF NICOTINIC HYDRAZIDE BY WAUGH-TYPE ENNEAMOLYBDOMANGANATE (IV) IN PERCHLORIC ACID MEDIUM”

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ABSTRACT: The kinetics of oxidation of the nicotinic hydrazide in acidic medium was studied spectrophotometrically at 468 nm. The reaction between nicotinic hydrazide and enneamolybdomanganate (IV) in aqueous acidic medium was studied spectrophotometrically at a constant ionic strength of 0.3 mol dm⁻³ at 27±0.2°C exhibits 1:1 stochiometry, Nicotinic hydrazide : [Mn⁴⁺Mo₉O₃₂]⁶⁻ under pseudo-first order condition. The main oxidative products were identified by spot test, FT-IR, NMR, Melting Point, LC-MS. The effect of [H⁺] ion and ionic strength of the reaction medium have been investigated. The reaction constants involved in the different steps of the mechanism are calculated. The activation parameters with respect to slow step of the mechanism are computed and discussed. A mechanism related to this reaction is proposed.

Key wards: Kinetics, Mechanism, Nicotinic hydrazide, Enneamolybdomanganate (IV).

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INTRODUCTION

Polyoxometalates (POM) have been studied in an extraordinarily broad range of areas including electrochemistry, catalysis, optics and medicine [1-3]. Many potential medicinal applications have been reported, such as anti-tumoral and anti-viral applications [4]. The diverse capability of (POM) as an important doubly function reagent (oxidative and catalytic properties) has been demonstrated with respect to many organic reactions [5]. This is particularly so with heteropolyanions containing higher valent transition ions as hetero atoms. In contrast Mn (IV) is present in a number of biologically important compounds [6]. The oxidant used in the present study [Mn⁴⁺Mo₉O₃₂]⁶⁻ is also strong oxidizing agent in acidic medium [7,8]. In the present study a two-electron transfer complimentary reaction between Waugh type enneamolybdomanganate (IV) and nicotinic hydrazide is investigated. (NH₄)₆[MnMo₉O₃₂]8H₂O 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 atom is coordinated to three molydbenum atoms and each molybdenum is also surrounded by six oxygen atoms in a much distorted octahedral geometry.
It can oxidize organic as well as inorganic substrates [9]. Literature survey reveals that the kinetics of oxidation of nicotinic hydrazide has been studied using selenium dioxide [10] Thallium (III) oxidants [11] in acidic medium. In view of the potential pharmaceutical importance of nicotinic hydrazide and lack of literature on the mechanism of its oxidation it is of immense interest to follow the oxidation kinetics of nicotinic hydrazide by [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$ in perchloric acid medium.

Nicotinic acid hydrazide or pyridine-3-carboxyhydrazide commercially known as nicotinic hydrazide (NIH). Recent studies have shown that nicotinic acid hydrazide could be considered as anti-inflammatory, analgesic agent [12] and as a novel pharmacaphore in the design of anticonvulsant drug [13]. Nicotinic acid hydrazide is one of such pyridine containing hydrazide which is an analogue of isoniazid the antituberculosis drugs.

MATERIALS AND METHODS

Chemicals

All chemicals used were of analytical reagent grade and double distilled water was used throughout the work. A solution of nicotinic hydrazide was prepared by dissolving a known amount of recrystallized sample in double distilled water. The purity of nicotinic hydrazide sample was checked by comparing its FT-IR spectrum with literature data and with its melting point160-163°C. The cobalt complex [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$ was prepared by the reported method [14] as follows 50 gm of ammonium molybdate was dissolved in 200 ml of water, excess of hydrogen peroxide as oxidant was added to it and the resultant solution was heated to 95°C. To this hot solution, 5 gm of MnSO$_4$.H$_2$O in 50 ml of water was added slowly with constant stirring. The resultant orange-red colored solution was boiled for 10 min and quickly filtered and cooled. The orange-red colored crystals were recrystallized thrice from hot (70°C) water. The solution of (NH$_4$)$_6$[Mn$^{IV}$Mo$_9$O$_{32}$] was standardized by treating known amount of its solution with excess of As$^{III}$ and back titrating As$^{III}$. The oxidation state of hetero atom was also confirmed to be four by iodometric method and standardized spectrophotometrically using Shimadzu UV-1800 spectrophotometer at wavelength 468nm[7-8]. The ionic strength was maintained using NaClO$_4$.HCIO$_4$ and NaCl AR grade.

Kinetic measurements

The kinetic measurements were performed on a ShimadzuUV-1800 UV-Visible spectrophotometer. The reaction between [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$ and nicotinic hydrazide was followed under pseudo-first order condition where as nicotinic hydrazide was always in excess over [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$ at a constant ionic strength of 0.3 mol dm$^{-3}$ in acidic medium at constant temperature 27±0.2°C. The reaction was initiated by mixing the [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$ and nicotinic hydrazide solutions, which also contains required concentration of HClO$_4$ and NaClO$_4$. The reaction was followed by measuring the absorbance of [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$ at 468 nm as a function of time. Beer’s law was tested for [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$ between the concentration 1.0×10$^{-3}$ and 5.0×10$^{-3}$ mol dm$^{-3}$ ($\varepsilon_{468} = 360±2$ mol dm$^{-3}$ cm$^{-1}$ ) under the experimental conditions [7-8].

Spectrophotometric measurements

The UV-Visible spectra of [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$complex and the reaction mixture were recorded by using ShimadzuUV-1800 UV-Visible spectrophotometer between the wavelength range 400-650 nm. The spectrum of the reaction mixture at various time intervals is shown in (Fig-1)

Stoichiometry and product Analysis

The stoichiometry was studied by keeping concentration of [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$ 1.0 × 10$^{-3}$ mol dm$^{-3}$ constant and varying the concentration of nicotinic hydrazide from 0.1× 10$^{-4}$ to 0.5× 10$^{-4}$ mol dm$^{-3}$ with constant concentration of 0.5 mol dm$^{-3}$ HClO$_4$. The reactants were equilibrated at 27±0.2°C for 24 hours in a nitrogen atmosphere. The progress of the reaction was followed by measuring the absorbance at 468 nm. The stoichiometry was found to be one mole of [Mn$^{IV}$Mo$_9$O$_{32}$]$^{6-}$ per mole of nicotinic hydrazide after completion of the reaction The reaction product was extracted with ethyl acetate and recrystallized from aqueous alcohol.

$$\text{O} \quad \text{NH}_2 \quad + \quad [\text{Mn}^{IV}\text{Mo}_9\text{O}_{32}]^{6-} \quad \text{H}^+ \quad \text{H}_2\text{O} \quad \rightarrow \quad \text{O} \quad \text{NH}_2 \quad + \quad [\text{Mn}^{IV}\text{Mo}_9\text{O}_{32}]^{8-} \quad \text{N}_2 \quad + \quad 8\text{H}^+$$
The purity was checked by melting point. The main oxidative product was identified by spot test and FT-IR spectrum which showed a band at (6) 1698 cm$^{-1}$ due to >C=O stretching of acid and broad band at (6)3071 cm$^{-1}$ due to O-H stretching. $^1$H NMR spectrum (400MHz DMSO), shows peaks δ 13.12 (s 1H), acidic OH (D$_2$O exchanged) 9.12 (s 1H), 8.29 (d 1H), 8.77 (d 1H) and 7.49 (dd 1H). Mass spectrum of product indicates the presence of nicotinic acid by molecular ion peak at m/z (M$^+$) 124 amu.

RESULTS AND DISCUSSION

Reaction order

The reaction orders have been determined from the slopes of log $k_{obs}$ versus log concentration plots by varying the concentrations of nicotinic hydrazide, [Mn$^{IV}$Mo$_6$O$_{19}$]$^{6-}$ and HClO$_4$ in turn while keeping other conditions constant. The concentration of [Mn$^{IV}$Mo$_6$O$_{19}$]$^{6-}$ was varied in the range 0.1×10$^{-3}$ to 2.0×10$^{-3}$ mol dm$^{-3}$ at fixed nicotinic hydrazide, [H$^+$] and ionic strength. The non-variation in the pseudo first order rate constant at various concentrations of [Mn$^{IV}$Mo$_6$O$_{19}$]$^{6-}$ indicates the order in [Mn$^{IV}$Mo$_6$O$_{19}$]$^{6-}$ as unity (Table1). The substrate nicotinic hydrazide concentration was varied in the range 0.2×10$^{-3}$ to 2.0×10$^{-3}$ mol dm$^{-3}$ at 27±0.2°C keeping all other reactants concentration and conditions constant. The apparent order in nicotinic hydrazide was found to be less than unity under the experimental conditions. The effect of increasing concentration of perchloric acid on the reaction rate at constant concentrations of nicotinic hydrazide and [Mn$^{IV}$Mo$_6$O$_{19}$]$^{6-}$ at constant ionic strength was studied. The rate constants were found to be increased with the increase in acid concentration and the order in acid was less than unity (Table1).

Effect of hydrogen ion concentration

The effect of hydrogen ion concentration on the rate of reaction was studied at constant nicotinic hydrazide, [Mn$^{IV}$Mo$_6$O$_{19}$]$^{6-}$ at ionic strength 0.3 mol dm$^{-3}$ at 27±0.2°C. The effect of hydrogen ion concentration on the reaction was studied in order to understand the nature of reactant species present in the solution. The concentration of [H$^+$] ion was varied between 0.01 to 1.0 mol dm$^{-3}$ keeping all other concentrations constant. It was found that the reaction rate increases on increase in concentration of [H$^+$] ions as shown in (Table 1). The order of [H$^+$] ion was found to be 0.64 as determined from the plot of log $k_{obs}$ versus log [H$^+$] ion.

Effect of ionic strength

The effect of ionic strength was studied by varying sodium perchlorate concentration in the reaction mixture. The ionic strength of the reaction medium was varied from 0.05 to 1.5 mol dm$^{-3}$, with all other reactant concentrations and other conditions being constant. It was found that as ionic strength increased, the rate of reaction decreased [15]. The plot of log $k_{obs}$ versus $1/2$ was linear with negative slope.

Effect of solvent polarity

The relative permittivity effect was studied by varying the percentage of acetonitrile from 10 to 40 % v/v in the reaction mixture with all other conditions being constant. The relative permittivities of the reaction mixtures were computed from the values of the pure solvent. It was found that the solvent polarity had negligible effect on the rate constant [16].

Test for free radicals

The reaction was studied in presence of added acrylonitrile to understand the intervention of free radicals in the reaction [17-18]. The intervention of free radicals was examined as follows. The reaction mixture, to which a known quantity of acrylonitrile scavenger had been added initially, was kept in an inert atmosphere for 1 h. When the reaction mixture was diluted with methanol, no precipitate resulted, indicating the absence of free radicals in the reaction mixture [19].

Effect of temperature

The effect of temperature on the reaction rate was studied by performing the kinetic run at four different temperatures 20, 25, 30, 35, 40 °C with keeping other experimental conditions constant. The rate constants were found to increase with increase in temperature in (Table 2). The activation energy corresponding to these rate constant was evaluated from the linear Arrhenius plot of log k versus 1/T and other activation parameteras. The activation parameters were $E_a$=32.08±0.2 kJ mol$^{-1}$, ΔH=29.61 kJ mol$^{-1}$, ΔG=38.64kJ mol$^{-1}$ and ΔS= -124.77 kJ mol$^{-1}$.

Polyoxometalate [Mn$^{IV}$Mo$_6$O$_{19}$]$^{6-}$ is a powerful oxidant in acidic medium [7,8] as it is exhibits many oxidation states under the experimental condition. The reduction product of [Mn$^{IV}$Mo$_6$O$_{19}$]$^{6-}$ is stable and not further reduction might be stopped. The water soluble [Mn$^{IV}$Mo$_6$O$_{19}$]$^{6-}$ complex is reported [14]. There are a few heteropolyoxometalates with Mn(IV) as hetero atoms, such as Na$_7$[Mn(Nb$_2$O$_{19}$)$_2$] 30H$_2$O [20] and (NH$_4$)$_6$[MnMo$_6$O$_{19}$] 8H$_2$O [14]. In all of these Mn(IV) complexes manganese is coordinated to six oxygen atoms in a slightly distorted octahedral arrangement.
Figure 1. Spectra of the reaction mixture at different time intervals at 27±0.2°C [Mn^{IV}Mo_{9}O_{32}]^{6−} 0.1×10^{-3} \text{mol dm}^{-3}, \text{nicotinic hydrazide} 0.2×10^{-2} \text{mol dm}^{-3}, \text{HClO}_4 0.5 \text{ mol dm}^{-3}\text{NaClO}_4 0.3 \text{ mol dm}^{-3}

Figure 2. UV-Vis spectra of [Mn^{IV}Mo_{9}O_{32}]^{6−} A) in water B) in 0.3 \text{ mol dm}^{-3}\text{HClO}_4 and C) reaction mixture [Mn^{IV}Mo_{9}O_{32}]^{6−} 0.5×10^{-3} \text{mol dm}^{-3}, \text{nicotinic hydrazide} 0.2×10^{-2} \text{mol dm}^{-3} \text{HClO}_4 0.5 \text{ mol dm}^{-3}\text{NaClO}_4 0.3 \text{ mol dm}^{-3}

Figure 3. Michaelis-Menten plot of 1/k_{obs} against 1/[nicotinic hydrazide] at different temperatures (conditions as in Table 2)
Table 1. Effect of concentration of enneamolybdomanganate (IV) ion, perchloric acid on the reaction between nicotinic hydrazide and enneamolybdomanganate (IV) at 27±0.2°C, I=0.3 mol dm⁻³.

<table>
<thead>
<tr>
<th>10⁻³ [Mn⁴⁺Mo₉O₃₂]⁶⁻ (mol dm⁻³)</th>
<th>10⁻³ [NIH] (mol dm⁻³)</th>
<th>[HClO₄] (mol dm⁻³)</th>
<th>10² kₗₒₛₜ(s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.0</td>
<td>0.50</td>
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<tr>
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<td>0.50</td>
<td>0.9</td>
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<td>0.9</td>
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<td>0.50</td>
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<td>0.9</td>
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<td>1.0</td>
<td>0.50</td>
<td>0.9</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0</td>
<td>1.00</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 2. Effect of temperature on rate for the oxidation of nicotinic hydrazide by [Mn⁴⁺Mo₉O₃₂]⁶⁻ in aqueous acidic medium

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>10² kₗₒₛₜ(s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>293</td>
<td>1.4</td>
</tr>
<tr>
<td>298</td>
<td>1.8</td>
</tr>
<tr>
<td>303</td>
<td>2.0</td>
</tr>
<tr>
<td>308</td>
<td>2.5</td>
</tr>
<tr>
<td>313</td>
<td>2.9</td>
</tr>
</tbody>
</table>

Table 3 Effect of concentration of nicotinic hydrazide on the reaction between nicotinic hydrazide and enneamolybdomanganate (IV) at different temperature [Mn⁴⁺Mo₉O₃₂]⁶⁻ 0.5×10⁻³ mol dm⁻³, HClO₄ 0.5 mol dm⁻³ NaClO₄ 0.3 mol dm⁻³

<table>
<thead>
<tr>
<th>Nicotinic hydrazide</th>
<th>298K</th>
<th>303K</th>
<th>308K</th>
<th>313K</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
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<td>1.8</td>
<td>2.2</td>
<td>2.5</td>
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<tr>
<td>0.04</td>
<td>1.8</td>
<td>2.0</td>
<td>2.5</td>
<td>2.9</td>
</tr>
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<td>2.9</td>
<td>3.6</td>
</tr>
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<td>3.3</td>
<td>3.9</td>
<td>4.9</td>
</tr>
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</table>

Each of these oxygen atoms with a structure of D₃ symmetry and is noncentrosymmetric [21]. The UV-Vis spectrum of the anion [Mn⁹⁺Mo₉O₃₂]⁶⁻ solution has an intense absorption, characteristic of charge transfer bands in the UV region. Another characteristic band is observed at 468nm with a shoulder at 484 nm [21]. The 468 nm absorption band is assigned to ⁴A₂g→⁴T₂g transition of Mn(IV) [21] the d-d band of [Mn⁴⁺Mo₉O₃₂]⁶⁻ at 468 nm in the visible spectra of [Mn⁴⁺Mo₉O₃₂]⁶⁻ was found to be susceptible to changes in hydrogen and metal cation concentrations. This property was used to determine the equilibrium constant for the binding of various metal cations.
Monovalent cations form 2:1 complexes, whereas di- and trivalent cations form 1:1 complexes replacing two protons from the anion in either cases. If the metal cation interact strongly with the oxygen atoms of the MnO₆ octahedral, the ligand field strength must change accordingly and the energy of $^4A_2g \rightarrow ^4T_2g$ splitting must be observed. When the pH of the solution is raised or when metal salt concentrations are raised, at least one cation bonds to the anion to replace two protons. Therefore the symmetry around the hetroatom must be lowered resulting in the appearance of the peak at 468 nm. The wavelength of this band was not shifted by different metal cations and both 1:1 and 2:1 complexes exhibited almost identical absorption spectra.

Spectroscopic evidence for the complex formation between nicotinic hydrazide and [MnMo₇O₃²]⁶⁻ was observed from UV-Vis spectral studies of the anion [MnMo₇O₃²]⁶⁻ which shows a peak at 468 nm and in presence of acid two isosbestic points are obtained at 435 and 520 nm due to its protonation (Fig-2 A and B respectively) At high metal ion concentrations the peak at 468 nm is reappeared [21] as a result of metal ion substitution on the anion at oxygen atoms of A type. In order to understand the interaction between the nicotinic hydrazide and [MnMo₇O₃²]⁶⁻ UV–Vis spectra of the reaction mixture was examined. The anion shows a characteristic peak at 468 nm in aqueous solution as in (Fig-2A) and on addition of 0.1 mol dm⁻³ perchloric acid the spectrum of protonated anion is obtained (Fig-2B) with two isosbestic points at 435 and 520 nm due to its protonation. To an acidic solution of the anion when nicotinic hydrazide is added the reappearance of the peak at 468 nm was not observed, instead there was considerable increase in the intensity of absorption about 504 nm (Fig-2C). The reappearance of peak at 468 nm in presence of nicotinic hydrazide is expected if the interaction of added nicotinic hydrazide would have been through oxygen atoms. An increase in the intensity of peak at 504 nm in presence of nicotinic hydrazide is also an indication of formation of complex between the [MnMo₇O₃²]⁶⁻ and nicotinic hydrazide. Such complex formation was also supported kinetically from the fractional order in nicotinic hydrazide (Table- 3) and Michaelis–Menten plot of $1/k_{obs}$ against $1/[$nicotinic hydrazide$]$ as shown in (Fig-3).

The hexaprotonated anion, [MnMo₇O₃²]⁶⁻ is quite stable only in aqueous solution, although it seems very difficult to obtain as a pure solution. pH-metric titration shows that the anion, [MnMo₇O₃²]⁶⁻ undergoes successive protonation in acidic solution as shown in equations one to six with pK₁ at 3.3 and pK₂ at 2.75 corresponding to mono and diprotonated species of [MnMo₇O₃²]⁶⁻ respectively[14]. Further protonation constants are very close to each other.

\[
\text{[MnMo₇O₃²]⁶⁻} + \text{H}^+ \rightleftharpoons \text{H [MnMo₇O₃²]⁵⁻}
\]
\[
\text{H [MnMo₇O₃²]⁵⁻} + \text{H}^+ \rightleftharpoons \text{H₂ [MnMo₇O₃²]⁴⁻}
\]
\[
\text{H₂ [MnMo₇O₃²]⁴⁻} + \text{H}^+ \rightleftharpoons \text{H₃ [MnMo₇O₃²]³⁻}
\]
\[
\text{H₃ [MnMo₇O₃²]³⁻} + \text{H}^+ \rightleftharpoons \text{H₄ [MnMo₇O₃²]²⁻}
\]
\[
\text{H₄ [MnMo₇O₃²]²⁻} + \text{H}^+ \rightleftharpoons \text{H₅ [MnMo₇O₃²]¹⁻}
\]
\[
\text{H₅ [MnMo₇O₃²]¹⁻} + \text{H}^+ \rightleftharpoons \text{H₆ [MnMo₇O₃²]⁰⁺}
\]

The hexaprotonated anion, [MnMo₇O₃²]⁶⁻ complex was treated with perchloric acid, which gives a deep brown coloured precipitate of hexaprotonated species. This hexaprotonated species [MnMo₇O₃²]⁶⁻ is unstable and undergoes deprotonation in aqueous solution containing 0.1 Mol.dm⁻³ of [H⁺] ion [14]. In present experimental conditions, only mono-protonated species were formed, which are the active oxidant species of the reaction. Further the order with respect to [H⁺] ion concentration was also found to be 0.86 from the plot of log $k_{obs}$ against log [H⁺] plot. The plot of $k_{obs}$ against [H⁺] was also found to be linear without any intercept indicating that only protonated form of the oxidant is the active species.
The formation of this complex was proved kinetically by a Michaelis Menten plot, that is a linear plot of log k versus 1/[MnO₆³⁻]. Sodium perchlorate and acetonitrile were used to vary the ionic strength and the solvent polarity respectively. The larger negative values of ΔS indicate that the activated complex in the transition state has a more rigid structure than the reactants in ground state.[22,23] The negative values of ΔS for radical reaction have been attributed to the nature of electron pairing and unpairing reactions and to the loss of degrees of freedom by the formation of a rigid transition state.
REFERENCES