

# CHAPTER-IV

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*Kinetics and mechanism of oxidation of benzoic acid hydrazide by bromate catalyzed by selenium(IV) in aqueous acidic medium.*

**Introduction:**

Selenium has the properties of a typical semiconductor and its more important electronic property is photoconductivity, for this reason it is used in producing photocells, rectifiers and photographic exposure meters. It is also used in xerographic reproduction, in glass industry, as degasified and as vulcanizing agent. During the last four decades it has been reported that selenium, its dioxide and some organoselenium compounds can be used as stoichiometric oxidant or oxidation catalyst [1-5]. Selenium dioxide has been in the center of our interest. Solid  $\text{SeO}_2$  is a one dimensional polymer, the chain consisting of alternating 'Se' and oxygen atoms. Each 'Se' atom, which is pyramidal bears a terminal oxide group. Selenium dioxide is considered as acidic oxide. It dissolves in water to form selenous acid. It is an important reagent in organic synthesis. Oxidation of paraldehyde and cyclohexanone with  $\text{SeO}_2$  gives glyoxal [6] and cyclohexane-1-2-dione [7] respectively. Selenium dioxide used as catalyst for oxidation of aldehyde [8-10] in presence of a secondary oxidant. Examples of selenium used as catalyst are oxidation of organosulfur compounds [11], azomethine compounds [12], benzyl amines [13], alkyl arene [14] and for epoxidation of alkenes [15-16]. Organoselenium compounds are used as the promoters of hydroperoxide oxidation of various groups of organic compounds.

**Product analysis:**

In 10 ml of  $0.6 \text{ mol dm}^{-3}$  hydrochloric acid  $0.045 \text{ m mol}$  (5.0 mg) catalyst and  $1 \text{ m mol}$  (0.136 g) of benzoic acid hydrazide were dissolved. To the resulting solution  $1 \text{ m mol}$  (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.

**Results:****Reaction order:**

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<sup>-3</sup> and at a constant ionic strength of 0.5 mol dm<sup>-3</sup> (Table 4.1). The pseudo-first-order plots were found to be linear (Table 4.1) on varying the concentration of oxidant between 0.5 x 10<sup>-3</sup> to 5.0 x 10<sup>-3</sup> mol dm<sup>-3</sup> keeping the concentration of catalyst and hydrazide constant at 1.0 x 10<sup>-4</sup> and 1.0 x 10<sup>-2</sup> mol dm<sup>-3</sup> respectively (Table 4.1) indicating the order in oxidant concentration is unity. The pseudo-first-order rate constants,  $k_{obs}$ , were fairly constant as the concentration of hydrazide was varied between 0.5 x 10<sup>-2</sup> to 5.0 x 10<sup>-2</sup> mol dm<sup>-3</sup> keeping all other concentrations constant (Table 4.2) therefore, the order in hydrazide concentration is also unity. The effect of catalyst concentration was studied between the concentration range of 1.0 x 10<sup>-5</sup> to 2.0 x 10<sup>-4</sup> mol dm<sup>-3</sup> and the plot of  $k_{obs}$  against [catalyst] (figure 4.1) was found to be linear indicating the first order dependence of reaction on [catalyst] (Table 4.3).

#### **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 [H<sup>+</sup>] was varied between 2.0 x 10<sup>-2</sup> to 0.4 mol dm<sup>-3</sup> (Table 4.4). The [H<sup>+</sup>] accelerates the rate of the reaction and the order in [H<sup>+</sup>] is found to be unity as determined from the plot of log  $k_{obs}$  against log [H<sup>+</sup>] (figure 4.2).

#### **Effect of ionic strength and temperature:**

The effects of ionic strength and temperature were studied keeping [hydrazide], [KBrO<sub>3</sub>], [catalyst] and [HCl] constant at 1.0 x 10<sup>-2</sup> mol dm<sup>-3</sup>, 1.0 x 10<sup>-3</sup> mol dm<sup>-3</sup>, 1.0 x 10<sup>-4</sup> mol dm<sup>-3</sup> and 0.1 mol dm<sup>-3</sup>, respectively. Sodium perchlorate was used to vary the ionic strength. The rate of the reaction remains unaffected with increasing ionic strength (from 0.1 to 0.5 mol dm<sup>-3</sup>) (Table 4.5). The effect of temperature on the reaction was studied at 20, 27, 30 and 40°C and the pseudo-first-order rate constants were found to be 3.0 x 10<sup>-4</sup>, 5.8 x 10<sup>-4</sup>, 7.3 x 10<sup>-4</sup> and 19 x 10<sup>-4</sup> s<sup>-1</sup> respectively (Table 4.6) and corresponding plots of log  $K_S$  and log  $K_S/T$  against 1/T and are shown in (figure 4.3 and 4.4). The activation parameters  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$  and  $-\Delta S^\ddagger$  were found to be 59.8 ± 6 kJ mol<sup>-1</sup>, 85.9 ± 6 kJ mol<sup>-1</sup> and 86.3 ± 7 JK<sup>-1</sup> mol<sup>-1</sup> respectively (Table 4.7).

#### **Effect of acrylonitrile:**

In order to understand the intervention of free radicals in the reaction the reaction was studied in presence of added acrylonitrile. There was no induced

polymerization of the acrylonitrile as there was no formation of the precipitate and also it did not affect the rate of the reaction.(Table 4.8)

**Effect of solvent polarity:**

The effect of solvent polarity on the reaction was studied by varying percentage of acetic acid from 2 to 40% v/v keeping hydrazide and bromate concentration constant at  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  respectively and catalyst concentration at  $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ . The kinetic data for the effect of solvent polarity is given in (Table 4.9).The dielectric constant of the reaction mixture were calculated by using the values for pure solvents (water and acetic acid) according to the formula.

$$D_{\text{mixture}} = V_1 D_1 + V_2 D_2$$

Where-  $D_1$  and  $D_2$  are dielectric constants of pure water and acetic acid at 298 K respectively and  $V_1$  and  $V_2$  are their respective volume fractions. The plot of  $-\log k_{\text{obs}}$  against  $1/D$  is shown in (figure 4.5). It was found that the decrease in the dielectric constant increases the rate of the reaction

**Table 4.1**

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

$10^4[\text{Se}^{\text{IV}}] = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ ,

$10^2[\text{Hydrazide}] = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{I}] = 0.5 \text{ mol dm}^{-3}$ .

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$10^3 [\text{KBrO}_3]$ mol dm <sup>-3</sup>	$10^3 k_{\text{obs}} \text{ s}^{-1}$
0.5	2.3
0.8	2.3
1.0	2.2
2.0	2.3
5.0	2.2

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**Table 4.2**

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

$10^4 [\text{Se}^{\text{IV}}] = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ ,

$10^3 [\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$ ,  $I = 0.5 \text{ mol dm}^{-3}$ .

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$10^2 [\text{Hydrazide}]$ mol dm <sup>-3</sup>	$10^3 k_{\text{obs}} \text{ s}^{-1}$
0.5	2.2
0.8	2.2
1.0	2.2
2.0	2.3
5.0	2.2

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**Table 4.3**

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

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

$[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$  and  $I = 0.5 \text{ mol dm}^{-3}$ .

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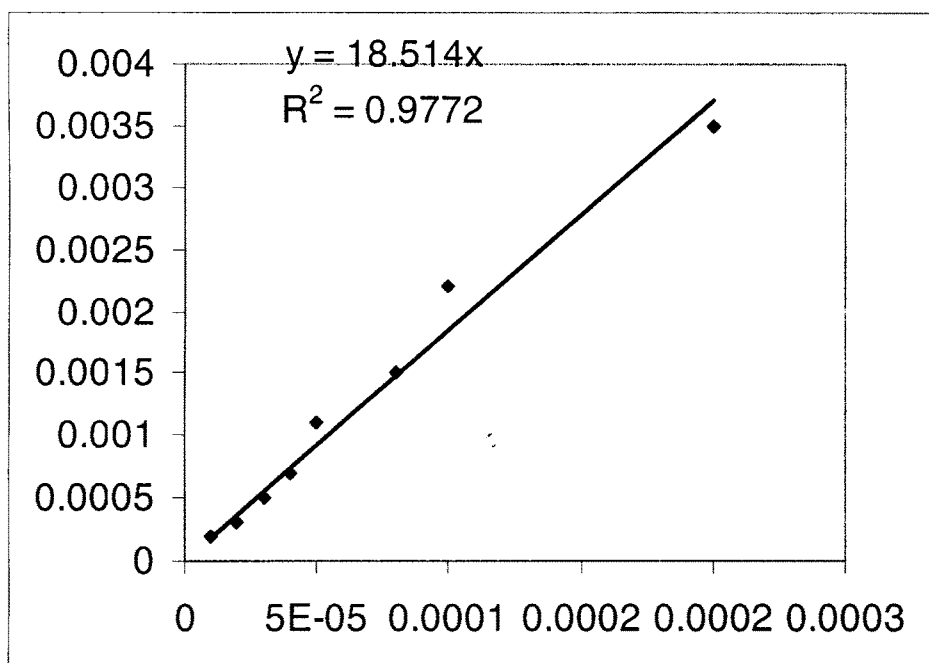
$10^4 [\text{Se}^{\text{IV}}]$ mol dm <sup>-3</sup>	$10^3 k_{\text{obs}} \text{ s}^{-1}$
0.1	0.2
0.2	0.3
0.3	0.5
0.4	0.7
0.5	1.1
0.8	1.5
1.0	2.2
2.0	3.5

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**Figure 4.1**

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

Conditions as in Table 4.3





**Table 4.4**

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

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

$10^4[\text{Se}^{\text{IV}}] = 1.0 \text{ mol dm}^{-3}$  and  $I = 0.5 \text{ mol dm}^{-3}$ .

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$10 [\text{HCl}]$ $\text{mol dm}^{-3}$	$10^3 k_{\text{obs}} \text{ s}^{-1}$
0.2	0.42
0.4	0.95
0.8	1.43
1.0	2.22
2.0	4.20
3.0	7.10
4.0	10.0

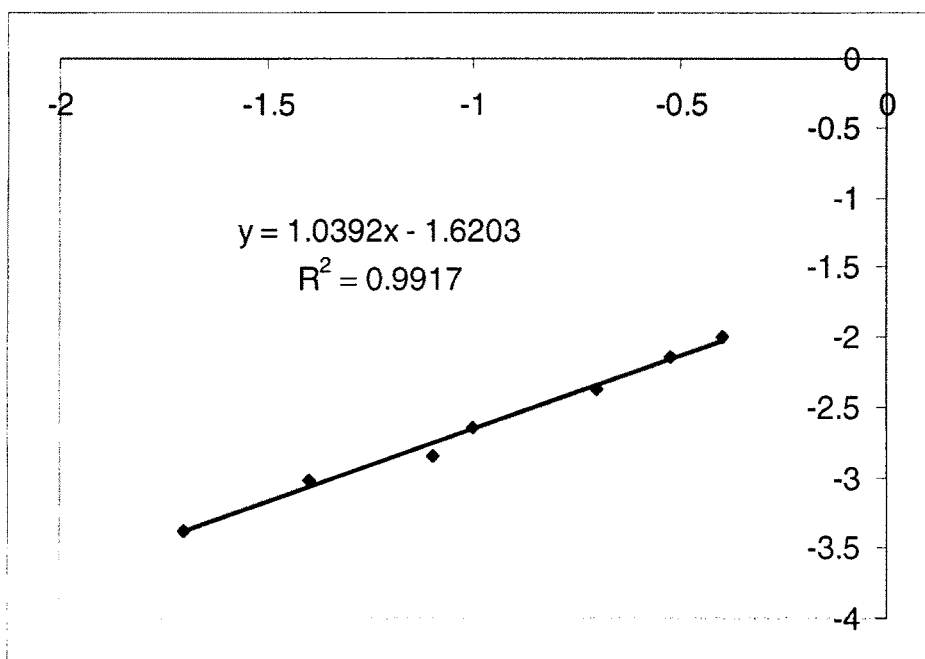
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**Figure 4.2**

Reaction order with respect to hydrogen ion concentration .

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

Conditions as in Table 4.4



**Table 4.5**

Effect of ionic strength on the oxidation of benzoic acid hydrazide by bromate catalysed by Selenium(IV) in aqueous acidic medium at 27<sup>0</sup> 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>                       $10^4$  [ Se<sup>IV</sup> ] = 1.0 mol dm<sup>-3</sup>

$10$ [ NaClO <sub>4</sub> ] mol dm <sup>-3</sup>	$10^3$ K <sub>obs</sub> S <sup>-1</sup>
0.5	2.2
0.8	2.2
1.0	2.3
2.0	2.2
5.0	2.2

**Table 4.6**

Effect of temperature on the oxidation of benzoic acid hydrazide by

bromate catalysed by Selenium(IV) in aqueous acidic medium

$10^2$  [ 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>

$10^4$  [ Se<sup>IV</sup> ] = 1.0 mol dm<sup>-3</sup>

I = 0.5 mol dm<sup>-3</sup>

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Temp	$10^4 K_{\text{obs}}$	$10^3$	$-\log K_{\text{obs}}$	$-\log ( K_{\text{obs}}/T )$
T (k)	S <sup>-1</sup>	( 1/T )		
293	3.0	3.41	3.51	5.31
300	5.8	3.31	3.24	5.11
303	7.3	3.30	3.13	5.02
313	19.0	3.19	2.71	4.66

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**Table 4.7**

Activation parameter for the oxidation of benzoic acid hydrazide by bromate catalysed by Se(IV) in aqueous acidic medium

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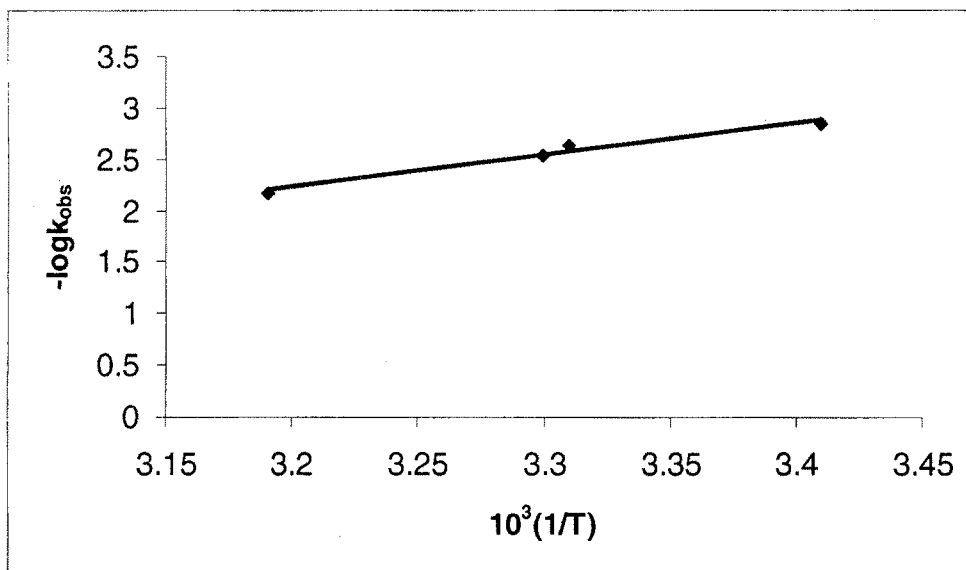
$E_a$ ( kJ mol <sup>-1</sup> )	65.1 ± 1
$H^\ddagger$ ( kJ mol <sup>-1</sup> )	59.8 ± 6
$S^\ddagger$ ( Jk <sup>-1</sup> mol <sup>-1</sup> )	-86.3 ± 6
$G^\ddagger$ ( kJ mol <sup>-1</sup> )	85.9 ± 7

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**Figure 4.3**

Effect of temperature on the oxidation of benzoic acid hydrazide by bromate catalysed by Selenium(IV) in aqueous acidic medium

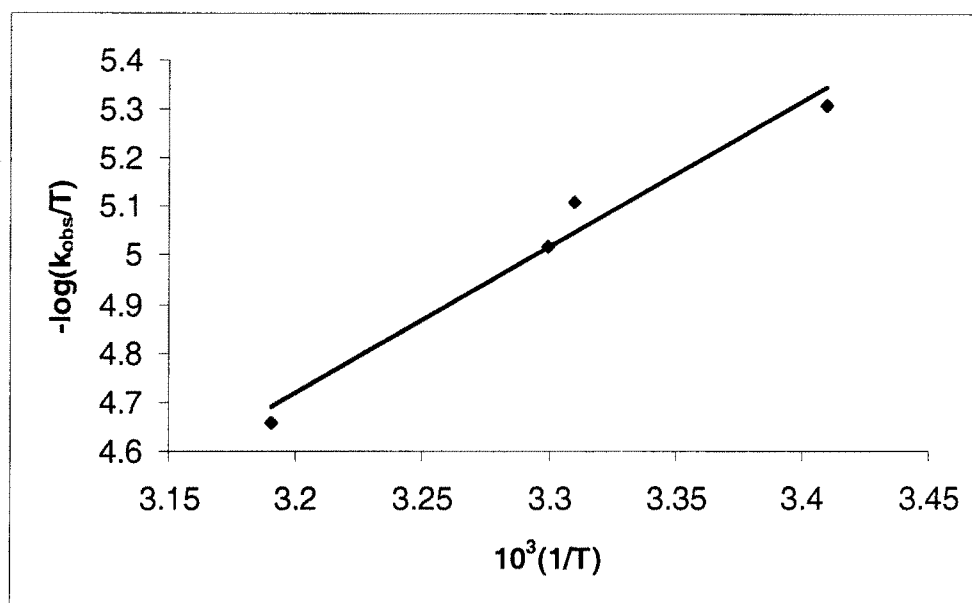
Conditions as in Table 4.6



**Figure 4.4**

Effect of temperature on the oxidation of benzoic acid hydrazide by bromate catalysed by Selenium(IV) in aqueous acidic medium

Conditions as in Table 4.6



**Table 4.8**

Effect of acrylonitrile concentration (% v/v ) on the oxidation of benzoic acid hydrazide by bromate catalysed by Selenium(IV) in aqueous acidic medium

at 27<sup>o</sup> C

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

$$[\text{HCl}] = 0.1 \text{ mol dm}^{-3} \quad 10^4 [\text{Se}^{\text{IV}}] = 1.0 \text{ mol dm}^{-3}$$

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

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% Acrylonitrile ( v/v )	$10^4 K_{\text{obs}}$ $\text{S}^{-1}$
0.0	23.0
0.5	23.2
1.0	23.2
2.0	23.4
3.0	23.3
4.0	23.3
5.0	23.3

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**Table 4.9**

Effect of solvent polarity (acetic acid) on the oxidation of benzoic acid hydrazide by bromate catalysed by Selenium(IV) in aqueous acidic medium

at 27<sup>0</sup> 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>       $10^4$  [ Se<sup>IV</sup> ] = 1.0 mol dm<sup>-3</sup>

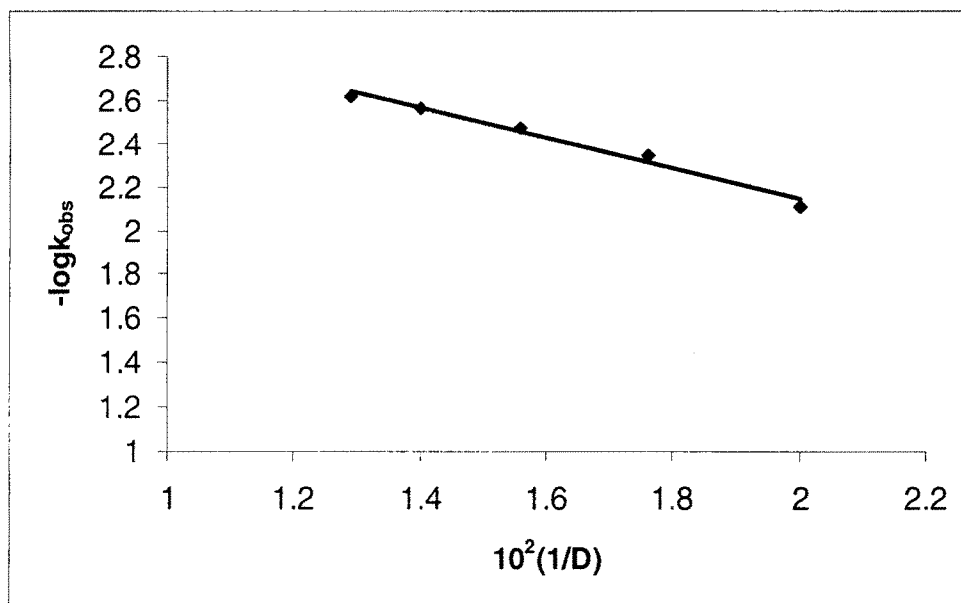
I = 0.5 mol dm<sup>-3</sup>

Acetic acid	D	$10^2(1/D)$	$10^3k_{\text{obs}} (\text{s}^{-1})$	$\log k_{\text{obs}}$
2%	77.05	1.29	2.39	-2.62
10%	71.25	1.40	2.74	-2.56
20%	64.0	1.56	3.35	-2.47
30%	56.75	1.76	4.60	-2.34
40%	49.5	2.0	7.67	-2.11

**Figure 4.5**

Effect of solvent polarity on the oxidation of benzoic acid hydrazide by bromate catalysed by Selenium(IV) in aqueous acidic medium at 27<sup>0</sup> C

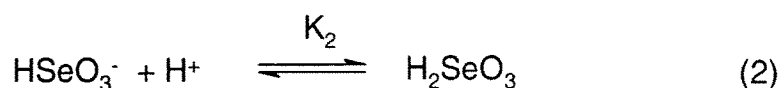
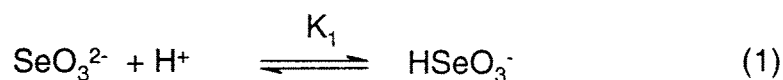
Conditions as in Table 4.9



### Discussion:

As mentioned in the earlier chapter the stoichiometry of bromate oxidations predicts either Br<sub>2</sub> or HOBr as the product of reaction but due to the oxidation potential [17] of HOBr or Br<sub>2</sub> of 0.7 and 1.97 V respectively indicate that the substrate, benzoic acid hydrazide, can be very easily oxidized by both of them 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 confirmed the formation of bromide as one of the product of the reaction. Therefore, the product of the reaction under the present 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.

Selenium(IV) in aqueous solution exists as SeO<sub>3</sub><sup>2-</sup> and undergo protonation [18] as given by equilibrium (1) and (2). The equilibrium constant for first equilibrium



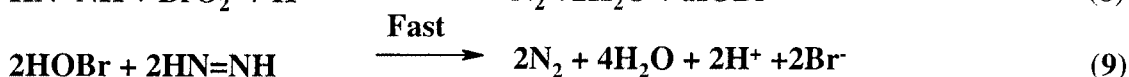
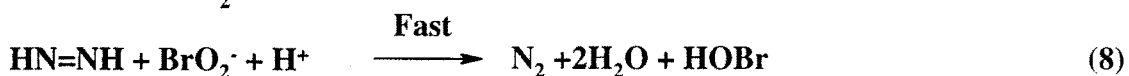
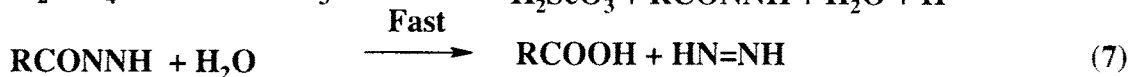
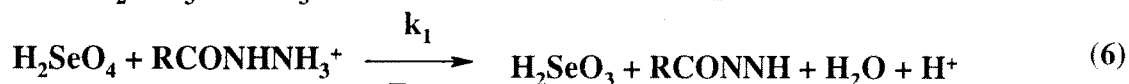
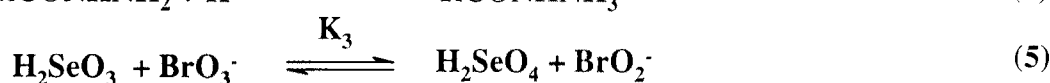
constant ( $K_1=2.1 \times 10^8$ ), is very high whereas that of the second protonation,  $K_2$ , is of the order  $4.16 \times 10^2 \text{ mol dm}^{-3}$ . Thus in acidic solutions ( $0.1 \text{ mol dm}^{-3}$ ) used in the present reaction the catalyst exists as protonated form, H<sub>2</sub>SeO<sub>3</sub>, which is the active species in the reaction.

Potassium bromate is a strong electrolyte and in aqueous solution it exists as BrO<sub>3</sub><sup>-</sup> which is also a strong acid thus its protonation would not be possible under the experimental conditions. Another possibility of explaining the presence of protonation prior equilibria is the involvement of an induction period. The bromate oxidations of one-electron oxidants were also found to involve induction period [17] due to initial hydrogen ion dependent reduction of bromate according to the equilibrium shown in equation 1. But in the present investigation there was no such



induction period which was also not observed by R. C. Thompson[19]. Therefore, the hydrogen ion dependence of the reaction is not due to the equilibrium (3). While in case of oxidation [17] of 12-tungstocobaltate(II) by bromate the reaction was predicted to be initiated by a third order slow step between the reductant and the oxidant generating  $\text{HBrO}_2$  thus leading to the occurrence of an induction period and also resulting in a complicated rate law in hydrogen ion concentration. Since, our reaction does not involve any induction period and also the hydrogen ion dependence is also not complicated, the reaction scheme predicted for 12-tungstocobaltate are not applicable.

The selenium (IV) catalyzed oxidation of benzoic acid hydrazide by bromate is found to be first order in oxidant, substrate, hydrogen ion concentration and the catalyst. Since, the uncatalyzed reactions do not occur under the experimental conditions the catalyzed reaction proceeds with the interaction of the catalyst and the oxidant. Therefore, the initiation of the reaction is the oxidation of the catalyst to its higher oxidation state by bromate which then effects the oxidation of the substrate. In the present study the reaction is not affected by the change in the ionic strength and hydrogen ion concentration effect is due to the protonation [20] of the benzoic acid hydrazide. Therefore, protonation of hydrazide occurs in a prior equilibrium and the protonated substrate is the active species in the reaction. Thus, the mechanism of the reaction involves oxidation of the catalyst, selenium (IV), to its higher oxidation state, selenium (VI), by bromate ion generating  $\text{HBrO}_2$ . Since the reaction did not follow the Michealis-Menten type of catalysis the oxidized form of the catalyst oxidizes the protonated hydrazide in the rate determining step as shown in Scheme I. Since test for free radicals was found to be negative the reaction proceeds without any intervention of free radicals. This observation was also supported by the product analysis in which benzoic acid was the only product obtained. The N-N -diacylhydrazine would have been obtained along with benzoic acid [21] as a result of free radical intervention in the reaction. Therefore the mechanism of reaction involves initial oxidation of the catalyst,  $\text{H}_2\text{SeO}_3$ , to its higher oxidation state which then reacts with the protonated form of the catalyst leading to products as shown in Scheme I.



### Scheme I

According to Scheme I the rate of the reaction is given by

$$\text{Rate} = k_1[\text{RCONHNH}_3^+][\text{H}_2\text{SeO}_4] \quad (10)$$

From equilibrium 4 of Scheme I substituting the value of  $[\text{RCONHNH}_3^+]$  in terms of  $[\text{RCONHNH}_2]$  we get

$$\text{Rate} = \frac{k_1 K_H [\text{RCONHNH}_2][\text{H}^+][\text{H}_2\text{SeO}_4]}{(1 + K_H[\text{H}^+])} \quad (11)$$

Then the  $[\text{H}_2\text{SeO}_4]$  from Equilibrium(5) of Scheme I is given by

$$[\text{H}_2\text{SeO}_4] = K_3 [\text{H}_2\text{SeO}_3][\text{BrO}_3^-] \quad (12)$$

Substituting the value of  $[\text{H}_2\text{SeO}_4]$  from equation (12) in equation (11) we get

$$\text{Rate} = \frac{k_1 K_H K_3 [\text{H}^+][\text{H}_2\text{SeO}_3][\text{RCONHNH}_2][\text{BrO}_3^-]}{(1 + K_H[\text{H}^+])} \quad (13)$$

Then,

$$k_{\text{obs}} = \frac{\text{Rate}}{[\text{RCONHNH}_2][\text{BrO}_3^-]} = \frac{k_1 K_H K_3 [\text{H}^+][\text{H}_2\text{SeO}_3]}{(1 + K_H[\text{H}^+])} \quad (14)$$

The mechanism of the reaction based on the kinetic results can be summarized as in Scheme I with corresponding rate law as given by equation 13 and value of  $k_{\text{obs}}$  by equation 14. According to Scheme 1 the protonated hydrazide is the active substrate species which leads to first order dependence of the rate of the reaction. The reaction is initiated by the oxidation of the catalyst to its higher oxidation state which in following step forms a complex with the hydrazide. The complex thus formed will decompose to generate a hydrazide cation radical

which will be converted into products by successive steps shown in Scheme 1. The decrease in the value of entropy of activation also supports formation of such a transition state.

**Conclusion:**

The reaction between  $\text{KBrO}_3$  and benzoic acid hydrazide in presence of selenium(IV) as a catalyst occurs through rate determining conversion of the catalyst to its higher oxidation state which then effects the oxidation of the substrate leading to the formation benzoic acid. In the present study the protonated forms of the hydrazide is the reactive species. The probable transition state was considered to be an interaction between the oxygen and nitrogen of the hydrazide moiety with the oxidized form of the catalyst.

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21. Shewale, S. A.; Phadkule, A. N.; Gokavi, G. S. Int J Chem Kinetics 2007, 40(3), 151-159.

### List of publication:

1. "Kinetics and Mechanism of Oxidation of Benzohydrazide by Bromate Catalysed by Vanadium (IV) in Aqueous Acidic Medium"  
S. A. Shewale, A. N. Phadkule and G. S. Gokavi\*  
**Int J Chem Kinetics** 2007, 40(3),151-159.

### Published contribution to academic conferences:

1. Poster presentation at UGC-SAP National Seminar on "Synthesis of New Materials For Industrial Applications" Hosted by Department of Chemistry, Shivaji University, Kolhapur, On 1<sup>st</sup> and 2<sup>nd</sup> Feb. 2008.  
"Kinetics and mechanism of oxidation of benzoic acid hydrazide by bromate catalysed by Selnium dioxide in aqueous acidic medium"



# Kinetics and Mechanism of Oxidation of Benzohydrazide by Bromate Catalyzed by Vanadium(IV) in Aqueous Acidic Medium

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**ABSTRACT:** The reaction between benzohydrazide and potassium bromate catalyzed by vanadium(IV) was studied under pseudo-first-order condition keeping large excess of hydrazide concentration over that of the oxidant. The initiation of the reaction occurs through oxidation of the catalyst vanadium(IV),  $\text{VO}^{2+}$ , to vanadium(V),  $\text{VO}_2^+$ , which then reacts with hydrazide to give N,N'-diacylhydrazine and benzoic acid as the products. The order in  $[\text{H}^+]$  is found to be two, and its effect is due to protonation and hydrolysis of oxidized form of the catalyst to form  $\text{HVO}_3$ . The oxidized form of the catalyst,  $\text{VO}_2^+$ , forms a complex with the protonated hydrazide as evidenced by the occurrence of absorption maxima at 390 nm. The rate of the reaction remains unaffected by the increase in the ionic strength. The activation parameters were determined, and data support the mechanism. The detailed mechanism and the rate equation are proposed for the reaction. © 2008 Wiley Periodicals, Inc. *Int J Chem Kinet* 40: 151–159, 2008

## INTRODUCTION

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 utilized to oxidize alcohols to

aldehydes, ketones, esters and carboxylic acids [1–9], and ethers [9b]. Conversion of sulfides to sulfoxides [10], hydroquinones to quinones [9,10], thiols to disulfides [11], and iodobenzene to iodoxybenzenes [12] have also been carried out by using bromate salts. Although the bromate itself is a strong oxidizing agent having a redox potential of 1.45 V, its 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 their corresponding higher oxidation state. The oxidized form of the catalyst will then effect the further conversion of the

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substrate into the product. Bromate ion is also used for volumetric 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(IV) [13] and 12-tungstocobaltate(II) [14] has also been studied by using bromate, and their mechanisms are predicted. Hydrazides, which are derivatives of both carboxylic acids and hydrazine, have been utilized as starting materials in organic synthesis [15]. The oxidative transformation with most oxidants gives corresponding acids and in some cases [15] esters or amides. Hydrazides have also been converted into *N-N*-diacylhydrazines with [15c] various oxidants. Formation of acids and their derivatives in the presence of different nucleophiles is the indication of direct two-electron transfer to the oxidant, whereas cyclization products generally involve a single electron transfer with intervention of a free radical. Vanadium(IV) in aqueous acidic medium is also known to be oxidized by bromate [13] to give vanadium(V) as the product. Since bromate is not oxidizing hydrazides, in the present study, the redox property of vanadium(IV)–bromate system is utilized to generate vanadium(V) in solution and then oxidizing the hydrazide.

## EXPERIMENTAL

### Materials

Reagent-grade chemicals and doubly distilled water were used throughout the work. The  $\text{KBrO}_3$  solution was prepared by dissolving  $\text{KBrO}_3$  (BDH) in water and standardized iodometrically. The hydrazide was prepared by esterification of the corresponding acids in ethanol followed by its conversion to hydrazide according to the reported procedure [16]. The solutions of hydrazide were prepared by dissolving required quantity in water. Ionic strength was maintained by using KCl, and to vary hydrogen ion concentration HCl (BDH) was used.

The catalyst vanadium(IV) was prepared by dissolving vanadyl sulfate (BDH) in water and standardized by titrating against potassium permanganate. The solution of vanadium(V) was prepared by dissolving ammonium vanadate (BDH) in hot water.

### KINETIC STUDIES

The reaction was studied under pseudo-first-order conditions keeping hydrazide concentration large excess

at constant temperature of  $27.0 \pm 0.1^\circ\text{C}$ . 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  $\log [\text{oxidant}]$  against time. The pseudo-first-order plots were linear for more than 90% completion of the reaction, and the rate constants were reproducible within  $\pm 6\%$ .

The reaction between vanadium(V) and benzo-hydrazide was also studied under similar conditions as that of vanadium(IV)-catalyzed reaction. The reaction was followed at 390 nm at which the complex formed between vanadium(V) and benzoic acid hydrazide absorbs. The pseudo-first-order rate constants of the decomposition of the complex were obtained by linear  $\log$  (absorbance) against time plots.

## RESULTS

### Stoichiometry

In 10 mL of  $0.6 \text{ mol dm}^{-3}$  hydrochloric acid, 35  $\mu\text{mol}$  (5 mg) catalyst and 2 mmol (0.272 g) of benzohydrazide were dissolved. To the resulting solution, 1 mmol (0.167 mg) of  $\text{KBrO}_3$  was added. The reaction mixture was stirred at  $27^\circ\text{C}$  for 5 min. The precipitate obtained was filtered, and ether was added to it. The insoluble part of the precipitate (140 mg) (product I) was washed with water and recrystallized from ethyl acetate-petroleum ether mixture. The recrystallized product I was dried, and its melting point (mp) was determined as  $238^\circ\text{C}$ . The soluble part of the precipitate (product II) in ether was washed with sodium bicarbonate solution and neutralized with hydrochloric acid. The solid obtained after neutralization (0.036 g) was washed with water and recrystallized from water. The recrystallized product II was dried, and the mp was determined as  $121^\circ\text{C}$ . By comparison of the reported [15b] mp values, the product I was found to be *N-N*-diacylhydrazine (mp  $238\text{--}240^\circ\text{C}$ ) of benzohydrazide and product II was found to be benzoic acid. Benzoic acid separated was filtered and recrystallized by water (mp  $121^\circ\text{C}$ ).

### Reaction Order

The uncatalyzed reaction did not occur under the experimental conditions. The catalyzed reaction was carried out under pseudo-first-order conditions keeping the

**Table I** Effect of Reactant Concentrations on the Rate of Reaction at 27°C

$10^2$ [Hydrazide] (mol dm <sup>-3</sup> )	$10^3$ [KBrO <sub>3</sub> ] (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}$ s <sup>-1</sup>
0.5	1.0	5.6
0.8	1.0	5.5
1.0	1.0	5.6
2.0	1.0	5.5
5.0	1.0	5.4
1.0	0.5	5.8
1.0	0.8	5.8
1.0	1.0	5.8
1.0	2.0	5.8
1.0	5.0	5.8

$10^4[\text{V}^{\text{IV}}] = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ , and  $I = 0.5 \text{ mol dm}^{-3}$ .

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  $0.5 \text{ mol dm}^{-3}$  (Table I). The pseudo-first-order plots were found to be linear on varying the concentration of oxidant between  $0.5 \times 10^{-3}$  and  $5.0 \times 10^{-3} \text{ mol dm}^{-3}$  keeping the concentration of catalyst and hydrazide constant at  $1.0 \times 10^{-4}$  and  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ , respectively (Table I), indicating the order in oxidant concentration is unity. The pseudo-first-order rate constants,  $k_{\text{obs}}$ , were fairly constant as the concentration of hydrazide was varied between  $0.5 \times 10^{-2}$  and  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$  keeping all other concentrations constant (Table I); therefore, the order in hydrazide concentration is also unity. To understand the effect of dissolved oxygen, separate kinetic runs were carried out for the standard run ( $[\text{KBrO}_3] = 1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{hydrazide}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{V}^{\text{IV}}] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ , and  $I = 0.5 \text{ mol dm}^{-3}$  at 27°C) under nitrogen atmosphere. There was no change in the value of pseudo-first-order rate constant indicating no effect of the dissolved oxygen on the reaction. The effect of catalyst concentration was studied between the concentration range of  $5.0 \times 10^{-5}$  to  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ , and the plot  $k_{\text{obs}}$  against [catalyst] was found to be linear indicating the first-order dependence of reaction on [catalyst] (Table II).

### Effect of Hydrogen Ion Concentration

The effect of hydrogen ion was studied to understand the nature of reactant species present in the solution. The  $[\text{H}^+]$  was varied from  $2.0 \times 10^{-2}$  to  $0.4 \text{ mol dm}^{-3}$  (Table III). The  $[\text{H}^+]$  accelerates the rate of the reaction, and the order in  $[\text{H}^+]$  is found to be slightly more

**Table II** Effect of Catalyst Concentration on the Reaction at 27°C

$10^4 [\text{V}^{\text{IV}}]$ (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )
0.5	2.3
0.8	3.8
1.0	5.8
2.0	12.1
3.0	19.1
4.0	24.3
5.0	31.9

$10^2[\text{Hydrazide}] = 1.0 \text{ mol dm}^{-3}$ ,  $10^3[\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ , and  $I = 0.5 \text{ mol dm}^{-3}$ .

than unity (1.09) as determined from the plot of  $\log k_{\text{obs}}$  against  $\log [\text{H}^+]$ . The plot of  $k_{\text{obs}}$  against  $[\text{H}^+]^2$  is linear ( $R^2 = 0.9978$ ) with an intercept indicating that the reaction involves both hydrogen ion-dependent and -independent paths to different extents. The rate of hydrogen ion-dependent path is considerably greater than that of the independent path as the values of slope and intercept were found to be  $4.2 \times 10^{-2}$  and  $2.6 \times 10^{-4}$ , respectively.

### Effect of Ionic Strength and Temperature

The effects of ionic strength and temperature were studied keeping [hydrazide],  $[\text{KBrO}_3]$ , [catalyst], and  $[\text{HCl}]$  constant at  $1.0 \times 10^{-2}$ ,  $1.0 \times 10^{-3}$ ,  $1.0 \times 10^{-4}$ , and  $0.1 \text{ mol dm}^{-3}$ , respectively. Potassium chloride was used to vary the ionic strength. The rate of the reaction remains unaffected with increasing ionic strength (from 0.1 to  $0.5 \text{ mol dm}^{-3}$ ). The effect of temperature on the reaction was studied at 20, 27, 30, and 40°C and the pseudo-first-order rate constants were found to be  $3.0 \times 10^{-4}$ ,  $5.8 \times 10^{-4}$ ,  $7.3 \times 10^{-4}$ , and  $19 \times 10^{-4} \text{ s}^{-1}$ , respectively. The activation parameters  $\Delta H^\ddagger$ ,  $\Delta G^\ddagger$ , and  $-\Delta S^\ddagger$  were found to be  $68.5 \pm 6 \text{ kJ mol}^{-1}$ ,

**Table III** Effect of Hydrogen Ion Concentration on the Reaction at 27°C

$10 [\text{HCl}]$ (mol dm <sup>-3</sup> )	$10^4 k_{\text{obs}}$ (s <sup>-1</sup> )
0.2	3.0
0.4	3.5
0.8	4.8
1.0	5.8
2.0	19.1
3.0	42.5
4.0	68.1

$10^2[\text{Hydrazide}] = 1.0 \text{ mol dm}^{-3}$ ,  $10^3 [\text{KBrO}_3] = 1.0 \text{ mol dm}^{-3}$ ,  $10^4[\text{V}^{\text{IV}}] = 1.0 \text{ mol dm}^{-3}$ , and  $I = 0.5 \text{ mol dm}^{-3}$ .

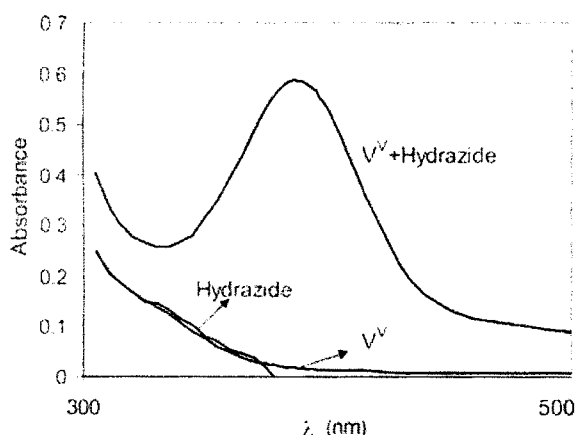
$105.4 \pm 6 \text{ kJ mol}^{-1}$ , and  $123.8 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

### Spectrophotometric Examination of Reaction Mixture

During the kinetic study, it was observed that a brown color complex was formed in the reaction mixture containing the highest catalyst concentration of  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ . Therefore, the reaction mixture was examined spectrophotometrically for formation of a complex in the course of the reaction. There was no change in the UV-vis spectrum of the mixture of the catalyst and the hydrazide. But when the vanadium(V), the oxidized form of the catalyst, was added to hydrazide the color of the solution changed from yellow to brown. Therefore, the spectra of only vanadium(V) ( $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ), hydrazide  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ , and in the presence of hydrazide  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  in  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid at an ionic strength of  $0.5 \text{ mol cm}^{-3}$  were recorded between 305 and 500 nm using an Elico SL159 spectrophotometer. A new absorption peak at 390 nm was observed for the mixture containing hydrazide and vanadium(V) (Fig. 1).

### Reaction Between Oxidized Form of the Catalyst, Vanadium(V), and Hydrazide

The formation of the complex between vanadium(V) and hydrazide was very rapid; therefore, the reaction between hydrazide and vanadium(V) was studied at 390 nm by following the decomposition of the complex formed. The concentration of hydrazide was kept at  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  and



**Figure 1** UV-vis spectra of vanadium(V) and the mixture of vanadium(V) and the hydrazide.  $[V^V] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $[\text{hydrazide}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ,  $[\text{HCl}] = 0.1 \text{ mol dm}^{-3}$ , and  $I = 0.5 \text{ mol dm}^{-3}$ .

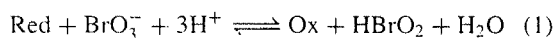
vanadium(V) and hydrochloric acid were varied between  $0.2 \times 10^{-3}$  to  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  and  $1.0 \times 10^{-2}$  to  $1.0 \times 10^{-1} \text{ mol dm}^{-3}$ , respectively. The pseudo-first-order rate constants were determined by linear ( $R^2 > 0.993$ )  $\log(\text{Abs.})$  against time plots. The pseudo-first-order rate constants for the decomposition of the complex were found to be constant when the concentration of the hydrazide was varied between  $0.5 \times 10^{-2}$  and  $5.0 \times 10^{-2} \text{ mol dm}^{-3}$  at constant concentration of vanadium(V), hydrochloric acid, and ionic strength of  $1.0 \times 10^{-3}$ , 0.1, and  $0.5 \text{ mol dm}^{-3}$ , respectively. The linearity of the pseudo-first-order plots and the constancy of pseudo-first-order rate constants as the hydrazide concentration was varied, indicating the first-order dependence of the reaction on both vanadium(V) and the hydrazide concentration. The effect of the hydrogen ion concentration was also studied on the decomposition of the vanadium(V)-hydrazide complex, and it was found that the rate of decomposition was independent of the hydrogen ion concentration.

### DISCUSSION

Oxidation of inorganic substrates by bromate ion has been studied [13,14], and the complexity in their mechanism strongly depends on the redox potential of the metal ion. The metal ions having  $E^\circ$  values more than 1.1 V are not directly oxidized by the bromate ion and involve [14] an induction period. The dependence of the rate of the reaction on acidity of the solution, for such reactions, is also complicated due to the formation of species like  $\text{HBrO}_2$ . On the other hand, the mechanism for the reduction of metal ions with  $E^\circ$  value less than 1.1 V does not involve any induction period [13], and metal ions are directly oxidized by bromate ion. For such reactions, the rate laws obtained are also simple and independent of the hydrogen ion concentration. The examples are bromate ion oxidation of  $[\text{Co}^{\text{II}}\text{W}_{12}\text{O}_{40}]^{6-}$  and  $\text{V}^{\text{IV}}$  with complex and simple rate law, respectively. The stoichiometry of these reported reactions also predicts  $\text{HOBr}_2$ ,  $\text{Br}_2$ , and  $\text{HOBr}$  as the products of the reduction of bromate. In the present investigation, the reaction between hydrazide and bromate occurs only in the presence of catalytic amount of  $\text{V}^{\text{IV}}$ . Therefore, the reaction is initiated by the oxidation of the catalyst ( $\text{V}^{\text{IV}}$ ) to its higher oxidation state ( $\text{V}^{\text{V}}$ ). The reaction between bromate and  $\text{V}^{\text{IV}}$  has been studied [13] earlier and found to follow a simple second-order rate law with an order of unity in both the reactant concentrations. The reaction was independent of the hydrogen ion concentration and the ionic strength variation. The mechanism also involves

intervention of  $\text{BrO}_2$ ,  $\text{HBrO}_2$ , and  $\text{HOBr}$  with bromine as the final products. In our work, the orders in bromate and the catalyst were found to be unity, which parallels the reported results. This indicates that the first step of the reaction between the catalyst and the bromate will be the oxidation of  $\text{V}^{\text{IV}}$  generating  $\text{BrO}_2$ . But the hydrogen ion dependence and the final product of the bromate reduction in the present study differ from that of the reported work. Therefore, identification of the product of bromate reduction was necessary. During the kinetic study, generation of bromine either in situ or at the end of the reaction was not observed, whereas, with the addition of silver nitrate to the reaction mixture, after completion of the reaction in sulfuric acid, precipitation of silver bromide occurred, confirming bromide as the product of the reaction. This might be due to the fact that even if  $\text{HOBr}$  or  $\text{Br}_2$  are formed during the course of the reaction, because of their respective oxidation potentials of 1.34 and 1.07 V, they can easily oxidize the hydrazide in acidic solutions with the formation bromide as the final product.

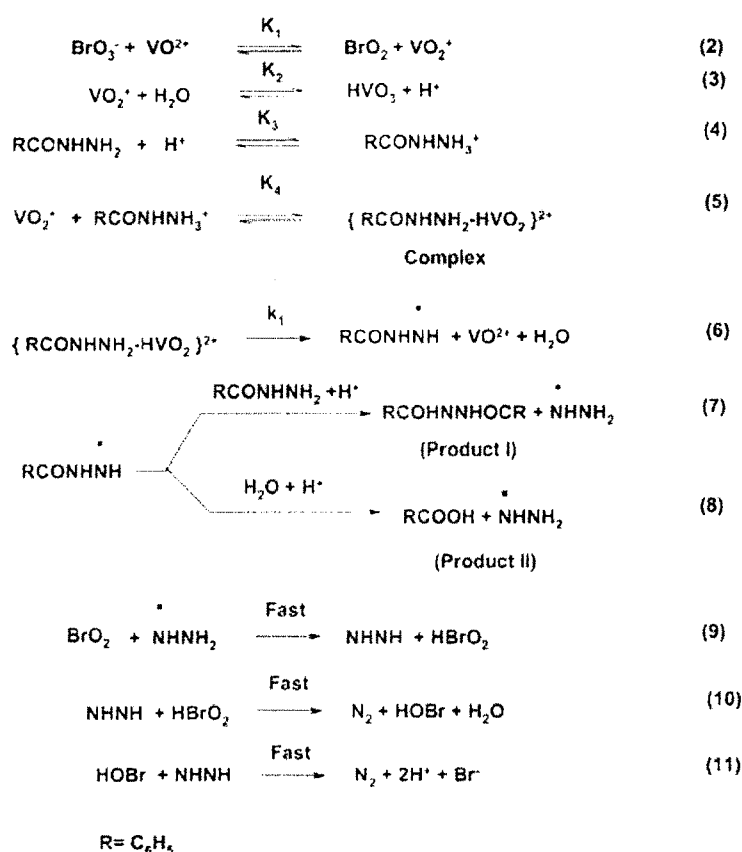
The plot of  $k_{\text{obs}}$  against  $[\text{H}^+]^2$  plot ( $R^2 = 0.9978$ ) was found to be linear with an intercept that is due to the simultaneous involvement of both hydrogen-dependent and the independent paths in the reaction. The hydrogen ion-dependent path of the reaction is due to prior protonation equilibria of the reactants, and the hydrogen ion-independent path is due to the participation of unprotonated reactant species. Potassium bromate is a strong electrolyte and in aqueous solution it dissociates to give  $\text{BrO}_3^-$  ion which is also a strong acid, thus its protonation would not be possible under the experimental conditions. Another possibility of explaining the presence of protonation prior equilibria is the involvement of an induction period. The bromate oxidations of one-electron reducing agents were also found to involve induction period [14] due to initial hydrogen ion-dependent reduction of bromate according to the equilibrium shown in Eq. (1). But in the present investigation, there was no



such induction period excluding the possibility of equilibrium (1). Therefore, the effect of  $[\text{H}^+]$  on the reaction is due to protonation prior equilibria of hydrazide and the oxidized form of the catalyst,  $\text{VO}_2^+$  ion. The monomeric form of vanadium (V),  $\text{VO}_2^+$  ion, is reported to be involved in various hydrogen ion-dependent equilibria [17] like formation of  $\text{HVO}_3$ ,  $\text{VO}_4^{3-}$ ,  $\text{HVO}_4^{2-}$ ,  $\text{H}_2\text{VO}_4^-$ , and  $\text{H}_3\text{VO}_4$ . In the present study, the range of pH of the solutions used is between 1 and 2 and the equilibria involving the vanadate ion,  $\text{VO}_4^{3-}$ , are possible only in aqueous solutions of pH

3–4. Therefore, under the reaction conditions, only formation of  $\text{HVO}_3$  as a result of hydrolysis of  $\text{VO}_2^+$  ion is considered. In acidic solutions, protonation of hydrazide [18] occurs and  $\text{VO}_2^+$  ion undergoes hydrogen ion-dependent hydrolysis to form  $\text{HVO}_3$ . The values of slope and intercept obtained from the plot of  $k_{\text{obs}}$  against  $[\text{H}^+]^2$  are  $4.2 \times 10^{-2}$  and  $2.6 \times 10^{-4}$ , respectively, and the ratio is found to be around  $1.6 \times 10^2$ . A very low value of intercept indicates that the rate law consists of a negligible  $[\text{H}^+]$ -independent term, and the linearity with high slope shows the presence of a term with second order in  $[\text{H}^+]$ . Thus, neglecting the hydrogen ion-independent term in comparison with that of hydrogen ion-dependent term, the effect of hydrogen ion on the reaction can be explained considering a prior protonation of hydrazide and formation of  $\text{HVO}_3$ .

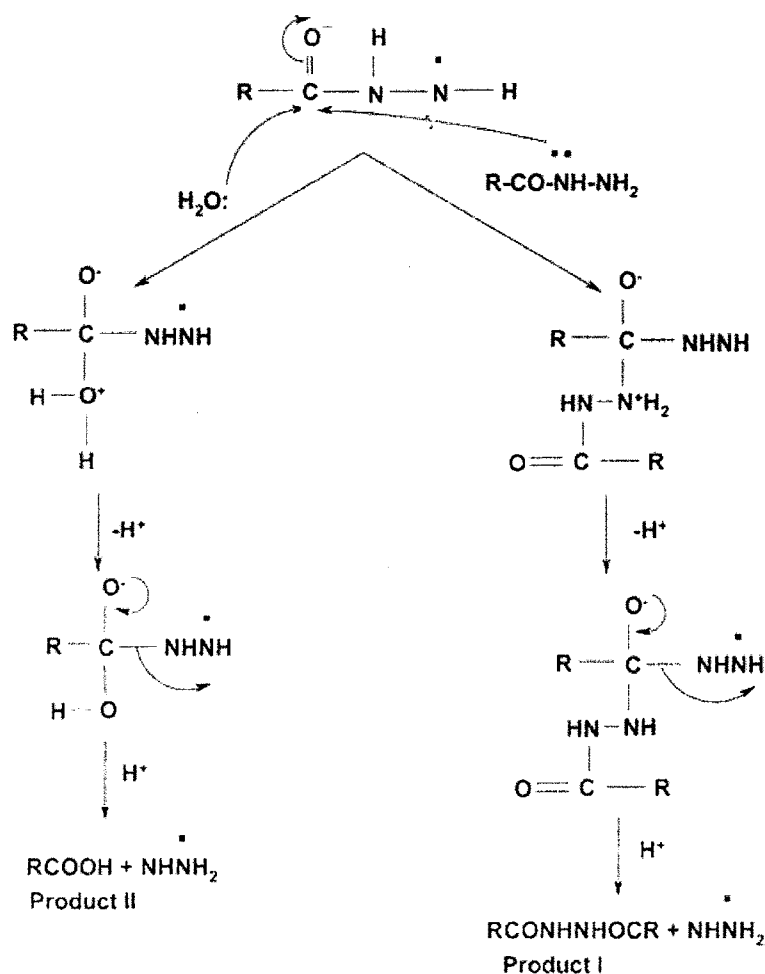
The  $\text{V}^{\text{IV}}$ -catalyzed oxidation of benzohydrazide by bromate is found to be first order in oxidant, substrate, and the catalyst. The order in hydrogen ion concentration is more than unity. Since the uncatalyzed reaction between bromate and hydrazide do not occur under the experimental conditions, the catalyzed reaction proceeds with the interaction of the catalyst and the oxidant. Therefore, the initiation of the reaction is the oxidation of the catalyst to its higher oxidation state by bromate, which then effects the oxidation of the substrate. The reaction is also not affected by the change in the ionic strength, and the hydrogen ion concentration effect is due to the reaction between protonated [18] benzohydrazide with unhydrolyzed oxidized form of the catalyst,  $\text{VO}_2^+$ . The protonation of hydrazide and hydrolysis of  $\text{V}^{\text{V}}$  occur in prior equilibria. Thus, the mechanism of the reaction involves oxidation of the catalyst ( $\text{V}^{\text{IV}}$ ) to its higher oxidation state ( $\text{V}^{\text{V}}$ ) by bromate ion-generating  $\text{BrO}_2$ . At comparatively high concentration of catalyst,  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ , a brown color was developed in the reaction mixture and disappeared. It was assumed that the  $\text{V}^{\text{V}}$  formed as a result of prior redox reaction between the catalyst and the oxidant might be forming a complex with the substrate. In a separate experiment, a mixture containing equal concentrations of  $\text{V}^{\text{V}}$  and benzohydrazide was examined spectrophotometrically. An absorption maxima for the mixture was observed at 390 nm, which was absent in the solutions containing only  $\text{V}^{\text{V}}$  or hydrazide under similar conditions (Fig. 1), which confirms the formation of a complex between the oxidized form of the catalyst and the substrate. The reaction between  $\text{V}^{\text{IV}}$  by bromate is fast [13], and the second-order rate constant for the oxidation is reported to be  $3.86 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Therefore, under the pseudo-first-order conditions employed in our study using catalytic amount of  $\text{V}^{\text{IV}}$  and large excess of bromate, the oxidation is expected to



Scheme 1

be very fast. Separate kinetic runs were also carried out to determine the rate constants of  $\text{V}^{\text{V}}$ -hydrazide complex formation and its decomposition. Even under second-order conditions at equal concentration of  $\text{V}^{\text{V}}$  and hydrazide, the formation of the complex was immediate as noticed by the rapid increase in the absorbance at 390 nm. Thus, the rate constant for the decomposition of the complex was measured by following the absorbance at 390 nm. The rate constant, under pseudo-first-order conditions keeping large excess of hydrazide than  $\text{V}^{\text{V}}$ , was found to be  $1.7 \times 10^{-4} \text{ s}^{-1}$ . Furthermore, the decomposition was also found to be independent of  $\text{V}^{\text{V}}$ , hydrazide, and hydrogen ion concentration. On the basis of kinetic data obtained, the mechanism in terms of the active species of reactants and the oxidized form of the catalyst is summarized in Scheme 1. According to Scheme 1, the reaction is initiated by the rapid oxidation of  $\text{V}^{\text{IV}}$  by bromate ion thus generating  $\text{VO}_2^+$  and  $\text{BrO}_2$  in the first step. The  $\text{VO}_2^+$  ion then gets hydrolyzed to form an vanadate ion,  $\text{HVO}_3$ . The protonated form of the substrate is formed in another prior equilibria as shown in the third

step of Scheme 1. In the following steps, the protonated hydrazide and the  $\text{VO}_2^+$  ion form a complex. The formation of the complex has been supported by the spectral changes occurring during the course of the reaction between  $\text{V}^{\text{V}}$  and hydrazide (Fig. 1). The complex formation even in equimolar concentrations of the  $\text{V}^{\text{V}}$  and the hydrazide (second-order conditions) occurs rapidly. The complex further decomposes to give hydrazide free radical regenerating the catalyst back with a rate constant  $1.7 \times 10^{-4} \text{ s}^{-1}$ . Considering the oxidation of catalyst by bromate as a fast equilibrium and decomposition of the complex formed between  $\text{VO}_2^+$  ion and the hydrazide as the rate-determining step, the rate law for the reaction can be written as in Eq. (12) and the expression for the  $k_{\text{obs}}$  by Eq. (13). According to Eq. (13), the values of pseudo-first-order rate constants ( $k_{\text{obs}}$ ) vary linearly with the catalyst concentration and the plot of  $k_{\text{obs}}$  against  $[\text{H}^+]^2$  is linear. The value of  $K_2$  is reported [17] to be  $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ , which can be neglected at high  $[\text{H}^+]$  but comparable at low  $[\text{H}^+]$ , thus making the overall order in hydrogen concentration to be slightly more than unity as



Scheme 2

observed.

$$\text{Rate} = \left( \frac{k_1 K_1 K_2 K_3 K_4 [\text{H}^+]^2}{([\text{H}^+] + K_2(1 + K_3[\text{H}^+]))} \right) \times [\text{BrO}_3^-][\text{Hydrazide}][\text{VO}^{2+}] \quad (12)$$

$$k_{\text{obs}} = \left( \frac{k_1 K_1 K_2 K_3 K_4 [\text{H}^+]^2}{([\text{H}^+] + K_2(1 + K_3[\text{H}^+]))} \right) [\text{VO}^{2+}] \quad (13)$$

Hydrazide-free radicals have been predicted in oxidations of hydrazide by one-electron oxidizing agents [19,20]. In one such study on oxidation of amino benzohydrazide by hydrogen peroxide mediated by myeloperoxidase [20], a ferric enzyme, it has been observed that the hydrazide-free radical produced also undergo slow oxidation by the dissolved oxygen. Therefore, the reaction was carried out in nitrogen atmosphere to know the effect of dissolved oxygen. It was found that there was no change in the pseudo-

first-order rate constant when the reaction was carried out in nitrogen atmosphere indicating no effect of the dissolved oxygen on the reaction. The stoichiometric analysis of the reaction mixture led to two major products *N,N'*-diacylhydrazine and benzoic acid. The formation of these two products in the present reaction can be explained due to the competitive nucleophilic attack on the carbonyl carbon of the hydrazide free radical by either another hydrazide molecule or water molecule producing *N,N'*-diacylhydrazine or benzoic acid, respectively, which is shown separately in Scheme 2. The formation of both the products generates  $\text{NHNH}_2$  free radical. The oxidized form of the catalyst is completely utilized in the rapid formation of the complex, which reduces its concentration in the solution to an insignificant extent, and the low concentration of the  $\text{NHNH}_2$  free radical formed makes the further possible interaction between them negligible. Therefore, the  $\cdot\text{NHNH}_2$  free radical produced preferably reacts with strong

one-electron oxidant  $\text{BrO}_2$  generated in the first equilibrium of Scheme 1, leading to the formation of  $\text{HBrO}_2$  and  $\text{NHNH}$ . The final product nitrogen is formed as a result of fast reactions of  $\text{NHNH}$  with intermediates of bromate,  $\text{HBrO}_2$ , and  $\text{HOBr}$  as shown in Scheme 1. The probable structure of the complex between the oxidized form of the catalyst and the hydrazide can be coordination of hydrazide ligand through oxygen and nitrogen atoms to the  $\text{V}^{\text{V}}$ . The moderate values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were both favorable [21] for electron transfer processes. The negative value of  $\Delta S^\ddagger$ , within the range for free radical reactions [22], has been ascribed to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom formerly available to the reactants upon the formation of rigid transition state.

## CONCLUSION

The reaction between  $\text{KBrO}_3$  and benzoic acid hydrazide in the presence of  $\text{V}^{\text{IV}}$  as a catalyst occurs through rate-determining conversion of the catalyst to its higher oxidation state which then effects the oxidation of the substrate leading to the formation of hydrazide free radical. Nucleophilic attack on the carbonyl oxygen by either another hydrazide molecule or by water leads to the formation of  $N,N'$ -diacylhydrazine and benzoic acid, respectively. In the present study, the protonated form of the hydrazide as well as unhydrolyzed form of the oxidized catalyst is the reactive species. The probable transition state was considered to be an interaction between oxygen and nitrogen of the hydrazide moiety with the oxidized form of the catalyst leading to the formation of a complex with absorption maxima at 390 nm.

## APPENDIX: DERIVATION OF RATE LAW

The rate of reaction is given by

$$\text{Rate} = k_1[\text{Complex}] \quad (\text{A1})$$

$$\text{Rate} = k_1 K_4[\text{VO}_2^+]_{\text{F}}[\text{RCONHNH}_3^+] \quad (\text{A2})$$

The total oxidized form of the catalyst,  $\text{VO}_2^+$  would be

$$[\text{VO}_2^+]_{\text{T}} = [\text{VO}_2^+]_{\text{F}} + [\text{HVO}_3] \quad (\text{A3})$$

where T and F indicate total and free  $[\text{VO}_2^+]$ .

According to equilibrium 3 of Scheme 1

$$[\text{HVO}_3] = K_2[\text{VO}_2^+]_{\text{F}}/[\text{H}^+] \quad (\text{A4})$$

$$\text{Therefore, } [\text{VO}_2^+]_{\text{T}} = [\text{VO}_2^+]_{\text{F}} + (K_2[\text{VO}_2^+]_{\text{F}}/[\text{H}^+])$$

$$\text{Then, } [\text{VO}_2^+]_{\text{F}} = [\text{VO}_2^+]_{\text{T}}/(1 + (K_2/[\text{H}^+]))$$

$$[\text{VO}_2^+]_{\text{F}} = [\text{VO}_2^+]_{\text{T}}[\text{H}^+]/([\text{H}^+] + K_2) \quad (\text{A5})$$

Substituting for concentration of  $[\text{VO}_2^+]$  in Eq. (A2)

$$\begin{aligned} \text{Rate} &= (k_1 K_2 K_4 [\text{VO}_2^+]_{\text{T}} [\text{H}^+] \\ &\quad \times [\text{RCONHNH}_3^+]) / ([\text{H}^+] + K_2) \quad (\text{A6}) \end{aligned}$$

Then from equilibrium 4 of Scheme 1, the total concentration of benzohydrazide can be obtained as

$$[\text{RCONHNH}_2]_{\text{T}} = [\text{RCONHNH}_2]_{\text{F}} + [\text{RCONHNH}_3^+] \quad (\text{A7})$$

$$\begin{aligned} [\text{RCONHNH}_2]_{\text{T}} &= [\text{RCONHNH}_2]_{\text{F}} \\ &\quad + K_3[\text{H}^+][\text{RCONHNH}_2]_{\text{F}} \end{aligned}$$

$$[\text{RCONHNH}_2]_{\text{T}} = [\text{RCONHNH}_2]_{\text{F}}(1 + K_3[\text{H}^+]) \quad (\text{A8})$$

$$[\text{RCONHNH}_2]_{\text{F}} = [\text{RCONHNH}_2]_{\text{T}} / (1 + K_3[\text{H}^+]) \quad (\text{A9})$$

and that of  $[\text{RCONHNH}_3^+]$  is given by

$$\begin{aligned} [\text{RCONHNH}_3^+] &= K_3[\text{H}^+][\text{RCONHNH}_2]_{\text{T}} / \\ &\quad (1 + K_3[\text{H}^+]) \quad (\text{A10}) \end{aligned}$$

Substituting the  $[\text{RCONHNH}_3^+]$  from Eq. (A10) in Eq. (A6) we get

$$\begin{aligned} \text{Rate} &= k_1 K_2 K_3 K_4 [\text{VO}_2^+]_{\text{T}} [\text{H}^+]^2 [\text{RCONHNH}_2]_{\text{T}} / \\ &\quad \{([\text{H}^+] + K_2)(1 + K_3[\text{H}^+])\} \quad (\text{A11}) \end{aligned}$$

Since,  $[\text{VO}_2^+]_{\text{T}}$  is obtained from fast equilibrium 2 of Scheme 1 and the  $[\text{VO}_2^+]_{\text{T}}$  is given by

$$[\text{VO}_2^+]_{\text{T}} = K_1[\text{BrO}_3^-][\text{VO}^{2+}] \quad (\text{A12})$$

Then, from Eqs. (A11) and (A12), we get

$$\begin{aligned} \text{Rate} &= k_1 K_1 K_2 K_3 K_4 [\text{BrO}_3^-][\text{VO}^{2+}][\text{H}^+]^2 \\ &\quad \times [\text{RCONHNH}_2]_{\text{T}} / \{([\text{H}^+] + K_2) \\ &\quad \times (1 + K_3[\text{H}^+])\} \quad (\text{A13}) \end{aligned}$$



Since  $[\text{RCONHNH}_2]_{\text{T}}$  is highly excess and considering its concentration as constant, we get

$$\text{Rate} = k_1 K_1 K_2 K_3 K_4 [\text{BrO}_3^-] [\text{VO}^{2+}] [\text{H}^+]^2 / (([\text{H}^+] + K_2)(1 + K_3[\text{H}^+]))$$

Then

$$k_{\text{obs}} = \text{Rate}/[\text{BrO}_3^-] = k_1 K_1 K_2 K_3 K_4 [\text{VO}^{2+}] [\text{H}^+]^2 / (([\text{H}^+] + K_2)(1 + K_3[\text{H}^+]))$$

or

$$k_{\text{obs}} = k_1 K_1 K_2 K_3 K_4 [\text{VO}^{2+}] [\text{H}^+]^2 / \{([\text{H}^+] + K_2)(1 + K_3[\text{H}^+])\} \quad (\text{A14})$$

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