

# Kinetics and Mechanism of Micellar Catalyzed Oxidation Reactions of Aliphatic Acid Hydrazides to their corresponding acids by Vanadium(V): A Mechanistic study

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## Abstract

The reaction between Vanadium (V) and Butyric and Isobutyric acid hydrazide is carried out in a mixture of perchloric acid and sodium perchlorate. The reaction proceeds through formation of complex with reactant, which decomposes in subsequent steps to give product. The various thermodynamic parameters were determined by studying the reaction at five different temperatures ranging from 30 to 50°C. Oxidation of hydrazides by Vanadium (V) proceeds through complex formation between hydrazide and the oxidant. Free radical formation can be confirmed by effect of acrylonitrile. The activation parameters were also determined and the mechanism is predicted.

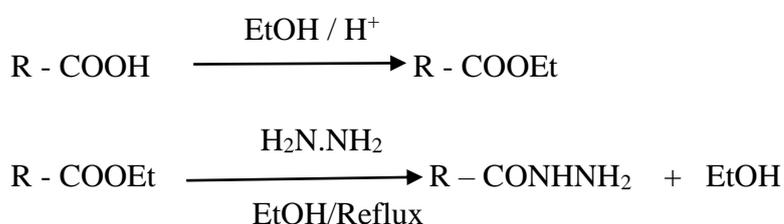
**Keywords:** Butyric acid hydrazide, Kinetics, Vanadium (V), Oxidation.

## Introduction:

Although the kinetics of oxidation of hydrazides by variety of oxidants has been studied, but their reactions with ammonium metavanadate in presence of micellar catalysts seem to have received much little attention. On the basis of literature survey and in the light of above discussion, it is clear that enough information regarding the mechanism of oxidation of aliphatic acid hydrazides is not known. Hence the study of kinetics of oxidation of aliphatic acid hydrazides by Vanadium (V) has been undertaken. The common oxidising agents used for organic substrates are  $K_2Cr_2O_7$  and  $KMnO_4$  etc. which are strong oxidising agents. On the other hand ammonium metavanadate is comparatively milder oxidising agent. This oxidant is used to oxidise organic substrates like hydrocarbons, ketones, aliphatic alcohols, aldehydes and aliphatic esters. The hydrazides selected for the kinetic study, belong to a homologous series, so that the effect of chain length on the reaction rate and on the mechanism of the reaction can be established. The hydrazides chosen for kinetic study are 1) n-Valeric acid hydrazide 2) iso-Valeric acid hydrazide.

## Experimental:

This work also includes the experimental part, preparation and purification of chemicals. The procedure followed for the synthesis of hydrazides is given below -



The pseudo first order reaction condition was used by keeping the concentration of hydrazide excess over that of oxidant. The progress of the reaction was followed at different time intervals by spectrophotometric measurement of absorbance due to complex formed between ammonium metavanadate and hydrazide in acid medium.

To study the oxidation of hydrazide, the reaction mixture was prepared by using requisite concentrations of ammonium metavanadate i.e. V(V), hydrazide, perchloric acid and sodium perchlorate in solution when and as required. The progress of reaction was followed by measuring optical density (O.D.) of the reaction mixture at 390 nm spectrophotometrically.  $\lambda_{max}$  was determined by varying wavelength, it was observed that maximum absorbance for both ammonium metavanadate and a mixture of hydrazide and ammonium metavanadate was obtained at 390 nm.

## Results and Discussion:

### *Effect of V(V) concentration:*

In order to investigate the effect of concentration of V(V) on rate of reaction, the reaction was carried out using different initial concentrations of ammonium metavanadate at 35°C and constant ionic strength, keeping the concentrations of hydrazide and perchloric acid unchanged.

An examination of data and log O.D. versus time plots make it clear that, oxidation of hydrazide at different initial concentrations of V(V) follows the first order kinetics because the log O.D. versus time plot in each case is linear with positive slope and intercept on log O.D. axis. The constancy of k values at different initial [V(V)] indicate the pseudo-first order kinetic behaviour of reaction.

### *Effect of hydrazide concentration:*

In order to study the effect of concentration of hydrazide on the rate of reaction, the reaction at different initial concentrations of substrate (hydrazide) was investigated. For this purpose the concentration of hydrazide was varied from  $2.5 \times 10^{-3}$  M to  $2.5 \times 10^{-2}$  M keeping temperature, ionic strength and concentrations of ammonium metavanadate and perchloric acid constant. The kinetic data of these runs and graphically presentations show that since the log O.D. against time plots are linear, the observed rate constant (k) was computed with respect to change in the concentration of hydrazide the value of pseudo-first order rate constant (k) depends on initial concentration of hydrazide and it increases with increase in [Hydrazide]. The order with respect to hydrazide is determined by plotting  $\log dA / dt$  versus log concentration of hydrazide which is a straight line, the slope of which gives an order of reaction. It is found to be fractional.

**Table 1: Order of reaction.**

Hydrazide	Order
n-VAH	0.65
iso-VAH	0.65

**Effect of Perchloric acid concentration:**

The effect of varying  $[\text{HClO}_4]$  on the rate of oxidation of hydrazide was studied over a range of perchloric acid concentration  $4.0 \times 10^{-2}$  M to  $10.0 \times 10^{-2}$  M, keeping concentrations of ammonium metavanadate and hydrazide constant.

From this data the log O.D. versus time graphs are plotted, from these plots it is observed that the values of rate constants remain almost constant between the range of hydrogen ion concentration studied.

**Effect of Sodium Perchlorate Concentration:**

In order to investigate the effect of ionic strength on specific rate of reaction, the reaction was studied by changing the concentration of sodium perchlorate which was not expected to give any secondary reactions and with assumption that it is completely dissociated. The results of this kinetic study of oxidation of acid hydrazides show that the specific rates of reactions are not influenced by increase in ionic strength. By varying the concentration of sodium perchlorate in the reaction mixture from 0.0 M to  $5.0 \times 10^{-2}$  M the effect of ionic strength was studied and it was observed that for the rates of reactions were almost constant during this variation of ionic strength.

**Effect of Temperature:**

To investigate the effect of temperature on the rate of reaction and as it was also essential to employ the results of kinetic runs in determination of various thermodynamic parameters of the reaction; the present oxidation reaction was carried out at five different temperatures ranging from 30 to  $50^\circ\text{C}$ . The pseudo-first order rate constants were calculated from the  $-\log$  O.D. against time plots. The activation parameters energy of activation ( $E_a$ ), Enthalpy of activation ( $\Delta H^\ddagger$ ) were calculated by plotting  $\log k$  versus  $1/T$  and  $\log k / T$  versus  $1/T$  respectively. From the slope of the plot  $1/T$  versus  $\log k$  energy of activation was calculated as  $E_a = -2.303 \times R \times \text{slope}$ . The slope of the plot  $1/T$  versus  $\log k / T$  is determined from which the enthalpy of activation for each hydrazide was calculated as

$\Delta H^\ddagger = -2.303 \times R \times \text{slope}$ . The entropy of activation  $\Delta S^\ddagger$  was calculated at each temperature by using the formula  $\Delta S^\ddagger = 4.576 (\log k - 10.573 - \log T + E_a / 4.576T)$

From the values of  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  the free energy of activation  $\Delta G^\ddagger$  was computed using the relation  $\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$ . The values of temperature coefficient were calculated by taking the ratios of first order rate constants for rise in temperature by  $10^\circ\text{C}$ .

**Table 2: Temperature Coefficient**

Hydrazide	$K_{40} / k_{30}$	$K_{45} / k_{35}$	$K_{50} / k_{40}$	Mean Values	
n-VAH	1.56	1.53	1.92	1.67	
Iso-VAH	1.40	1.43	1.57	1.47	
	Temperature	$E_a$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
Hydrazide	Coefficient	$\text{KJ mol}^{-1}$	$\text{KJ mol}^{-1}$	e.u.	$\text{KJ mol}^{-1}$
n-VAH	1.67	66.24	52.65	-27.85	88.54

iso-VAH	1.47	60.31	65.47	-31.27	105.77
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### ***Test for intervention of free radical:***

It is already seen that, the order of reaction with respect to V(V) is one. The possibility of formation of free radical during the course of reaction was confirmed by testing the reaction mixture with acrylonitrile and mercuric chloride solutions. The reaction mixture becomes turbid in presence of 10 percent acrylonitrile and white suspension is formed. The formation of white suspension is indicative of polymerisation of acrylonitrile, it was also observed that, the reaction mixture reduces mercuric chloride (a white precipitate of mercurous chloride was obtained) spontaneously. However, blank experiments showed that, there was neither polymerisation of acrylonitrile nor the reduction of mercuric chloride in the absence of either V(V) or hydrazide under identical experimental conditions. Hence induced polymerisation of acrylonitrile and spontaneous reduction of mercuric chloride in reaction mixture only indicates that, the present reaction involves the formation of free radical or radical ions during its path.

### ***Determination of stoichiometry of the reaction:***

The stoichiometry of the reaction is of paramount importance in elucidation of reaction mechanism, hence it was considered necessary to determine the number of moles of V(V) consumed by one mole of hydrazide in oxidation reaction under investigation. The stoichiometry of the reaction was determined by spectrophotometric method. A set of five reaction mixtures containing a known excess of V(V) over hydrazide in the presence of  $5.0 \times 10^{-2}$  M perchloric acid and  $5.0 \times 10^{-2}$  M sodium perchlorate was kept in a thermostat at  $35^{\circ}\text{C}$  for 48 hours. A blank experiment without hydrazide was carried out concurrently using identical quantities of V(V), perchloric acid and sodium perchlorate after volume correction with water for hydrazide solution. In the spectrophotometric method 5 ml from each reaction mixture and blank were diluted to 50 ml using the same measuring flask and optical density of V(V) in diluted solutions was measured at 390 nm as usual. The actual difference in optical density (-dD) due to consumption of V(V) for the formation of complex with hydrazide in each reaction mixture was determined by considering the dilution factor i.e.  $-dD = 10 (D_s - D_o)$  Where,  $D_o$  and  $D_s$  are the optical densities of diluted solutions in blank and in presence of substrate (hydrazide) respectively. The decrease in concentration (-dC) of V(V) in each case was calculated from decrease in its optical density (-dD) and molar extinction coefficient ( $\epsilon$ ) by using the expression  $-dC = -dD / \epsilon$ . Finally, the moles of V(V) needed in oxidation of one mole of hydrazide were calculated in each case by using the relation

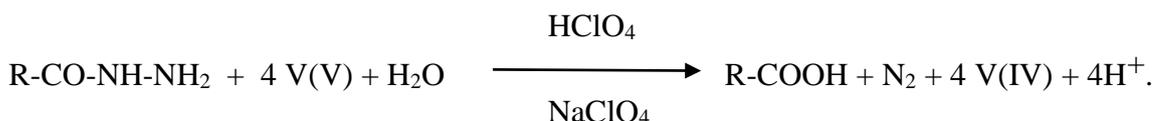
$$\text{Mole ratio} = -[V(V)] / [\text{Hydrazide}]_o$$

Where moles of V(V) consumed in a particular reaction,  $-[V(V)] = -dC$

The value of  $-[V(V)] / [\text{Hydrazide}]_o$  for different experiments is found to be 4 or nearly equal to 4. Therefore it is concluded that 4 moles of ammonium metavanadate were required for oxidation of one mole of hydrazide.

**IDENTIFICATION OF OXIDATION PRODUCTS:**

Finally considering the products of oxidation, observed mole ratio and material balance, the oxidation of hydrazide can be represented by the stoichiometric equation.



The above equation not only consistent with stoichiometry and products of reaction, but also it explains the observed gradual decrease in k values with increase in time, which can be attributed to increasing proportions of H<sup>+</sup> ions with the progress of the reaction.

**Table 3: Effect of H<sub>2</sub>SO<sub>4</sub>, [HYD] = 1.0 x 10<sup>-2</sup> M, [NaClO<sub>4</sub>] = 5.0 X 10<sup>-2</sup> M, [AMV] = 5.0 x 10<sup>-4</sup> M Temp = 35<sup>o</sup>C λ<sub>max</sub> = 390 nm**

[H <sub>2</sub> SO <sub>4</sub> ] x 10 <sup>2</sup> N	n-VAH k x 10 <sup>-5</sup> sec <sup>-1</sup>	iso-VAH k x 10 <sup>-5</sup> sec <sup>-1</sup>
1.0	4.78	10.1
2.5	13.4	28.3
5.0	15.4	34.0
7.5	18.6	42.2
10.0	21.9	52.7

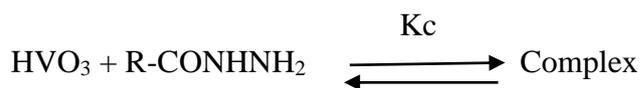
**Table 4: Thermodynamic parameters**

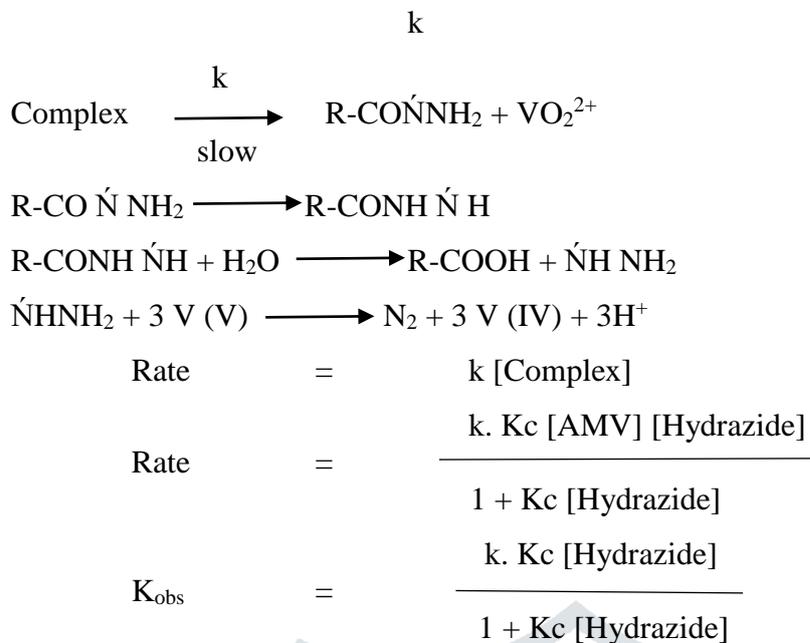
Hydrazide	ΔH <sup>#</sup> cal mol <sup>-1</sup>	ΔS <sup>#</sup> cal mol <sup>-1</sup>	ΔG <sup>#</sup> cal mol <sup>-1</sup>	Ea cal mol <sup>-1</sup>
n-VAH	12584.17	-27.85	21161.97	15833.17
iso-VAH	15650.13	-31.27	25281.29	14414.59

The oxidation products identified in these reactions were corresponding acids and nitrogen.

A perusal of the order of reactivity of hydrazides studied indicates that there is no significant difference in their reactivity, but slightly increase in the reactivity with increase in the chain length is observed. It is also observed that branching in the molecule makes the molecule more reactive than its straight chain isomer.

Taking into consideration the close similarity in the kinetic behaviour n-valeric and iso-valeric acid hydrazides it can be suggested that oxidation of these hydrazides by vanadium (v) proceeds through complex formation between hydrazide and the oxidant. Thus on the basis of kinetic evidences the following mechanism can be proposed.





Micellar catalysis and inhibition have received considerable attention in view of the analogies drawn between micellar and enzyme catalysis. Micelles are formed in aqueous solutions by surfactants, which possess water solubilizing moiety and water-insoluble portion. Micelles increases rate of bimolecular reactions by concentrating both reactants at their surfaces. Three factors may account for the rate enhancement of an organic reaction in aqueous solution when the reactants are incorporated into or onto a micelle: approximation effects, electrostatic effects, and medium effects. Due to these factors, a significant amount of systematic kinetic results have been reported on the effect of micelles on various organic reactions during the few decades. The aliphatic acid hydrazides oxidation by vanadium(V) ( $\text{H}_2\text{SO}_4$ ) has been carried out in anionic surfactants, namely sodium lauryl sulphate (SLS). The reaction rate increases with increasing [SLS] up to  $45.0 \times 10^{-3} \text{ mol dm}^{-3}$  and remains constant at higher [SLS]. This may be due to the dilution effect. The role of SLS micelles in catalysis can be explained by incorporation = solubilization of vanadium(V)- acid hydrazide system in the Stern layer of SLS micelles through electrostatic and hydrophobic interactions. These results are in good agreement with our previous observations.

**Table 5: Effect of varying [SLS] on the oxidation of aliphatic acid hydrazide by vanadium(V).**

Reaction conditions:  $[\text{V(V)}] = 20.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $[\text{Hydrazide}] = 50.0 \times 10^{-3} \text{ mol dm}^{-3}$ ,

$[\text{H}_2\text{SO}_4] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$  Temperature =  $35^\circ\text{C}$

[SLS] ( $\text{mol dm}^{-3}$ )	$k_{\text{obs}} \times 10^{-4} (\text{s}^{-1})$
0	3.1
5	3.4
10	3.9
15	4.0
20	4.2
25	4.5
30	4.9
35	5.3

40	5.8
45	6.3
50	6.4
60	6.4
70	6.4

### Conclusions:

A perusal of literature revealed that anionic species are stabilized by cationic micelles, cationic species by anionic micelles and neutral molecules by nonionic micelles accordingly exhibit catalytic effect. Micelles may catalyze or inhibit a reaction. In this study we have used an anionic surfactant, SLS, which has a catalytic effect i.e. the rate of oxidation of aliphatic acid hydrazide by vanadium(V) in presence of SLS has been enhanced. The micellar catalysis is due to the ability of micelles to concentrate both reactants at their surface.

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