

## **CHAPTER -IV**

**Kinetics and Mechanism of  
Oxidation of benzoic acid  
hydrazide by bromate catalyzed  
by octamolybdomanganate (II)  
( $[\text{MnMo}_8\text{O}_{27}]^{4-}$ ) in aqueous  
acidic medium**

Potassium and sodium bromate are stable solids and easily handled as compared with liquid bromine and hypobromous acid solutions. The product of bromate oxidation is bromide ion, which can be safely recycled thus making the methods of their oxidations environmentally benign than the metal ion oxidations. Bromates have been used for various organic oxidative transformations[1-16]. Although the bromate itself is a strong oxidizing agent having a redox potential [17] of 1.45 V, the oxidations generally require a catalyst due to the slowness of the uncatalyzed reactions under normal conditions. The catalysts used for bromate oxidations are in their lower oxidation state, which will be oxidized to the corresponding higher oxidation state. The oxidized form of the catalyst [15,16 ] will then affect the further conversion of the substrate into the product. Bromate ion is also used for volumetric[18] determination of inorganic ions having the redox potential < 0.8 V and for the ions exceeding this value of the potential the analysis of the ions becomes difficult due to their slow oxidation. Kinetics of oxidation of inorganic reductants like vanadium(V)[19] and 12-tungstocobaltate(II)[20] have also been studied by using bromate and their mechanisms are predicted. Hydrazides, derivatives of both carboxylic acids and hydrazine have been utilized as starting materials in organic synthesis [21]. The oxidative transformation with most oxidants give corresponding acids and in some cases [21] esters or amides. Hydrazides have also been converted into N-N-diacylhydrazines with [22,23] various oxidants. Formation of acids and their derivatives in presence of different nucleophiles is the indication of direct two-electron transfer to the oxidant, while cyclization products generally involve a single electron transfer with intervention of a free radical.

Polyoxometalate (POM) anions are used [25] in almost all aspects of chemistry and material science due to their tunable physical and chemical properties. These anions are used as oxidants and catalysts [26] (both redox and acid) for various organic transformations. The electron transfer reactions of POM anions are generally outer-sphere in nature as the hetero atom is surrounded by the oxometalate moiety thus making the free access to the hetero atom difficult for other reactants. The mechanistic studies involving POM are concentrated on

the Keggin type anion[25], as an oxidant containing hetero atom in its higher oxidation state and variety of organic and inorganic substrates have been oxidized by these POMs. In comparison with Keggin and Dawson type of salts, less attention is given to other type of POM anions. In continuation [16,27-37] of our interest in the electron transfer reactions involving POMs and their utilization as redox catalysts the present study of oxidation of benzoic acid hydrazide by bromate in presence of octamolybdomanganate(II) ( $[\text{MnMo}_8\text{O}_{27}]^{4-}$ ). Octamolybdomanganate(II) consists of a sheet structure in which  $\text{MoO}_6$  units are polymerized around  $\text{Mn}(\text{OH}_2)_4$  groups with sharing of common oxygen atoms.

The reaction was studied under pseudo-first-order conditions keeping hydrazide concentration excess at constant temperature of  $27.0 \pm 0.1^\circ\text{C}$ . 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  $\log [\text{Oxidant}]$  against time. The pseudo-first-order plots were linear for more than 70% completion of the reaction and the rate constants were reproducible within  $\pm 6\%$ .

### Stoichiometry and product analysis

In 10 ml of  $0.6 \text{ mol dm}^{-3}$  hydrochloric acid  $40 \mu\text{mol}$  ( 5.0 mg) catalyst and 1 m mol (0.136 g ) of benzoic acid hydrazide were dissolved. To the resulting solution 1m mol (0.167 mg) of  $\text{KBrO}_3$  was added. The reaction mixture was stirred at  $27^\circ\text{C}$  for five minutes. The benzoic acid separated was filtered and recrystallized by water. The m.p. of the recrystallized product was found to be  $121^\circ\text{C}$  (lit M. P.  $121^\circ\text{C}$  ). Therefore the stoichiometry of the reaction was found to be two moles of oxidant per three moles of the hydrazide.

### Reaction orders

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  $0.1 \text{ mol dm}^{-3}$  and at a constant ionic strength of  $0.5 \text{ mol dm}^{-3}$ . The pseudo-first-order plots were found to be linear and the pseudo-first-order rate constants,  $k_{\text{obs}}$ , were fairly constant as the concentration of hydrazide was varied between  $0.5 \times 10^{-2}$  to  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$  keeping concentration of oxidant and catalyst constant at  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  respectively. (Table I), indicating the order in reductant to be unity. The pseudo-first-order plots of  $\log [\text{BrO}_3^-]$  against time were linear up to more than 70 % completion of the reaction and values of  $k_{\text{obs}}$  were found to be constant with the increase in concentration of the oxidant between  $0.4 \times 10^{-3}$  to  $2.0 \times 10^{-3} \text{ mol dm}^{-3}$  keeping concentration of hydrazide and catalyst constant at  $1.0 \times 10^{-2}$  and  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  respectively (Table I) indicating an order of unity in oxidant concentration also. The effect of catalyst concentration was studied between the concentration range of  $4.0 \times 10^{-5}$  to  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$  (Table 2) and the order in catalyst concentration was found to be 1.5 as determined from the slope of plot  $-\log k_{\text{obs}}$  against  $-\log [\text{catalyst}]$ .

#### **Effect of hydrogen ion concentration.**

The effect of hydrogen ion was studied in order to understand the nature of reactant species present in the solution. The concentration of  $[\text{H}^+]$  was varied between 0.03 to  $0.3 \text{ mol dm}^{-3}$  keeping concentration of reductant, oxidant and catalyst constant at  $1.0 \times 10^{-2}$ ,  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  respectively, (Table 4.3) and the plot of  $k_{\text{obs}}$  against  $[\text{H}^+]$  was found to be linear indicating the first order dependence of reaction on  $[\text{H}^+]$ .

**Table 4.1**

Effect of reactant concentrations on the rate of reaction at 27 °C.

 $10^4 [\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-} = 1.0 \text{ mol dm}^{-3}$      $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$      $I = 0.5 \text{ mol dm}^{-3}$ .

$10^2 [\text{Hydrazide}]$ $\text{mol dm}^{-3}$	$10^3 [\text{KBrO}_3]$ $\text{mol dm}^{-3}$	$10^3 k_{\text{obs}} \text{ s}^{-1}$
0.5	1.0	1.7
0.8	1.0	1.9
1.0	1.0	1.9
2.0	1.0	1.9
5.0	1.0	1.4
1.0	0.4	1.4
1.0	0.8	1.6
1.0	1.0	2.1
1.0	2.0	2.9
1.0	4.0	4.0

**Table 4.2**

Effect of catalyst concentration on the reaction at 27°C.

$10^2$  [Hydrazide] = 1.0 mol dm<sup>-3</sup>       $10^3$  [KBrO<sub>3</sub>] = 1.0 mol dm<sup>-3</sup>  
[HCl] = 0.1 mol dm<sup>-3</sup> and      I = 0.5 mol dm<sup>-3</sup>

$10^4$ [Mn <sup>II</sup> Mo <sub>8</sub> O <sub>27</sub> ] <sup>4-</sup> mol dm <sup>-1</sup>	$10^3$ k <sub>obs</sub> s <sup>-1</sup>
0.2	0.2
0.4	0.6
0.8	1.4
1.0	2.1
2.0	6.4
3.0	11.2

**Table 4.3**

Effect of hydrogen ion concentration on the reaction at 27°C.

$10^2 [\text{Hydrazide}] = 1.0 \text{ mol dm}^{-3}$        $10^3 [\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$ ,

$10^4 [\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-} = 1.0 \text{ mol dm}^{-3}$ ,       $I = 0.5 \text{ mol dm}^{-3}$ .

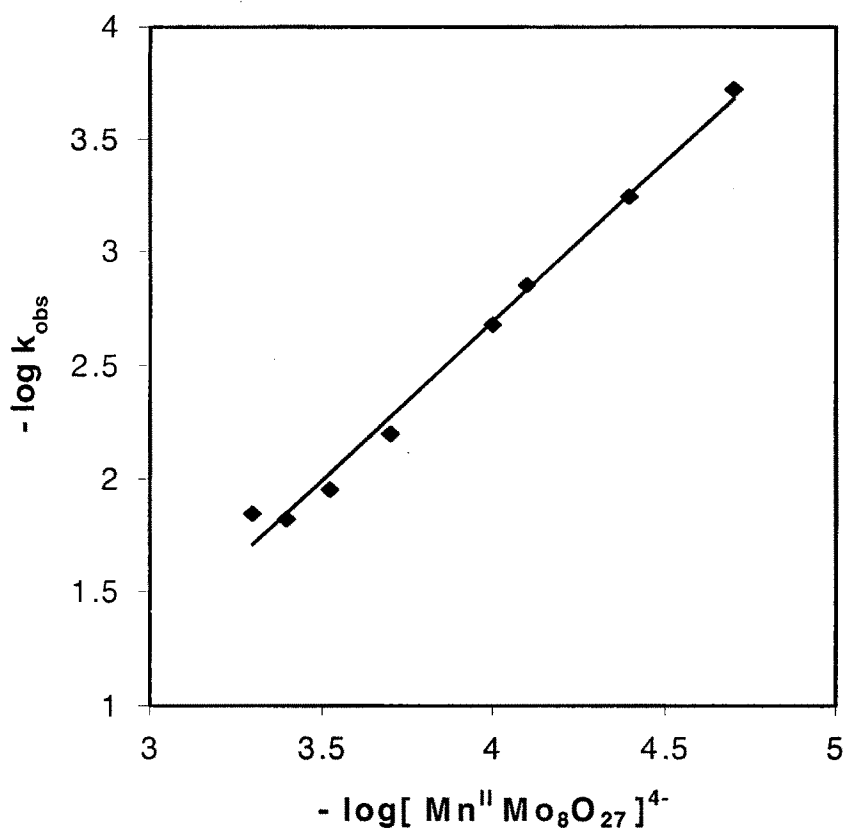
$10 [\text{HCl}]$ $\text{mol dm}^{-3}$	$10^3 k_{\text{obs}} \text{ s}^{-1}$
0.3	0.8
0.6	1.5
1.0	1.9
2.0	3.8
3.0	6.7

**Figure 4.1**

Reaction order with respect to catalyst.

Graph of  $-\log k_{\text{obs}}$  against  $-\log [\text{Catalyst}]$

Conditions as in Table 4.2.



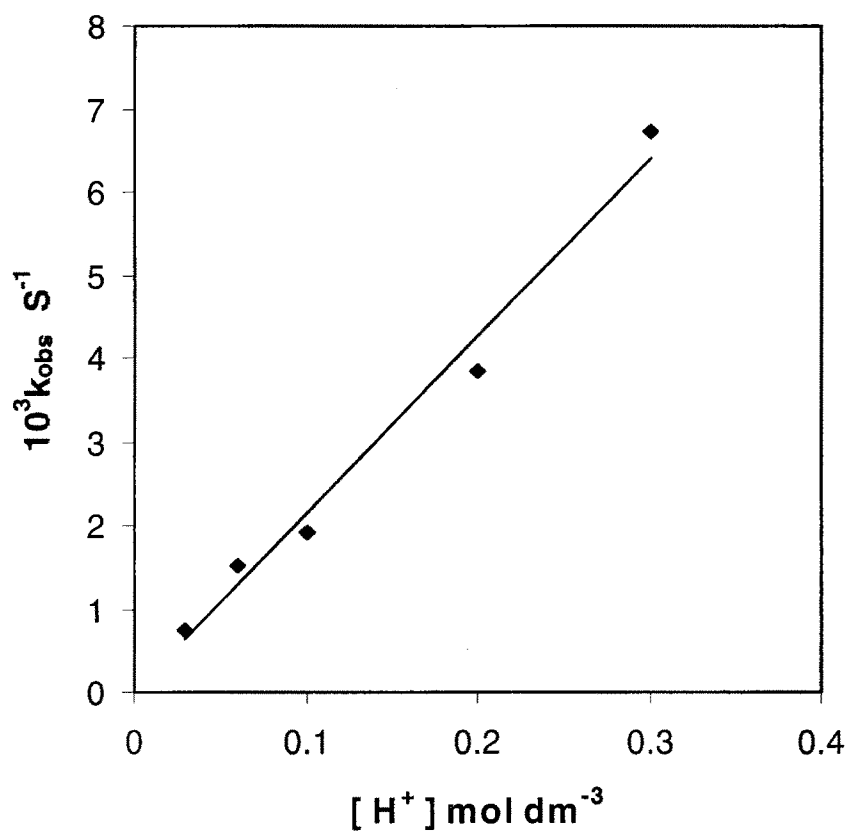


**Figure 4.2**

Reaction order with respect to hydrogen ion concentration.

Graph of  $k_{\text{obs}}$  against  $[\text{H}^+]$

Conditions as in Table 4.3



### Effect of ionic strength, solvent polarity and temperature

The effects of ionic strength, solvent polarity and temperature were studied by keeping [hydrazide], [KBrO<sub>3</sub>], [catalyst] and [HCl] constant at  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$  and  $2.0 \text{ mol dm}^{-3}$ , respectively. Potassium chloride and acetonitrile were used to vary the ionic strength and solvent polarity respectively. The rate of the reaction remains constant with increasing ionic strength (from 0.05 to 0.5  $\text{mol dm}^{-3}$ ). The dielectric constant of reaction mixtures were computed (Table 4.6) from the dielectric constant values of pure solvents using formula,

$$D = V_1D_1 + V_2D_2$$

Where  $V_1$  and  $V_2$  are the volume fractions and  $D_1$  and  $D_2$  are dielectric constants of water( 78.5) and acetonitrile( 37.0) respectively. The plot of  $\log k_{\text{obs}}$  versus  $1/D$  was found to be linear with positive slope. (Figure 4.3).The effect of temperature on the reaction was studied at 20, 27, 30 and 40°C and the pseudo-first-order rate constants were determined (Table 4.8). The activation parameters  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$  and  $-\Delta S^\ddagger$  were also determined (Table 4.9) from graph of  $\log k_{\text{obs}}$  and  $\log k_{\text{obs}}/T$  against  $1/T$  (Figure 4.4 and 4.5).

### Test for free radical intervention

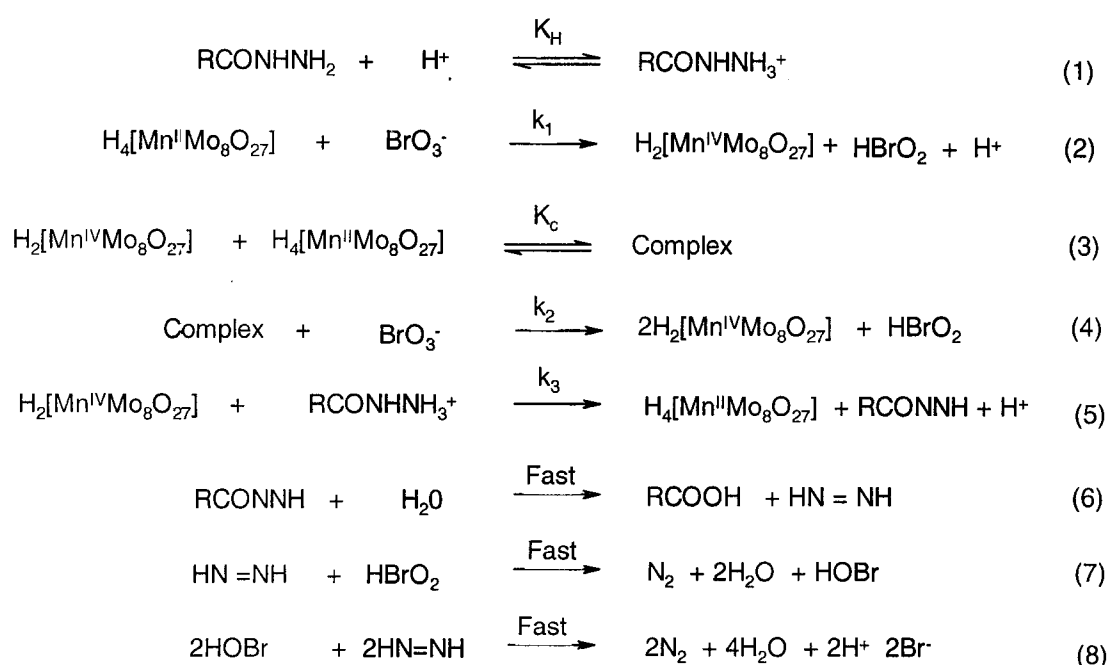
The reaction was also studied in presence of added acrylonitrile to understand the intervention of free radicals in the reaction. There was no effect of added acrylonitrile on the reaction and also no precipitate due to the polymerization of the added acrylonitrile was observed, thus confirming the absence of any free radical formation in the reaction.

### Discussion

Oxidation of manganese(II) in presence of molybdate ion, by bromate has been studied and found to follow an autocatalytic mechanism by the product,  $[\text{MnMo}_9\text{O}_{32}]^{\delta-}$ , was predicted. The reaction was initiated by the oxidation of manganese(II) and the stoichiometry predicts  $\text{Br}_2$  as the product of reduction of

bromate. The oxidation potential[20] of  $\text{Br}_2$  is 1.97 V indicating that it can very easily oxidizes the substrate, benzoic acid hydrazide, in acidic solutions. The test for formation of bromide ion was carried out in sulphuric acid solution instead of hydrochloric acid by adding silver nitrate to the reaction mixture after completion of the reaction. The precipitation of silver bromide confirms the formation of bromide as one of the product of the reaction. Therefore, the product of the reaction under the experimental conditions is bromide ion. 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 accelerating effect of hydrogen ion concentration on the reaction with an order of unity in its concentration is due to the various protonation equilibria of the oxidant and the catalyst. The protonation constants of polyoxomolybdates like the anion  $[\text{MnMo}_9\text{O}_{32}]^{6-}$  are generally high ( $\text{pK}_a = 3.0$ ) and 90 % of the anion is in the protonated form below the  $\text{pH} = 2$ . Therefore, since the present study was carried out between the hydrogen ion concentration range of 0.03 to 0.3, the catalyst  $[\text{MnMo}_8\text{O}_{27}]^{4-}$  will be in its protonated form. Potassium bromate is a strong electrolyte and in aqueous solution it exists as  $\text{BrO}_3^-$  which is also a strong acid thus its protonation would not be possible under the experimental conditions. Another possibility of protonation prior equilibria due to the involvement of an induction period, as observed in bromate oxidations, is also ruled out as no such induction period was observed. Therefore, the accelerating effect of hydrogen ion concentration is due to the prior protonation of the substrate, benzoic acid hydrazide and its protonated form is the active species. Since, the uncatalyzed reaction does not occur under the experimental conditions, the catalyzed reaction proceeds with the interaction of the catalyst and the oxidant. The order in both oxidant and reductant were found to be unity whereas, the order in catalyst concentration was also found to be more than unity (1.5). The order of more than unity in catalyst concentration is due to autocatalytic nature of its oxidation by bromate as reported earlier in which the oxidized form of the catalyst undergo complexation with the un-oxidized form of the catalyst resulting in an induction period. The non-occurrence of induction period in the present study, is due to the

pseudo-first-order conditions utilized and the product of oxidation of the catalyst,  $[\text{MnMo}_8\text{O}_{27}]^{2-}$ , reacts rapidly with the substrate without its accumulation. Therefore, the initiation of the reaction is the autocatalytic oxidation of the catalyst to its higher oxidation state by bromate which then forms complex with the catalyst. The substrate is oxidized in the following steps both by the oxidized form of the catalyst and its complex with the catalyst remaining. On the basis of kinetic results, considering the protonated form of the catalyst and the bromate ion as the active species, the initiation of the reaction takes place by the oxidation of protonated catalyst,  $\text{H}_4[\text{Mn}^{\text{II}}\text{Mo}_8\text{O}_{27}]$ , to its higher oxidation state  $\text{H}_2[\text{Mn}^{\text{IV}}\text{Mo}_8\text{O}_{27}]$ . The oxidized form of the catalyst  $\text{H}_2[\text{Mn}^{\text{IV}}\text{Mo}_8\text{O}_{27}]$  forms a complex with the free catalyst in a prior equilibria. The oxidized form of the catalyst oxidize the substrate in slow step to give product as shown in Scheme 1.



**Scheme I**

The rate of reaction is given by,

$$\text{Rate} = k_3 [ \text{H}_2[\text{Mn}^{\text{IV}} \text{Mo}_8\text{O}_{27}] ] \cdot [ \text{RCONHNH}_3^+ ]$$

Substituting for [ RCONHNH<sub>3</sub><sup>+</sup> ] from equilibrium 1 of scheme I,

$$\text{Rate} = \frac{k_3 K_H [ \text{H}^+ ] [ \text{H}_2[\text{Mn}^{\text{IV}} \text{Mo}_8\text{O}_{27}] ] [ \text{RCONHNH}_3^+ ]}{( 1 + K_H [ \text{H}^+ ] )} \quad (9)$$

From equation 2 and equilibrium 3 of scheme I the [ H<sub>2</sub>[Mn<sup>IV</sup> Mo<sub>8</sub>O<sub>27</sub>] ] is given by

$$\begin{aligned} [\text{H}_2[\text{Mn}^{\text{IV}} \text{Mo}_8\text{O}_{27}]] &= k_1 [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] [ \text{BrO}_3^- ] + k_2 [ \text{Complex} ] [ \text{BrO}_3^- ] \quad (10) \\ &= k_1 [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] [ \text{BrO}_3^- ] + k_2 K_C [ \text{H}_2[\text{Mn}^{\text{IV}} \text{Mo}_8\text{O}_{27}] ] \\ &\quad [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] [ \text{BrO}_3^- ] \\ &= [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] [ \text{BrO}_3^- ] ( k_1 + k_2 K_C [ \text{H}_2[\text{Mn}^{\text{IV}} \text{Mo}_8\text{O}_{27}] ] ) \\ &= [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] [ \text{BrO}_3^- ] ( k_1 + k_1 k_2 K_C [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] ) \\ &= k_1 [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] [ \text{BrO}_3^- ] ( 1 + k_2 K_C [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] ) \end{aligned}$$

Substituting the value of [ H<sub>2</sub>[Mn<sup>IV</sup> Mo<sub>8</sub>O<sub>27</sub>] ] into the rate equation we get,

$$\text{Rate} = \frac{k_1 k_3 K_H [ \text{RCONHNH}_2 ] [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] [ \text{BrO}_3^- ] [ 1 + k_2 K_C [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ]}{( 1 + K_H [ \text{H}^+ ] )} \quad (11)$$

$$k_{\text{obs}} = \frac{\text{Rate}}{[ \text{RCONHNH}_2 ] [ \text{BrO}_3^- ]} = \frac{k_1 k_3 K_H [ \text{H}^+ ] [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] ( 1 + k_2 K_C [ \text{H}_2[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}] ] )}{( 1 + K_H [ \text{H}^+ ] )} \quad (12)$$

**Table 4.5**

Effect of ionic strength on the oxidation of benzoic acid hydrazide by bromate catalyzed by  $[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-}$  in aqueous acidic medium at 27<sup>0</sup> C.

$10^2 [\text{hydrazide}] = 1.0 \text{ mol dm}^{-3}$        $10^3 [\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$

$[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$        $10^4 [\text{Mn}^{\text{II}}] = 1.0 \text{ mol dm}^{-3}$

$I = 0.5 \text{ mol dm}^{-3}$

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$10 [\text{KCl}]$ $\text{mol dm}^{-3}$	$10^3 k_{\text{obs}}$ $\text{s}^{-1}$
0.5	2.3
0.8	1.7
1.0	2.3
2.0	2.3
5.0	2.6

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**Table 4.6**

Effect of dielectric constant of medium on the oxidation of benzoic acid hydrazide by bromate catalyzed by  $[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-}$  in aqueous acidic medium at 27<sup>0</sup> C.

$10^2 [\text{hydrazide}] = 1.0 \text{ mol dm}^{-3}$        $10^3 [\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$   
 $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$                $10^4 [\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-} = 1.0 \text{ mol dm}^{-3}$   
 $I = 0.5 \text{ mol dm}^{-3}$

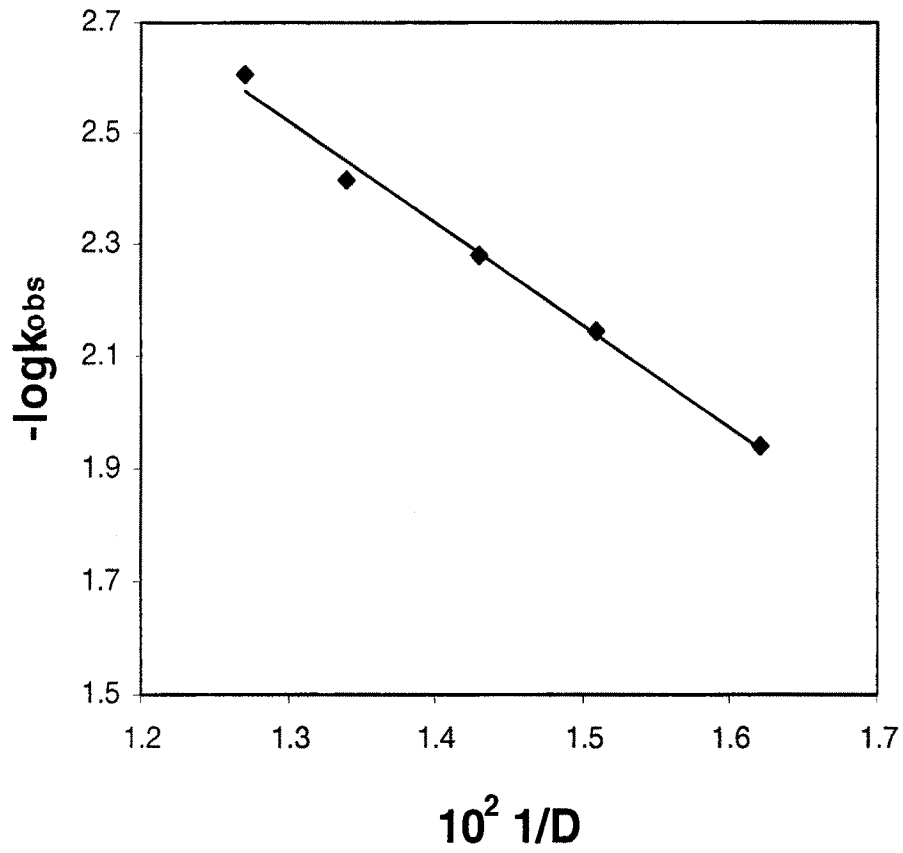
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% Acetonitrile (V/V)	Dielectric constant (D)	$10^3 k_{\text{obs}}$ $\text{S}^{-1}$	$-\log k_{\text{obs}}$	$10^2 1/D$
0	78.50	2.5	2.6038	1.27
10	74.35	3.8	2.4168	1.34
20	69.90	5.3	2.2781	1.43
30	66.05	7.2	2.1432	1.51
40	61.90	11.5	1.9393	1.62

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**Figure 4.3**

Effect of dielectric constants of medium on the oxidation of benzoic acid hydrazide by bromate catalysed by  $[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-}$  in aqueous acidic medium, conditions as in Table 3.5





**Table 4.7**

Effect of acrylonitrile concentration (% v/v ) on the oxidation of benzoic acid hydrazide by bromate catalyzed by  $[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-}$  in aqueous acidic medium at 27<sup>0</sup> C

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

$$10^3 [\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$$

$$[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$$

$$10^4 [\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-} = 1.0 \text{ mol dm}^{-3}$$

$$I = 0.5 \text{ mol dm}^{-3}$$

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% Acrylonitrile ( v/v )	$10^3 k_{\text{obs}}$ $\text{S}^{-1}$
2	2.3
4	2.3
6	2.5
8	2.1
10	2.5

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**Table 4.8**

Effect of temperature on the oxidation of benzoic acid hydrazide by bromate catalyzed by  $[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-}$  in aqueous acidic medium.

$10^2 [\text{hydrazide}] = 1.0 \text{ mol dm}^{-3}$        $10^3 [\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$

$[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$                        $10^4 [\text{Mn}^{\text{II}}] = 1.0 \text{ mol dm}^{-3}$

$I = 0.5 \text{ mol dm}^{-3}$

Temp T (K)	$10^3 k_{\text{obs}}$ $\text{S}^{-1}$	$10^3$ (1/T)	- log $k_{\text{obs}}$	- log ( $k_{\text{obs}}/T$ )
293	1.3	3.41	2.87	5.34
300	2.1	3.33	2.67	5.15
303	2.7	3.30	2.57	5.05
313	4.8	3.19	2.32	4.82

**Table 4.9**

Activation parameters for the oxidation of benzoic acid hydrazide by bromate catalyzed by  $[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-}$  in aqueous acidic medium.

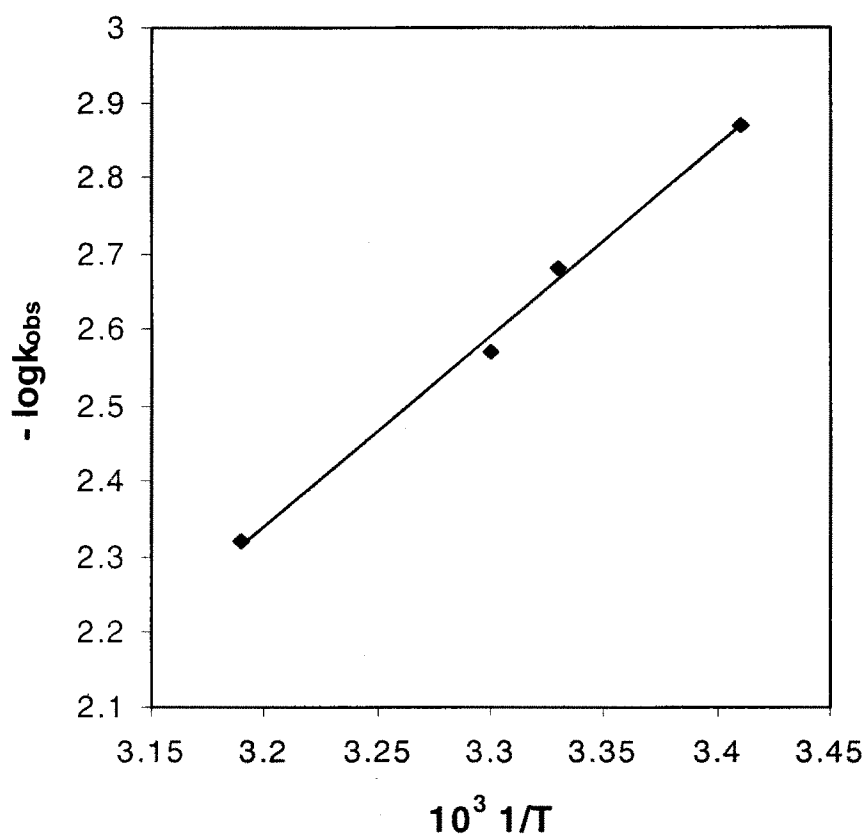
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$E_a$ ( $\text{kJ mol}^{-1}$ )	$48.49 \pm 1$
$\Delta H^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$51.39 \pm 6$
$\Delta S^\ddagger$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$-142.80 \pm 7$
$\Delta G^\ddagger$ ( $\text{kJ mol}^{-1}$ )	$94.23 \pm 6$

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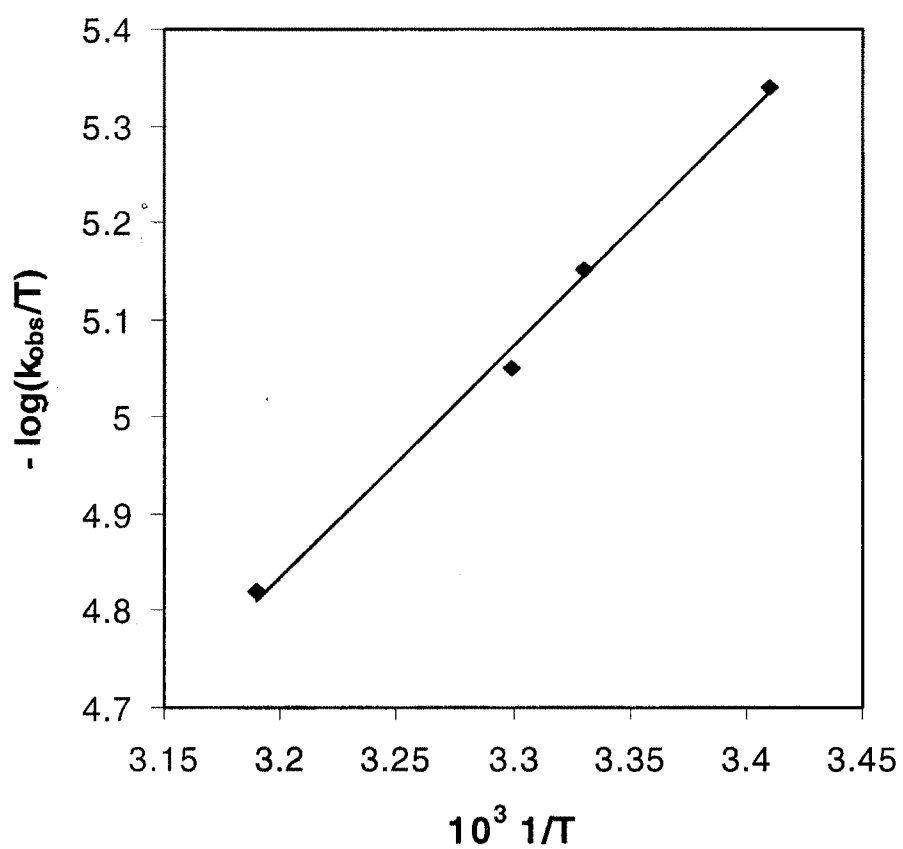
**Figure 4. 4**

Effect of temperature on the oxidation of benzoic acid hydrazide by bromate catalyzed by  $[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-}$  in aqueous acidic medium, conditions as in Table 4.8



**Figure 4.5**

Effect of temperature on the oxidation of benzoic acid hydrazide by bromate catalyzed by  $[\text{Mn}^{\text{II}} \text{Mo}_8\text{O}_{27}]^{4-}$  in aqueous acidic medium, conditions as in Table 4.8.



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