CHAPTER -III

Kinetics and Mechanism of oxidation of benzoic acid hydrazide by bromate catalyzed by Anderson type hexamolybdochromate(III) in aqueous acidic medium.

Polyoxomolybdates of the Keggin structure, $H_{3+x}PV_xMo_{12-x}O_{40}$ (x=0-2), have been utilized as oxidation catalysts for both gas-phase and liquid-phase oxidations[1], the earliest use was as co-catalysts in Wacker type oxidations of terminal alkenes,[2] followed later on by various catalytic oxidations of halides,[3] alcohols, ketones and amines,[4] phenols,[5] (alkyl)aromatics,[6] dienes,[7] alkanes,[8] and sulfur containing compounds.[9] From a mechanistic point of view there is now quite abundant information indicating that the polyoxomolybdates act as electron-transfer oxidants toward one of the reaction components, commonly, the organic substrate or oxidant. The specific complete reaction pathway, thus, much depends on the both the targeted oxidative transformation and the oxidant employed. Although Keggin and Dawson type polyoxomolybdates have been utilized as oxidation catalysts Anderson type compounds have not received[10] less attention.

The Anderson structure may be described as an isopolyoxometalate containing a crown of six octahedrons sharing edges. The centre may be occupied or not. In chromium containing compound, there are six hydrogen atoms, the positions of which are considered to be the six –OH groups bridging the central atom to the molybdenum containing crown octahedrons. Perloff[11] investigated the detailed structure of the heteropoly salt of $Na_3[CrMo_6O_{24}].8H_2O$ and established that the anion has the same structure as $[TeMo_6O_{24}]^{6-}$ anion with an excellent agreement and concluded that hydrogen atoms of the anion are bonded to oxygen atoms which are coordinated to Cr atom

Potassium or sodium bromate are strong oxidizing reagents used in various organic transformation[12]. The product of these oxidations is mainly bromide ion which can be safely treated and recycled. The oxidations by bromate are generally slow and in presence of a catalyst they proceed with a measurable rate. In continuation of our work on organic oxidations catalysed by polyoxometalates[13] we now present our studies on a novel system; the oxidation of benzoic acid hydrazide by bromate catalysed by an Anderson-type polyoxomolybdate, sodium hexamolybdochromate (III). Hydrazides, which are derivatives of both carboxylic acids and hydrazine have been utilized as starting materials inorganic synthesis[14]. The oxidative transformation of hydrazides with most oxidants give corresponding acids[15] and in some cases[16] esters or amides.Hydrazides have also been converted into N-N-diacylhydrazines with various oxidants[17].

The reaction was studied under pseudo-first-order conditions keeping hydrazide concnetration large excess at constant temperature of 25.0 ± 0.1°C. The reaction was initiated by mixing the previously thermostatted solutions of oxidant, catalyst and substrate, which also contained the required amount of hydrochloric acid, potassium chloride and doubly distilled water. The reaction was followed by titrating the reaction mixture for unreacted oxidant 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 90% completion of the reaction and the rate constants were reproducible within ± 6%.

Stoichiometry and product analysis:

In 10 ml of 0.6 mol dm^{-3} hydrochloric acid 40 μmol (5.0 mg) catalyst and 1 m mol (0.136 g) of benzoic acid hydrazide were dissolved. To the resulting solution 1 m mol (0.167 mg) of $KBrO_3$ was added. The reaction mixture was stirred at 27 °C for five minutes. The benzoic acid separated was filtered and recrystallized by water. The m.p. of the recrystallized product was found to be 121°C (lit M. P.121°C).Therefore the stoichiometry of the reaction is found to be two moles of oxidant per three moles of the hydrazide.

Reaction order With Reactants concentration:

The uncatalyzed reaction did not occur under the experimental conditions. The catalyzed reaction was carried out under pseudo-first-order keeping the concentration of hydrazide large excess at a constant concentration of HCl at 0.1 mol dm^{-3} and at a constant ionic strength of 0.5 mol dm^{-3}. The pseudo-first-order plots were found to be linear and the pseudo-first-order rate constants, k_{obs}, were fairly constant as the concentration of oxidant and hydrazide were varied (Table 3.1), indicating the order in reductant and oxidant to be unity each.

Effect of catalyst concentration:

The effect of catalyst concentration was studied between the concentration range of 5.0 x 10^{-5} to 5.0 x 10^{-4} mol dm^{-3} keeping [hydrazide], [$KBrO_3$], and [HCl] constant at 1.0 x 10^{-2} mol dm^{-3}, 1.0 x 10^{-3} mol dm^{-3}, and 0.1 mol dm^{-3},respectively (Table 3.2) and the plot of k_{obs} against [catalyst] was found to be linear indicating the first order dependence of reaction on [catalyst] as shown in Figure 3.1.

Effect of hydrogen ion concentration:

The effect of hydrogen ion was studied keeping [hydrazide], [$KBrO_3$], and [catalyst] constant at 1.0 x 10^{-2} mol dm^{-3},1.0 x 10^{-3} mol dm^{-3}, and 1.0 x 10^{-4} mol dm^{-3},respectively in order to understand the nature of reactant species present in the solution. The concentration of [H^+] was varied between 0.04 to 0.4 mol dm^{-3} (Table 3.3). The [H^+] accelerates the rate of the reaction and the order in [H+] was found to be more than unity (1.7) as shown in figure 3.2.

Effect of ionic strength, solvent polarity and temperature:

The effects of ionic strength, solvent polarity and temperature were studied keeping [hydrazide], [$KBrO_3$], [catalyst] and [HCl] constant at 1.0 x 10^{-2} mol dm^{-3}, 1.0 x 10^{-3} mol dm^{-3}, 1.0 x 10^{-4} mol dm^{-3} and 2.0 mol dm^{-3}, respectively. Potassium chloride and acetonitrile were used to vary the ionic strength and solvent polarity, respectively. The rate of the reaction is constant with increasing ionic strength from 0.1 to 0.5 mol dm^{-3} (Table 3.4).The dielectric constant of reaction mixtures were computed(Table 3.5) from the dielectric constant values of pure solvents using formula as,

$$D = V_1D_1 + V_2D_2$$

Where V_1 and V_2 are the volume fractions and D_1 and D_2 are dielectric constants of pure water(78.5) and acetonitrile(37.0) respectively. The plot of logk_{obs} versus 1/D was found to be liner with positive slope.(Figure 3.3) The effect of temperature on the reaction was studied at 20,25,30 and 40°C and the pseudo-first-order rate constants were determined (Table 3.7). The activation parameters E_a, $\Delta H^{\#}$, $\Delta G^{\#}$ and $-\Delta S^{\#}$ were also determined, (Table3.8) from graph of $\log k_{obs}$ and $\log k_{obs}/T$ against 1/T (Figure 3.4 and 3.5).

Test for free radical intervention

The reaction was also studied in presence of added acrylonitrile to understand the intervention of free radicals 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 (Table3.6).

Table 3.1

Effect of reactant concentrations on the rate of reaction at 25 °C.

10^4 [$H_6Cr^{III}Mo_6O_{24}$]$^{3-}$ = 1.0 mol dm^{-3} [HCl] = 0.1 mol dm^{-3} I = 0.5 mol dm^{-3}.

10^2 [Hydrazide] mol dm^{-3}	10^3 [$KBrO_3$] mol dm^{-3}	10^3 k_{obs} s^{-1}
0.5	1.0	1.2
0.6	1.0	1.3
0.7	1.0	1.2
0.8	1.0	1.2
1.0	1.0	1.3
3.0	1.0	1.1
4.0	1.0	1.1
5.0	1.0	1.1
1.0	0.4	1.2
1.0	0.6	1.2
1.0	2.0	1.3
1.0	3.0	1.2
1.0	4.0	1.3

Table 3.2

Effect of catalyst concentration on the reaction at 25°C.

10^2[Hydrazide] = 1.0 mol dm^{-3} 10^3[$KBrO_3$] = 1.0 mol dm^{-3}

[HCl] = 0.1 mol dm^{-3} and I = 0.5 mol dm^{-3}

10^4 [$H_6Cr^{III}Mo_6O_{24}$]$^{3-}$ mol dm^{-1}	10^3 k_{obs} s^{-1}
0.5	0.4
0.8	0.7
1.0	1.2
2.0	1.7
3.0	2.7
4.0	3.2
5.0	3.7

Table 3.3

Effect of hydrogen ion concentration on the reaction at 25°C.

10^2[Hydrazide] = 1.0 mol dm^{-3} 10^3[$KBrO_3$] = 1.0 mol dm^{-3}

10^4[$H_6Cr^{III}Mo_6O_{24}$ $]^{3-}$ = 1.0 mol dm^{-3} I = 0.5 mol dm^{-3}.

10 [HCl] mol dm^{-3}	10^3 k_{obs} s^{-1}
0.4	0.2
0.8	0.8
1.0	1.3
1.5	2.2
2.0	3.3
2.5	4.8
3.0	5.9
4.0	10.5

Figure 3.1

Reaction order with respect to catalyst. Graph of k_{obs} against [Catalyst]

Conditions as in Table 3.2

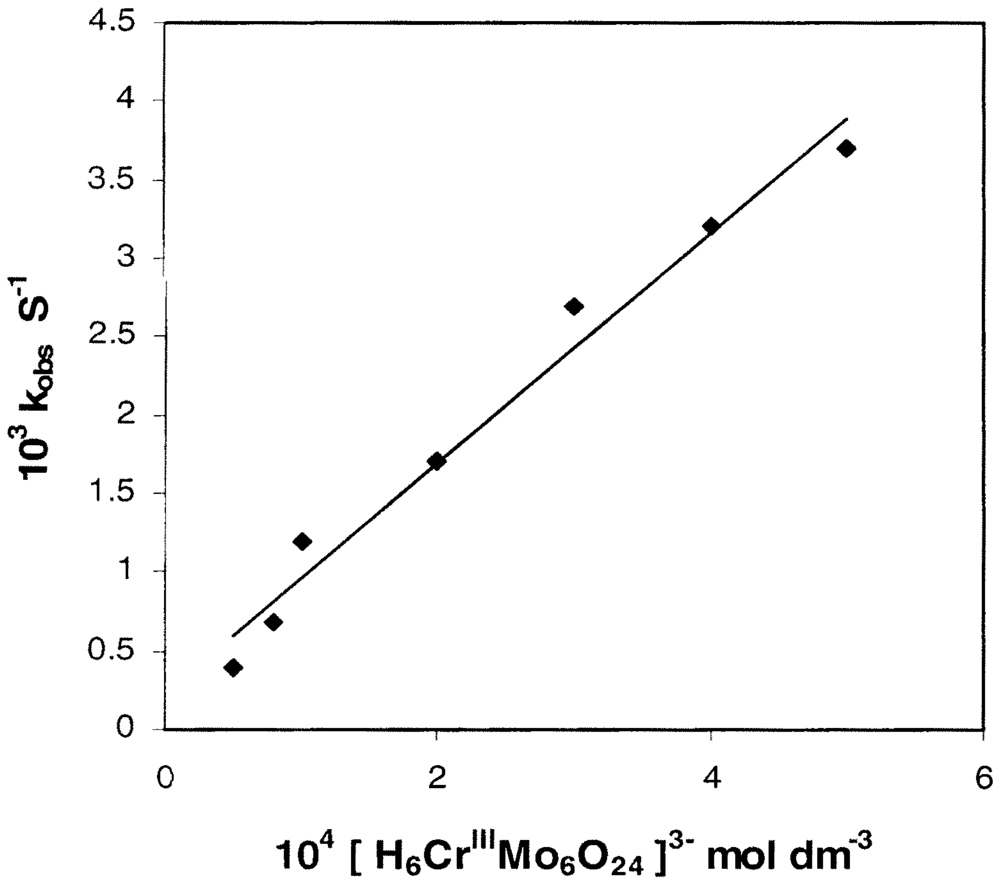


Figure 3.2

Reaction order with respect to hydrogen ion concentration.

Graph of [H^+ $]^2$/ k_{obs} against [H^+]

Conditions as in Table 3.3

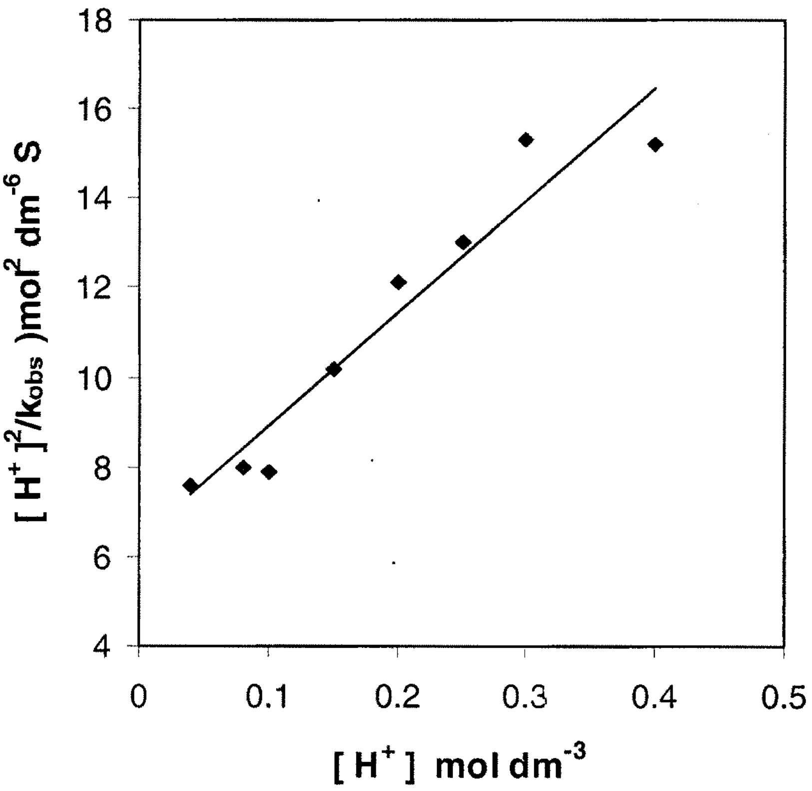


Table 3.4

Effect of ionic strength on the oxidation of benzoic acid hydrazide by bromate catalyzed by [H_6Cr^{III} Mo_6O_{24} $]^{3-}$ in aqueous acidic medium at 25^0 C.

10^2 [hydrazide] = 1.0 mol dm^{-3} 10^3 [$KBro_3$]= 1.0 mol dm^{-3}

[HCl] = 0.1 mol dm^{-3} 10^4[H_6Cr^{III} Mo_6O_{24} $]^{3-}$ = 1.0 mol dm^{-3}

I = 0.5 mol dm^{-3}.

10 [KCl] mol dm^{-3}	10^3k_{obs} S^{-1}
0.5	1.2
0.8	1.2
1.0	1.2
2.0	1.1
5.0	1.4

Table 3.5

Effect of dielectric constant of medium on the oxidation of benzoic acid hydrazide by bromate catalysed by [H_6Cr^{III} Mo_6O_{24} $]^{3-}$ in aqueous acidic medium at 25^0 C

10^2[hydrazide] = 1.0 mol dm^{-3} 10^3 [$KBro_3$]= 1.0 mol dm^{-3}

[HCl] = 0.1 mol dm^{-3} 10^4[H_6Cr^{III} Mo_6O_{24} $]^{3-}$ = 1.0 mol dm^{-3}

I = 0.5 mol dm^{-3}.

% Acetonitrile (V/V)	Dielectric constant (D)	10^3k_{obs} s^{-1}	-log k_{obs}	$10^2 1/D$
0	78.5	1.0	2.9913	1.27
10	74.35	1.3	2.8794	1.34
20	69.9	1.7	2.7773	1.43
30	66.05	2.9	2.5436	1.51
40	61.9	3.8	2.4168	1.62

Table 3.6

Effect of acrylonitrile concentration (% v/v) on the oxidation of benzoic acid hydrazide by bromate catalysed by [$H_6Cr^{III} Mo_6O_{24}$ $]^{3-}$ in aqueous acidic medium at 25^0 C.

10^2[hydrazide] = 1.0 mol dm^{-3} 10^3 [$KBro_3$]= 1.0 mol dm^{-3}

[HCl] = 0.1 mol dm^{-3} 10^4[$H_6Cr^{III} Mo_6O_{24}$ $]^{3-}$= 1.0 mol dm^{-3}

I = 0.5 mol dm^{-3}.

% Acrylonitrile (v/v)	10^3 k_{obs} S^{-1}
2	1.3
4	1.3
6	1.3
8	1.2
10	1.3

Table 3.7

Effect of temperature on the oxidation of benzoic acid hydrazide by bromate catalysed by [$H_6Cr^{III}Mo_6O_{24}$]$^{3-}$ in aqueous acidic medium

10^2[hydrazide] = 1.0 mol dm^{-3} 10^3[$KBro_3$]= 1.0 mol dm^{-3}

[HCl] = 0.1 mol dm^{-3} 10^4[$H_6Cr^{III}Mo_6O_{24}$]$^{3-}$ = 1.0 mol dm^{-3}

I = 0.5 mol dm^{-3}.

Temp T (K)	10^3 k_{obs} S^{-1}	10^3 (1/T)	- log k_{obs}	- log (k_{obs}/T)
293	0.9	3.41	3.05	5.51
298	1.3	3.35	2.89	5.36
303	1.9	3.30	2.72	5.20
313	3.8	3.19	2.42	4.92

Table 3.8

Activation parameters for the oxidation of benzoic acid hydrazide by bromate catalysed by [$H_6Cr^{III}Mo_6O_{24}$]$^{3-}$ in aqueous acidic medium

Ea (kJ mol^{-1})	50.71± 1
$\Delta H^{\#}$ (kJ mol^{-1})	51.66 ± 6
$\Delta S^{\#}$ (Jk^{-1} mol^{-1})	-138.36 ± 7
$\Delta G^{\#}$ (kJ mol^{-1})	96.80 ± 6

Figure 3.3

Effect of dielectric constants of medium on the oxidation of benzoic acid hydrazide by bromate catalysed by [$H_6Cr^{III}Mo_6O_{24}$]$^{3-}$ in aqueous acidic medium Conditions as in Table 3.5

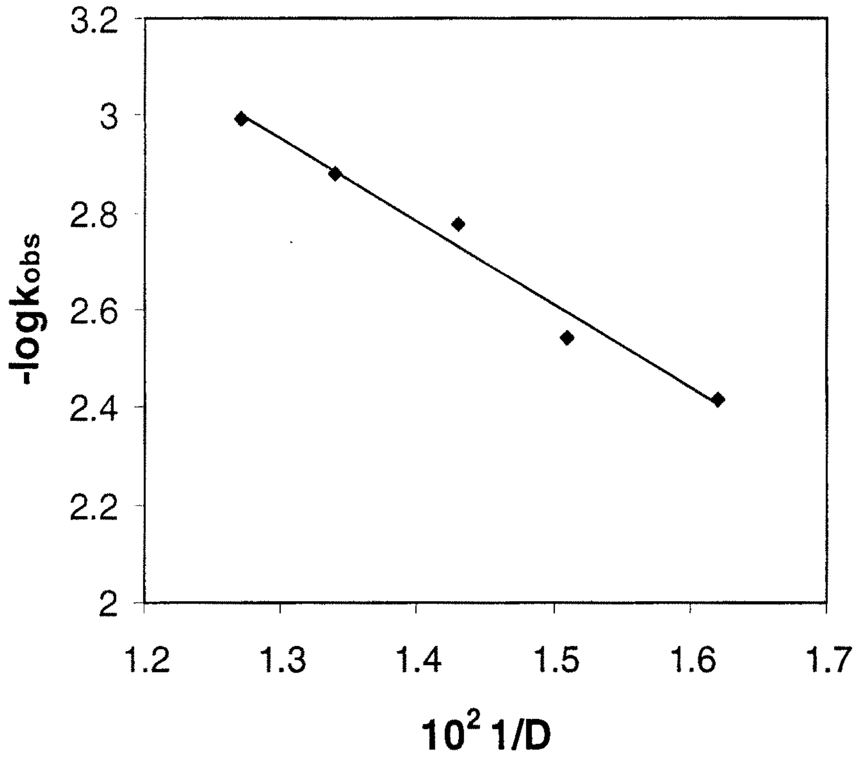


Figure 3.4

Effect of temperature on the oxidation of benzcic acid hydrazide by bromate catalysed by [$H_6Cr^{III}Mo_6O_{24}$ $]^{3-}$ in aqueous acidic medium

Conditions as in Table 3.7

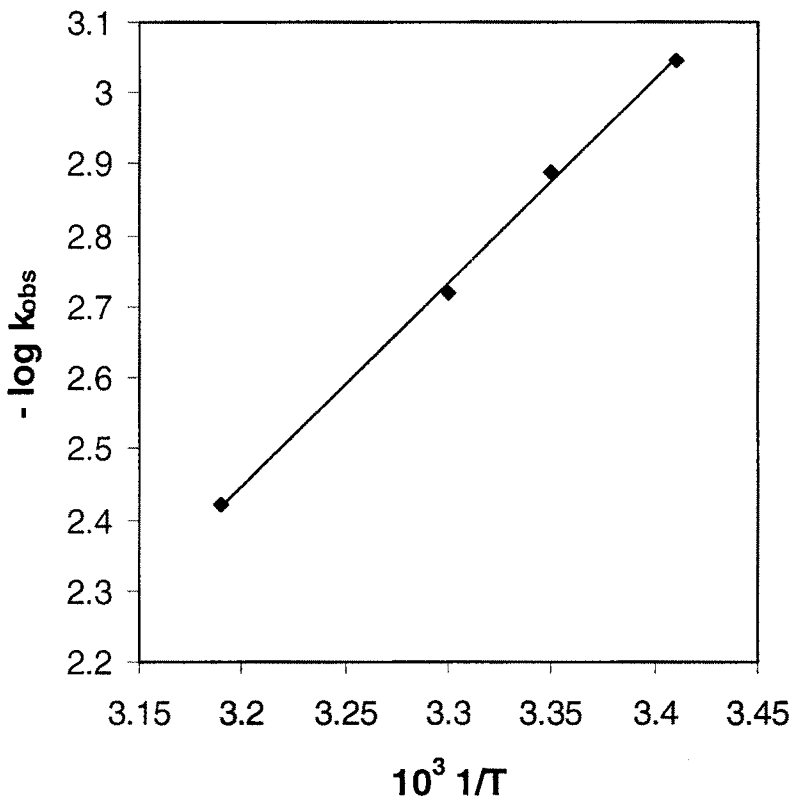
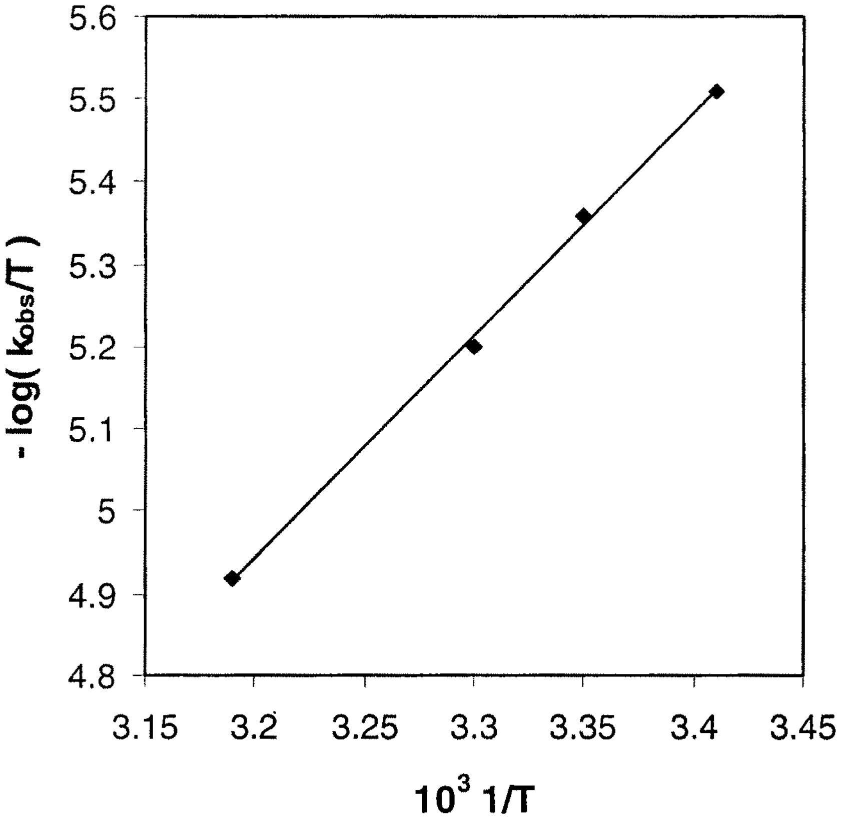


Figure 3.5

Effect of temperature on the oxidation of benzoic acid hydrazide by bromate catalysed by [$H_6Cr^{III}Mo_6O_{24}$]$^{3-}$ in aqueous acidic medium. Conditions as in Table 3.7



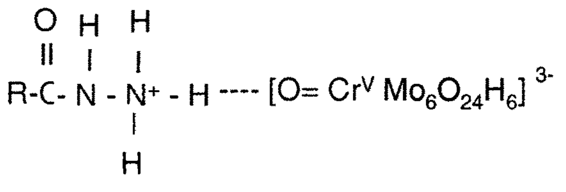
Discussion

Oxidation of inorganic substrates like V^{IV} and $[Co^{II}W_{12}O_{40}]^{6-}$ by bromate have been studied [18,19] and their stoichiometry predicts either Br_2 or HOBr as the product of reduction of bromate. The oxidation potential of HOBr or Br_2 were respectively 1.34 and 1.07 V indicating that the substrate, benzoic acid hydrazide, can be very easily oxidized by both of them in acidic solutions. Therefore, in order to confirm the end product of the oxidant, either bromide or bromine, the test for formation of bromide ion was carried out in sulphuric acid solution instead of hydrochloric acid. Addition of silver nitrate to the reaction mixture, after completion of the reaction, results in formation of silver bromide precipitate which confirmed bromide as one of the product of the reaction. It is also noticed during the kinetic studies and the stoichiometric analysis that no bromine was evolved further confirming the bromide ion as the only product. The reaction is found to be first order in oxidant as the pseudo-first-order plot of $\log[KBrO_3]$ against time is linear(Figure 1) and first order in substrate concentration as evidenced by the constancy in the pseudo-first-order rate constants between the concentration range 0.5×10^{-2} to 5.0×10^{-2} mol dm^{-3} (Table 1). The plot of pseudo-first-order rate constant against concentration of the catalyst was also found to be linear ($R^2 = 0.977$) indicating the order in catalyst is unity. Since, the uncatalyzed reaction does not occur under the experimental conditions the catalyzed reaction proceeds with the interaction of the catalyst and the oxidant. In the present study, the catalyst is a heteropolyoxometalate in which the hetero atom Cr^{III} is buried within the six molybdate octahedrons which does not favor the formation of a complex between the catalyst and the substrate, thus making it as an innert redox catalyst. Therefore, the initiation of the reaction occurs by the oxidation of the catalyst to its higher oxidation state by bromate in a prior fast step which then effects the oxidation of the substrate. In acidic solutions, the stable oxidation states of chromium are Cr^{VI} and Cr^{III}. Intervention of either Cr^{V} or Cr^{IV} is predicted in most of the oxidations of Cr^{III} by various oxidizing agents and these are stabilized[20] in presence of ligands like 2-ethyl-2-hydroxy butyric acid. The former is a two-electron oxidant whereas the later is a one-electron oxidant. In absence of stabilizing ligands like 2-ethyl-2-

hydroxybutyric acid the oxidation of a substrate by Cr^{IV} produce Cr^{III} as a result of one-electron change, thus leading to the generation of a free radical. Since, in the present study test for formation of free radical was negative it was assumed that the oxidized form of the catalyst undergo two-electron change. Therefore, oxidation of molybdochromate by bromate result into formation of Cr^{V}-molybdate which then abstracts two electrons from the hydrazide without any intervention of free radical. In order to confirm the formation of Cr^{V}-molybdate the FTIR spectrum of the green compound obtained by treating Cr^{III}-molybdate with bromate in hydrochloric acid was investigated. The FTIR of the green product obtained shows that the peak corresponding to M-O_c-M at 643 cm^{-1} (Figure 3.6A) was splitted into two peaks (Figure 3.6B) due to change in the oxidation state of hetero atom Cr^{III}. There was also a new peak at 829 cm^{-1} corresponding to the Cr^{V}=O. Such type of oxidation of Cr^{III} polyoxometalates has also been reported while studying the preparation[21] of chromium substituted heteropolytungstate anions. Therefore, the Cr^{III}-molybdate under the experimental conditions gets oxidized to Cr^{V}-molybdate according to the equation 1.

$$H[H_6Cr^{III}Mo_6O_{24}]^{3-} + BrO_3^- \longrightarrow [O{=}Cr^{V}Mo_6O_{24}]^{3-} + HBrO_2 \qquad (1)$$

The effect of hydrogen ion concentration is due to involvement of various protonation equilbria and the order in $[H^+]$ of more than unity indicates involvement of two protonation equilibria. Potassium bromate is a strong electrolyte and in aqueous solution it exists as BrO_3^- which is also a strong acid therefore protonation of the oxidant does not occur under the present experimental conditions employed. The substrate hydrazide undergo protonation[22] in acidic solution which explains the first-order dependence of the rate of reaction on $[H^+]$. The second order in $[H^+]$ can be explained by the protonation equilibria of the the catalyst. The Anderson type polyoxometalates are known to undergo selective protonation[23] at the oxygen atom shared by two Mo atoms. Since, the catalyst prepared is $[H_6Cr^{III}Mo_6O_{24}]^{3-}$ there will be three successive protonation and the monoprotonated form will be the active species in the present reaction. Therefore, the effect of the [H^+] on the reaction is due to the protonation of hydrazide as well as that of the catalyst in prior equilibria. The kinetic data obtained can be satisfactorily explained by considering protonated form of the substrate and monoprotonated form of the catalyst. The mechanism of the reaction based on the kinetic results can be summarized as in Scheme I in terms of active protonated forms of the substrate and the catalyst and their respective formation equilibria. According to Scheme 1 the reaction is initiated by the oxidation of the catalyst to its higher oxidation state Cr^V by bromate in a prior equilibrium. The Cr^V-molybdate then oxidizes the hydrazide to an intermediate RCONNH, acyl diimide. Such diimide intermediates are proposed[14] in oxidation of hydrazides by various oxidizing agents. The nucleophilic attack of water molecule on the carbonyl carbon of the acyl diimide give benzoic acid and another intermediate NH-NH. The formation of Cr^V is supported by the changes observed in the IR spectrum of the oxidized catalyst (Figure 3.6) as compared with that of the catalyst. The probable transition state would be the interaction between the oxygen atom of the oxidized form of the catalyst and the hydrogen atom of the ammonium group of the hydrazide moiety as shown below. The effect of ionic strength on the rate qualitatively explains the reaction between charged ions of a similar kind, as shown in Scheme I. Increasing the acetonitrile content in the reaction medium leads to an increase in the rate of the reaction. Since the probable transition state is less solvated and as it is larger in size, it will be more stable in the medium of higher relative permittivity [24], as observed. The decrease in the value of entropy of activation also supports formation of such a transition state.



$$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{H}{|}}{N}{-}\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N^+}}{-}H \text{----} [O{=}Cr^V Mo_6O_{24}H_6]^{3-}}$$

Scheme I:

$$RCONHNH_2 + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} RCONHNH_3^+$$

$$[H_6Cr^{III}Mo_6O_{24}]^{3-} + H^+ \overset{K_2}{\rightleftharpoons} H[H_6Cr^{III}Mo_6O_{24}]^{2-}$$

$$H[H_6Cr^{III}Mo_6O_{24}]^{2-} + H^+ \overset{K_3}{\rightleftharpoons} H_2[H_6Cr^{III}Mo_6O_{24}]^-$$

$$H_2[H_6Cr^{III}Mo_6O_{24}]^- + H^+ \overset{K_4}{\rightleftharpoons} H_3[H_6Cr^{III}Mo_6O_{24}]$$

$$H[H_6Cr^{III}Mo_6O_{24}]^{2-} + BrO_3^- \overset{K_5}{\rightleftharpoons} [H_6\overset{\overset{O}{\|}}{Cr^V}Mo_6O_{24}]^{3-} + HBrO_2$$

$$\overset{\overset{O}{\|}}{[}H_6Cr^VMc_6O_{24}]^{3-} + RCONHNH_3^+ \xrightarrow{k_1} [H_6Cr^{III}Mo_6O_{24}]^{3-} + RCONNH + H_2O + H^+$$

$$RCONNH + H_2O \xrightarrow{\text{Fast}} RCOOH + HN{=}NH$$

$$HN{=}NH + HBrO_2 \xrightarrow{\text{Fast}} N_2 + 2H_2O + HOBr$$

$$2\ HOBr + 2\ HN{=}NH \xrightarrow{\text{Fast}} 2\ N_2 + 4H_2O + 2H^+ + 2Br^-$$

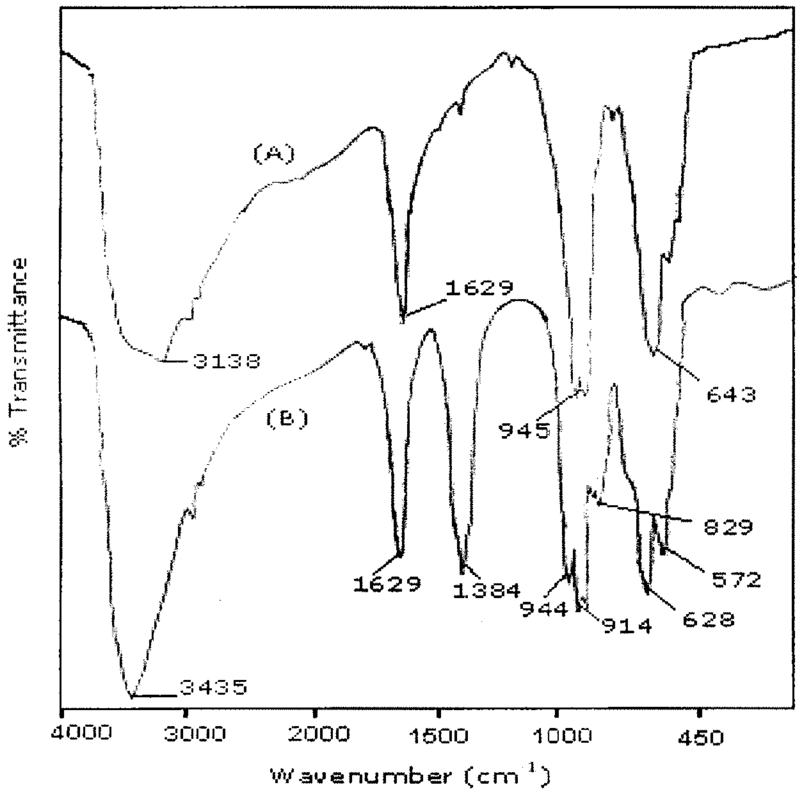
Scheme I

$$\text{Rate} = \frac{k_1K_1K_2K_5[H^+]^2[RCONHNH_2][BrO_3^-][H_6Cr^{III}Mo_6O_{24}]^{3-}}{(1 + K_1[H^+])(1 + K_2[H^+] + K_2K_3[H^+]^2 + K_2K_3K_4[H^+]^3)} \qquad (2)$$

$$k_{obs} = \frac{k_1K_1K_2K_5[H^+]^2[H_6Cr^{III}Mo_6O_{24}]^{3-}}{(1 + K_1[H^+])(1 + K_2[H^+] + K_2K_3[H^+]^2 + K_2K_3K_4[H^+]^3)} \qquad (3)$$

Figure 3.6

FT-IR Spectra of (A) hexamolybdochromate (III) and
(B) hexamolybdochromate (V)



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