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1. "Kinetics and Mechanism of Oxidation of Benzoic Acid Hydrazide by Bromate Catalysed by Anderson Type Hexamolybdochromate(III) in Aqueous Acidic Medium"

   S. D. Kadam, A. R. Supale and G. S. Gokavi*

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2. "Kinetics and mechanism of oxidation of benzoic acid hydrazide by bromate catalysed by octamolybdomanganate(II)($[MnMo_8O_{27}]^{4-}$)"

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   "Kinetics and Mechanism of Oxidation of Benzoic Acid Hydrazide by Bromate Catalysed by Anderson Type Hexamolybdochromate(III) in Aqueous Acidic Medium"

Kinetics and Mechanism of Oxidation of Benzoic Acid Hydrazide by Bromate Catalyzed by Anderson Type Hexamolybdochromate(III) in Aqueous Acidic Medium

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The reaction between benzoic acid hydrazide and potassium bromate catalyzed by Anderson type hexamolybdochromate(III) was carried out under pseudo-first-order condition keeping large excess of hydrazide concentration over that of the oxidant. The reaction is accelerated by the hydrogen ion concentration due to the involvement of the prior protonation equilibria of both catalyst and the hydrazide. The protonated forms of the catalyst and the substrate are the active species in the reaction. The initiation of the reaction occurs through oxidation of the catalyst $H[CrMo_6O_{24}H_6]^{2-}$ to $[O = Cr^VMo_6O_{24}H_6]^{3-}$ which then reacts with the hydrazide to give product without any intervention of free radical. The oxidized form of the catalyst $[O = Cr^VMo_6O_{24}H_6]^{3-}$ was isolated and characterized by its FTIR spectra. The rate of the reaction also increases with increase in ionic strength and the decrease in the relative permittivity of the medium. Along with the effect of ionic strength and relative permittivity the activation parameters determined also support the mechanism. The detailed mechanism and the rate equation are proposed for the reaction.

1. Introduction

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 heterogeneous and homogeneous

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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 available 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] much 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 catalyzed by polyoxometalates [13] we now present our studies on a novel system: the oxidation of benzoic acid hydrazide by bromate catalyzed by an Anderson-type polyoxomolybdate, sodium hexamolybdochromate(III). Hydrazides, which are derivatives of both carboxylic acids and hydrazine have been utilized as starting materials in organic 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].

2. Experimental

2.1 Materials and reagents

Reagent grade chemicals and doubly distilled water were used throughout the work. The $KBrO_3$ solution was prepared by dissolving $KBrO_3$ (BDH) in water standardized iodometrically. The hydrazides were prepared by esterification of the corresponding acids in ethanol followed by their conversion to hydrazides according to the reported [18] procedure. The solutions of hydrazides were pre-

pared by dissolving them in water. Ionic strength was maintained using KCl, and to vary hydrogen ion concentration HCl (BDH) was used.

2.2. Catalyst preparation and characterization

The catalyst Sodium hexamolybdochromate (III) was prepared by the previously reported method [11]. The pH of a solution containing 14.5 g of $Na_2MoO_4 \cdot 2H_2O$ in 30 ml of water was adjusted to 4.5 with concentrated HNO_3. A second solution was made by dissolving 4.0 g of $Cr(NO_3)_3 \cdot 9H_2O$ in 5 ml of water. Both the solutions were mixed together, and the mixture was boiled for 1 min and filtered while hot. The filtrate was set aside for crystallization and crystals started to appear in 1 hr. The solution was allowed to stand for 2 weeks before the precipitate was filtered off and washed several times with cold water. Reddish purple crystals were obtained.

The complex $Na_3[CrMo_6O_{24}H_6] \cdot 8H_2O$ was studied by AAS analysis. 100 mg of the recrystallized sample was dissolved in doubly glass-distilled water. 5 ml of this stock solution was diluted to 100 ml and used for AAS analysis of Cr and Mo metals using Perkin-Elmer AAnalyst-300. The complex $Na_3[CrMo_6O_{24}H_6] \cdot 8H_2O$ shows (Theoretical): Na-5.6303 % (5.6052 %), Cr-4.2227 % (4.2242 %) and Mo-46.217 % (46.2109 %).

2.3 Characterization of oxidized form of catalyst

During kinetic studies, it was observed that the purple color of the catalyst changed to green in presence of bromate. The green colored product was crystallized form the solution and FTIR spectra was recorded. The FTIR of the green product obtained shows that the peak corresponding to $M-O_c-M$ of Cr^{III}-molybdate at 643 cm^{-1} (Fig. 2(A)) was splitted into two peaks (Fig. 2(B)) due to the change in the oxidation state of hetero atom Cr^{III}. There was also a new peak at 829 cm^{-1} corresponding to the $Cr^V = O$.

2.4 Kinetic measurements

The reaction was studied under pseudo-first-order conditions keeping hydrazide concentration large excess at constant temperature of 25.0 ± 0.1 °C. The reaction was initiated by mixing the previously thermostated 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 (Fig. 1) were linear for more than 70 % completion of the reaction and the rate constants were reproducible within ± 6 %.
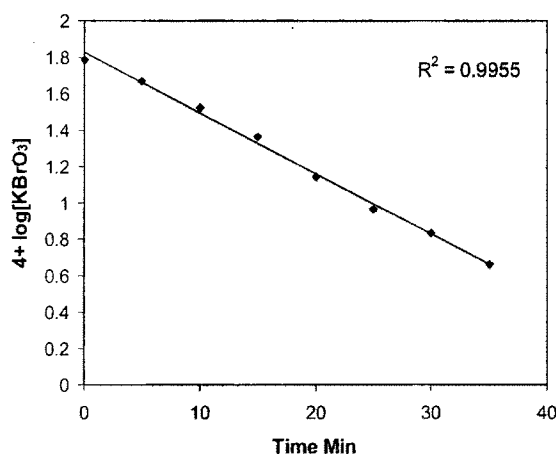
Fig. 1. Pseudo-first-order plot of log [KBrO$_3$] against time at 25 °C. 10^2[Hydrazide] = 1.0 mol dm^{-3}, 10^3[KBrO$_3$] = 1.0 mol dm^{-3}, 10^4[H$_6$Cr^{III} Mo$_6$O$_{24}$]$^{3-}$ = 1.0 mol dm^{-3}, [HCl] = 0.1 mol dm^{-3} and I = 0.5 mol dm^{-3}.

2.5 Stoichiometry and product analysis

In 10 ml of 0.6 mol dm^{-3} hydrochloric acid 40 µg mol (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.

3. Results

3.1 Reaction orders

The uncatalyzed reaction did not occur under the experimental conditions. The catalyzed reaction was carried out under pseudo-first-order conditions 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} (Table 1). The pseudo-first-order plots were found to be linear (Fig. 1) and the pseudo-first-order rate constants, k_{obs}, were fairly constant as the concentration of oxidant and hydrazide were varied (Table 1), indicating the order in reductant and oxidant to be unity each. The effect of catalyst concentration was studied between the concentration range of 5.0 × 10^{-5} to 5.0 × 10^{-4} mol dm^{-3} and the plot of k_{obs} against [catalyst] was found to be linear (R^2 = 0.977) indicating the first order dependence of reaction on [catalyst] (Table 2).

Table 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} and I = 0.5 mol dm^{-3}.

10^2 [Hydrazide] mol dm^{-3}	10^2 [KBrO$_3$] mol dm^{-3}	$10^3\ k_{obs}$ s^{-1}
0.5	0.1	1.2
0.6	0.1	1.3
0.7	0.1	1.2
0.8	0.1	1.2
1.0	0.1	1.3
3.0	0.1	1.1
4.0	0.1	1.1
5.0	0.1	1.1
1.0	0.04	1.2
1.0	0.06	1.2
1.0	0.2	1.3
1.0	0.3	1.2
1.0	0.4	1.3

Table 2. Effect of catalyst concentrations 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$_6$Cr^{III} Mo$_6$O$_{24}$]$^{3-}$ mol dm^{-3}	$10^3\ k_{obs}$ 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. Effect of hydrogen ion concentrations 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$_6$Cr^{III} Mo$_6$O$_{24}$]$^{3-}$ = 1.0 mol dm^{-3} and 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

3.2 Effect of hydrogen ion concentration.

The effect of hydrogen ion concentration was studied 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^{-5} (Table 3). The [H$^+$] accelerates the rate of

Table 4. Effect of acetonitrile content 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$_6$Cr^{III} Mo$_6$O$_{24}$]$^{3-}$ = 1.0 mol dm^{-3}, [HCl] = 0.1 mol dm^{-3} and I = 0.5 mol dm^{-3}.

Acetonitrile (% v/v)	10^3 k_{obs} s^{-1}
2.0	1.3
4.0	1.3
6.0	1.3
8.0	1.2
10	1.3

the reaction and the order in [H$^+$] was determined from the slope of log k_{obs} against log [H$^+$] plot (R^2 = 0.992). The order in [H$^+$] was found to be more than unity (1.7).

3.3 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 × 10^{-2} mol dm^{-3}, 1.0 × 10^{-3} mol dm^{-3}, 1.0 × 10^{-4} mol dm^{-3} and 0.1 mol dm^{-3}, respectively. Potassium chloride and acetonitrile were used to vary the ionic strength and solvent polarity, respectively. The rate of the reaction increases with increasing ionic strength (from 0.1 to 0.5 mol dm^{-3} and percentage of acetonitrile (from 0 to 40 % v/v). The effect of temperature on the reaction was studied at 20, 25, 30 and 40 °C and the pseudo-first-order rate constants were found to be 0.9 × 10^{-3}, 1.3 × 10^{-3}, 1.91 × 10^{-3} and 3.83 × 10^{-3} s^{-1} respectively. The activation parameters $\Delta H^{\#}$, $\Delta G^{\#}$ and $- \Delta S^{\#}$ were found to be 51.6 ± 6 kJ mol^{-1}, 96.8 ± 6 kJ mol^{-1} and 138.4 ± 7 JK^{-1} mol^{-1} respectively.

3.4 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 rate of the reaction (Table 4) 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.

4. Discussion

Oxidation of inorganic substrates like V^{IV} and [Co^{II}W$_{12}$O$_{40}$]$^{6-}$ by bromate have been studied [19, 20] 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 (Fig. 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 [21] 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} (Fig. 2(A)) was splitted into two peaks (Fig. 2(B)) 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 [22] of chromium substituted heteropolytungstate anions. Therefore, the Cr^{III}-molybdate under the experimental conditions gets oxidized to Cr^{V}-molybdate according to the Eq. 1.

$$H[H_6Cr^{III}Mo_6O_{24}]^{3-} + HBrO_3 \rightarrow [O = Cr^{V}Mo_6O_{24}]^{3-} + HBrO_2 \qquad (1)$$
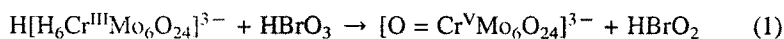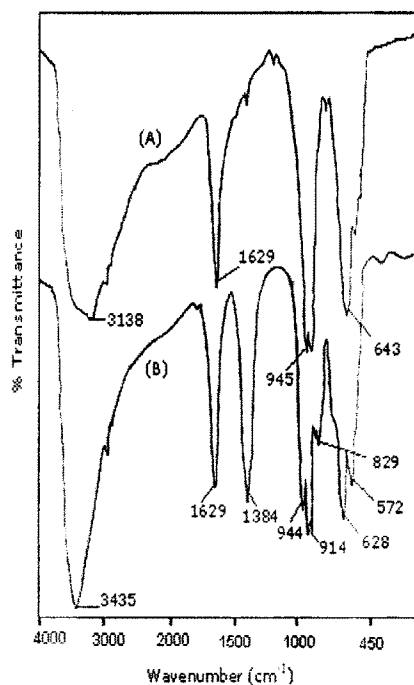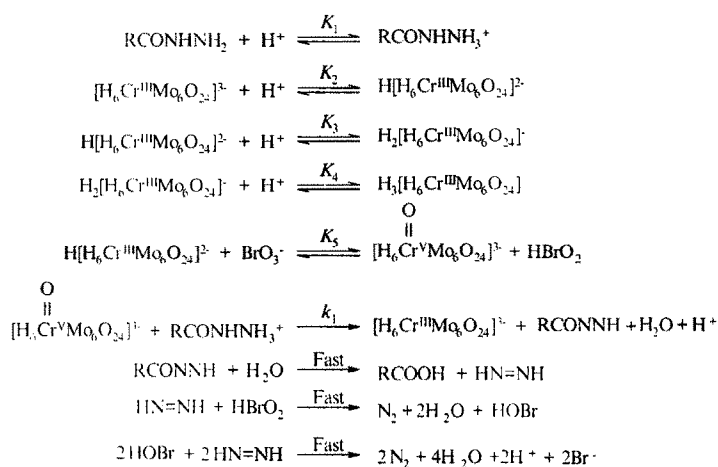
Fig. 2. FTIR Spectra of (A) hexamolybdochromate (III) and (B) hexamolybdochromate (V).

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 [23] 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 catalyst. The Anderson type polyoxometalates are known to undergo selective protonation [24] at the oxygen atom shared by two Mo atoms. Since, the catalyst prepared is [H$_6$Cr^{III}Mo$_6$O$_{24}$]$^{3-}$ 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.
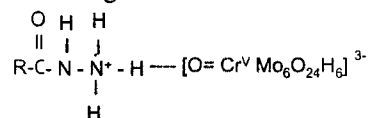
$$RCONHNH_2 + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} RCONHNH_3^+$$

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

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

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

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

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

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

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

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

Scheme 1

$$Rate = \frac{k_1 K_1 K_2 K_5 [H^+]^2 [RCONHNH_2][BrO_3^-][H_6Cr^{III}Mo_6O_{24}]^{3-}}{(1 + K_1[H^+])(1 + K_2[H^+] + K_2K_3[H^+]^2 + K_2K_3K_4[H^+]^3)} \quad (2)$$

$$k_{obs} = \frac{k_1 K_1 K_2 K_5 [H^+]^2 [H_6Cr^{III}Mo_6O_{24}]^{3-}}{(1 + K_1[H^+])(1 + K_2[H^+] + K_2K_3[H^+]^2 + K_2K_3K_4[H^+]^3)} \quad (3)$$

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 1 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 (Fig. 1) 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

$$\begin{array}{c} O \quad H \quad H \\ \parallel \quad \mid \quad \mid \\ R\text{-}C\text{-}N\text{-}N^+\text{-}H \cdots [O= Cr^V Mo_6O_{24}H_6]^{3-} \\ \mid \\ H \end{array}$$

qualitatively explains the reaction between charged ions of a similar kind, as shown in Scheme 1. 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 [25], as observed. The decrease in the value of entropy of activation also supports formation of such a transition state.

Appendix

According to Scheme 1

$$\text{Rate} = k_1 \,[\text{RCONHNH}_3]^+ [\,\overset{\overset{\textstyle O}{\textstyle \|}}{\text{H}_6\text{Cr}^V\text{Mo}_6\text{O}_{24}}]^{2-}$$

$$= k_1 K_5 [\text{RCONHNH}_3]^+ [\text{H}\{\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}\}]^{2-} [\text{BrO}_3]^-$$

From first equilibrium step of Scheme 1

$$[\text{RCONHNH}_2]_t = [\text{RCONHNH}_2]_f + K_1 [\text{H}^+][\text{RCONHNH}_2]_f$$

$$[\text{RCONHNH}_2]_f = [\text{RCONHNH}_2]_T / (1 + K_1 [\text{H}^+])$$

and

$$[\text{RCONHNH}_3]^+ = K_1 [\text{H}^+][\text{RCONHNH}_2]_f = K_1 [\text{H}^+][\text{RCONHNH}_2] / (1 + K_1 [\text{H}^+])$$

Then From the protonation equilibria of the catalyst, equilibria with K_2, K_3, and K_4, we have

$$[\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}]^{3-}_T = [\text{H}\{\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}\}]^{2-} + [\text{H}_2\{\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}\}]^- + [\text{H}_3\{\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}\}]$$

$$[\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}]^{3-}_T = [\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}]^{3-}_f (1 + K_2 [\text{H}^+] + K_2 K_3 [\text{H}^+]^2 + K_2 K_3 K_4 [\text{H}^+]^3)$$

$$[\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}]^{3-}_f = [\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}]^{3-}_T / (1 + K_2 [\text{H}^+] + K_2 K_3 [\text{H}^+]^2 + K_2 K_3 K_4 [\text{H}^+]^3)$$

$$[\text{H}\{\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}\}^{2-}] = K_2 [\text{H}^+][\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}]^{3-}_T / (1 + K_2 [\text{H}^+] + K_2 K_3 [\text{H}^+]^2 + K_2 K_3 K_4 [\text{H}^+]^3)$$

Substituting the values of $[\text{RCONHNH}_3]^+$ and $[\text{H}\{\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}\}]^{2-}$ in the rate expression we get

$$\text{Rate} = \frac{k_1 K_1 K_2 K_5 [\text{H}^+]^2 [\text{RCONHNH}_2][\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}]^{3-} [\text{BrO}_3]^-}{(1 + K_1 [\text{H}^+])(1 + K_2 [\text{H}^+] + K_2 K_3 [\text{H}^+]^2 + K_2 K_3 K_4 [\text{H}^+]^3)}$$

$$\frac{\text{Rate}}{[\text{BrO}_3]^-} = \frac{k_1 K_1 K_2 K_5 [\text{H}^+]^2 [\text{RCONHNH}_2][\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}]^{3-}}{(1 + K_1 [\text{H}^+])(1 + K_2 [\text{H}^+] + K_2 K_3 [\text{H}^+]^2 + K_2 K_3 K_4 [\text{H}^+]^3)}$$

Since due to pseudo-first-order conditions employed [RCONHNH_2] is also constant. Therefore, the observed pseudo-first-order rate constant is given by

$$k_{obs} = \frac{k_1 K_1 K_2 K_5 [\text{H}^+]^2 [\text{H}_6\text{Cr}^{III}\text{Mo}_6\text{O}_{24}]^{3-}}{(1 + K_1 [\text{H}^+])(1 + K_2 [\text{H}^+] + K_2 K_3 [\text{H}^+]^2 + K_2 K_3 K_4 [\text{H}^+]^3)}$$

References

1. M. T. Pope, *Isopoly and Heteropoly Anions*. Springer, Berlin, Germany (1983).
A. Muller, *Polyoxometalate Chemistry*. Kluwer Academic, Dordrecht, The Netherlands (2001).
I. V. Kozhevnikov, *Catalysis by Polyoxometalates*. Wiley, Chichester, U.K. (2002).
C. L. Hill and C. M. Prosser-McCartha, Coord. Chem. Rev. **143** (1995) 407.

N. Mizuno and M. Misono, **Chem. Rev. 98** (1998) 171.

R. Neumann, Prog. Inorg. **Chem. 47** (1998) 317.

2. K. I. Matveev, Kinet. Catal. **18** (1977) 716.

K. I. Matveev and I. V. Kozhevnikov, Kinet. Catal. **21** (1980) 855.

J. R. Grate, D. R. Mamm, and S. Mohajan, Mol. Eng. **3** (1993) 205.

H. Grennberg, K. Bergstad, and J. E. Backvall, J. Mol. Catal. **113** (1996) 355.

T. Yokota, S. Fujibayashi, Y. Nishyama, S. Sakaguchi, and Y. Ishii, J. Mol. Catal. **114** (1996) 113.

K. Bergstad, H. Grennberg, and J. E. Backvall, **Organometallics 17** (1998) 45.

3. R. Neumann and I. Assael, **J. Chem Soc., Chem. Commun.** (1998) 1285.

O. Branytskaya and R. Neumann, **J. Org. Chem. 68** (2003) 9510.

4. J. M. Bregault, B. El Ali, J. Mercier, J. Martin, C. C. Martin, and R. Acad, Sci. II **309** (1989) 459.

B. El Ali, J. M. Bregault, J. Mercier, J. Martin, C. Martin, and O. Convert, J. **Chem. Soc., Chem. Commun.** (1989) 825.

A. Atlamsani, M. Ziyad, and J. M. Bregault, J. Chim. Phys., Phys. Chim. Biol. **92** (1995) 1344.

A. M. Khenkin and R. Neumann, **J. Org. Chem. 67** (2002) 7075.

R. Ben-Daniel and R. Neumann, **Angew. Chem., Int. Ed. 42** (2003) 92.

R. Neumann and M. Levin, **J. Org. Chem. 56** (1991) 5707.

R. Ben-Daniel, P. L. Alsters, and R. Neumann, J. Org. **Chem. 66** (2001) 8650.

L. El Aakel, F. Launay, A. Atlamsani, and J. M. Bregeault, **Chem. Commun.** (2001) 2218.

A. M. Khenkin, I. Vigdergauz, and R. Neumann, Chem. Eur. J. **6** (2000) 875.

5. O. A. Kholdeeva, A. V. Golovin, R. I. Maksimovskaya, I. V. Kozhevnikov, and J. Mcl, Catal. **75** (1992) 235.

M. Lissel, H. Jansen van de Wal, and R. Neumann, Tetrahedron Lett. **33** (1992) 1795.

I. G. Kolesnik, E. G. Zhizhina, and K. I. Matveev, J. Mol. Catal. A **153** (2000) 147.

6. A. M. Khenkin and R. Neumann, **J. Am. Chem. Soc. 124** (2002) 4198.

R. Neumann and M. de la Vega, J. Mol. Catal. **84** (1993) 93.

K. Nomiya, H. Yanagibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu, and Y. Shimizu, J. Mol. Catal. A **114** (1996) 181.

A. M. Khenkin and R. Neumann, **Angew. Chem., Int. Ed. 39** (2000) 4088.

A. M. Khenkin, L. Weiner, Y. Wang, and R. Neumann, J. Am. Chem. Soc. **123** (2001) 8531.

7. R. Neumann and M. Lissel, **J. Org. Chem. 54** (1989) 4607.

R. Neumann and M. Levin, **J. Am. Chem. Soc. 114** (1992) 7278.

8. A. M. Khenkin and R. Neumann, **J. Am. Chem. Soc. 123** (2001) 6437.

9. R. D. Gall, M. Faraj, and C. L. Hill, **Inorg. Chem. 33** (1994) 5015.

I. V. Kozhevnikov, V. I. Simagina, G. V. Varnakova, and K. I. Matveev, Kinet. Catal. **20** (1979) 506.

B. S. Dzhumakaeva, V. A. Golodov, and J. Mol, Catal. **35** (1986) 303.

M. K. Harrup and C. L. Hill, **Inorg. Chem. 33** (1994) 5448.

M. K. Harrup and C. L. Hill, J. Mol. Catal. A. **106** (1996) 57.

R. D. Gall, C. L. Hill, and J. E. Walker, J. Catal. **159** (1996) 473.

10. A. M. Khenkin and R. Neumann, **Adv. Synth. Catal. 344** (2002) 1017.

11. A. Perloff, Inorg. **Chem. 9** (1970) 2228.

12. F. Shirini F. M. A. Zolfigol, and A. R. Abri, Lett. Org. Chem. **3** (2006) 292.

B. F. Mirjalili, M. A. Zolfigol, A. Bamoniri, Z. Zaghaghi, and A. Hazar, Acta. Chim. Slov. **50** (2003) 563.

L. Metsger and S. Bittner, **Tetrahedron 56** (2000) 1905.

13. S. P. Mardur, S. B. Halligudi, and G. S. Gokavi, Catal. Lett. **96** (2004) 165.

S. P. Mardur and G. S. Gokavi, Catal. Commun. **8** (2007) 279.

14. M. Kocevar, P. Mihorko, and S. Polanc, J. Org. Chem. **60** (1995) 1466.
T. G. Back, S. Collins, and R. G. Kerr, J. Org. Chem. **46** (1981) 1564.
R. V. Hoffman and A. Kumar, J. Org. Chem. **49** (1984) 4014.
15. T. L. Ho, H. C. Ho, and C. M. Wong, Synthesis (1972) 562.
J. Schnyder and M. Rttenberg, Helv. Chim. Acta. **58** (1975) 521.
J. Tsuji, H. Takayanagi, and Y. Toshida, Chem. Lett. (1976) 147.
16. J. B. Aylward and R. O. C. Norman, J. Chem. Soc. (1968) 2399.
J. Tsuji, S. Hayakawa, and H. Takayanagi, Chem. Lett. (1975) 437.
J. Tsuji, T. Nagashima, N. T. Qui, and H. Takayanagi, Tetrahedron **36** (1980) 1311.
R. V. Hoffman and A. Kumar, J. Org. Chem. **49** (1984) 4014.
17. W. A. F. Gladstone, J. Chem. Soc. (C) (1969) 1571.
P. P. Kulkarni, A. J. Kadam, U. V. Desai, R. B. Mane, and P. P. Wadgaonkar, J. Chem. Res. (S) (2000) 184.
V. K. Jadhav, P. P. Wadgaonkar, and M. M. Salunkhe, J. Chin. Chem. Soc. **45** (1998) 831.
18. A. I. Vogel, *A Textbook of Practical Organic Chemistry, Including Qualitative Analysis*. 3rd Edn, ELBS and Longmann Group (1975).
19. R. C. Thompson, Inorg. Chem. **10** (1971) 1892.
20. M. Ali, Transition Met. Chem. **28** (2003) 345.
21. A. M. Hasure and G. S. Gokavi, Transition Met. Chem. **29** (2004) 231.
22. C. Rong and F. C. Anson, Inorg. Chem. **33** (1994) 1064.
23. P. V. Krishna Rao, M. S. Frank, and A. K. Ramaiah, React. Kinet. Cat. Lett. **9** (1978) 159.
M. Shibata, P. Zuman, and J. Electroanal, Chem. **420** (1997) 79.
24. D. Honda, S. Ikegami, T. Inoue, T. Ozeki, and A. Yagasaki, Inorg. Chem. **46** (2007) 1464.
25. E. S. Amis, *Solvent effects on the Reaction Rates and Mechanism*. Academic Press, New York (1966).