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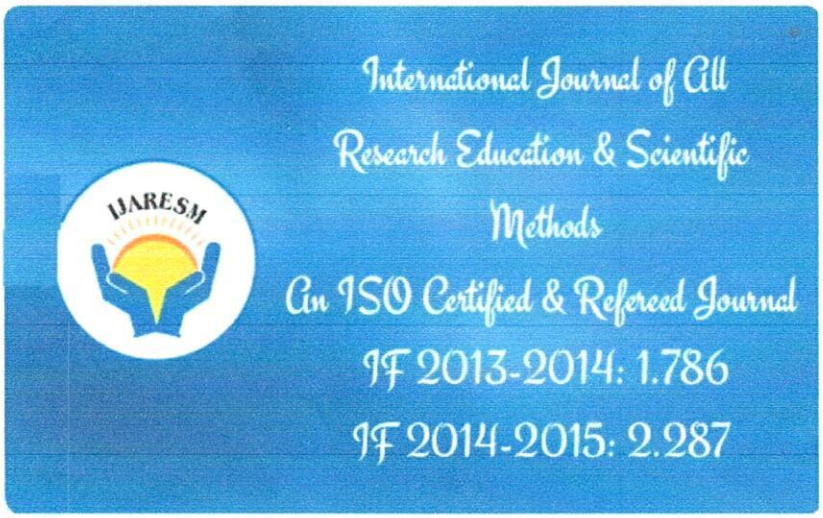

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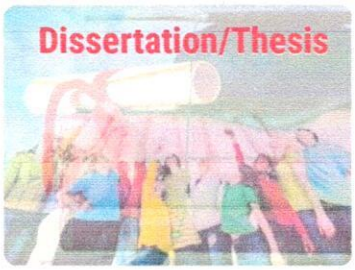

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Spectroscopic Study for Kinetic and Mechanistic Determination for Oxidation of Benzoic Acid Hydrazide by Ammonium Metavanadate

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ABSTRACTS

Chemical kinetics deals with the rate at which the chemical reactions take place and the influence of various factors such as concentration, temperature, pressure catalysts etc., on the reaction rates. Different chemical reactions occur at different rates. Hydrazides are derivatives of carboxylic acids. They have been extensively used in various fields of chemistry; therefore it is pertinent to understand the mechanism of their oxidation. Literature survey reveals that kinetics of oxidation of by vanadium (V) is not extensively studied. Therefore kinetic study of benzoic acid hydrazide by vanadium (V) was undertaken. The reactions between vanadium (V) and Benzoic acid hydrazide (BAH), were studied in sulphuric acid medium under pseudo first order condition. The formation of complex between the reactants, which decomposes in the subsequent step to give products. The reaction proceeds by one electron transfer with intervention of free radical. Increase in hydrazide concentration has no effect on the specific rate. Increase in acid concentration increases the reaction rate and decreases with decrease in dielectric constant. The effect of temperature was studied between 30 to 55 oC. The activation parameters were determined and the values support the proposed mechanism as evidenced by considerable decrease in e ntropy of activation. (-ΔS # = 156.71, J K-1 mol-1

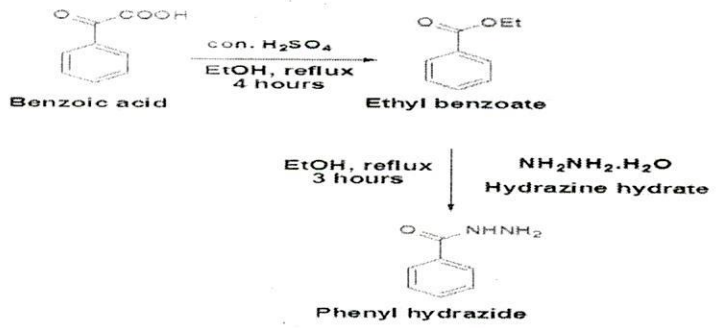
Key words: BAH, hydrazides, hydrazines. Pseudo-first order, vanadium (V)

INTRODUCTION

Hydrazides in organic chemistry are a class of organic compounds shairing a common functional group characterized by a nitrogen to nitrogen covalent bond having four substituents with at least one of them being an acyl group. The general structure for an hydrazide is (R1=O)R2-N-N-R3R4. A related class of compounds called hydrazines do not carry an acyl group. Hydrazides are derivatives of Carboxylic acids and hydrazines.Since hydrazides find extensive use in various fields of chemistry1, especially pharmaceutical Chemistry2, it is necessary to study kinetically by using spectroscopic methods and to understand the mechanism of their oxidation.

The kinetics and Mechanism of oxidation of benzoic acid hydrazides has been well studied.Ammonium metavanadate being one of the most versatile oxidizing agents, reacting with diverse substrates. The oxidation of benzoic acid hydrazides continues to be of interest. The oxidant used is a versatile that deserves further investigation. Literature survey reveals that, although several oxidants are used for oxidation of hydrazides and their mechanisms have been established, there is no report on the oxidation of benzoic acd hydrazide by Amonium etavanadateThe reaction of hydrazides with most oxidants give the corresponding acids1 and in some cases2 esters or amides. Ammonium metavanadate salts are well known oxidants3 in organic synthesis.

MATERIAL AND METHOD



Ethyl ester of benzoic acid was prepared by esterification. Then hydrazide was prepared by using the prescribed procedure[3].An equimolar mixture of ethyl ester and hydrazine hydrate(B.D.H. 99%) was refluxed for 15 minutes. Then enough absolute ethanol was added through the condenser to get clear solution and further refluxed for 5 hours. The excess of hydrazine hydrate, solvent ethanol and other unreacted material was removed by distilling the solution under reduced pressure. The hydrazide was recrystallised from ethanol. Then it was stored in amber colored bottles kept in dark place.

Ammonium metavanadate, sulphuric acid and salt used were of AR grade. Double distilled water was used throughout the experiment. The 0.01 M stock solution of ammonium metavanadate was prepared by dissolving accurately weighed and calculated quantity of ammonium metavanadate in hot double distilled water using pyrex glass measuring flask. The vanadium (V) solution was standardized against standard ferrous ammonium sulphate solution by using diphenylamine. Similarly the stock solution of sodium perchlorate was prepared by dissolving equivalent quantities of sodium carbonate and perchloric acid (70% E. Merck) in water to maintain ionic strength. Standard BAH solution was prepared by dissolving its hydrazide in ethanol-water6:4 proportion system. In case of Vanadium (V) oxidation of hydrazide, the ionic strength was maintained using sodium perchlorate. In a particular experiment the oxidant vanadium and substrate hydrazide are taken in separate conical flasks along with required quantities of sulphuric acid and sodium perchlorate and then both are kept in a thermostat at 35+-0.1^{o}C for half an hour. The kinetic experimental study was followed by mixing thermally equilibrated solution of reactants and transferring the reaction mixture to 1cm^3 cuvette. The progress of reaction was followed by, measuring absorbance of the reaction mixture at 415 spectrophotometrically using UV-Vis. Spectrophotometer ELICO-(INDIA) S.L.159 in sulphuric acid medium using water as a reference solvent.. The reaction was studied under pseudo-first order condition in which, concentration of benzoic acid hydrazide was in excess as compared to that of oxidant ammonium metavanadate. The reaction is found to proceed through formation of complex between vanadium (V) and benzoic acid hydrazide. The pseudo-first order rate constant K was obtained by plotting the log of absorbance at 415 against time for hydrazide and was found to be fairly constant at different concentrations of vanadium (V).

RESULTS AND DISCUSSION

The Experimental results are interpreted and the specific reaction rate constants for various concentration of Substrate, Oxidant, medium of the reaction, salt and temperature of the reaction are determined by graphical method are:

Sr.	Effect of Substrate	[BAH] x 10^3M.	1.0	2.0	4.0	5.0	6.0	8.0	10
1	[hydrazide]	k x 10^4sec^{-1}	2.57	2.73	2.73	2.65	2.65	2.38	2.07
	Effect of oxidant	[AMV] x 10^4M.	1.0	2.0	4.0	5.0	6.0	8.0	10.0
2	[AMV]	k x 10^4sec^{-1}	2.50	2.50	2.46	2.65	2.73	2.57	2.61
	Effect of Medium	[H_2SO_4] x 10^2M.	0.5	1.0	2.0	3.0	4.0	5.0	
3	[H_2SO_4]	k x 10^4sec^{-1}	1.73	2.65	2.88	2.99	3.19	3.30	
	Effect of Ionic Strength	[$NaClO_4$] x 10^1M.	0.5	1.0	2.0	3.0	4.0	5.0	
4	[$NaClO_4$]	k x 10^4sec^{-1}	2.57	2.65	2.65	2.76	2.80	2.65	

	Effect of	Temperature	3.0	35	40	45	50	55	
5	Temperature	°C	1.77	2.65	3.42	5.03	6.14	8.44	

The various Energy parameters calculated are:

Sr.	Thermodynamic Parameter		
1	Temperature Coefficient		1.83
2	Energy of Activation	Ea(KJ mol^{-1})	51.11
3	Enthalpy of Activation	$\Delta H^{\#}$ (KJ mol^{-1})	46.32
4	Entropy of Activation	$\Delta S^{\#}$ (J $K^{-1}mol^{-1}$)	-156.71
5	Free Energy of Activation	$\Delta G^{\#}$ (KJ mol^{-1})	98.5

1. Effect of Reactant Concentration:

The reaction is found to proceed through formation of complex between vanadium (V) and hydrazide. The specific rate of oxidation is independent of concentration of oxidant and substrate. The order is unity with oxidant concentration. The specific rate of oxidation decreases with increase in concentration of substrate hydrazide. The decrease in rate constant as the concentration of benzoic acid hydrazide increases can be attributed to greater stability of the complex in alcoholic medium probably due to solvation[16]. This is evident from initial absorbance values of the complex with different hydrazide concentrations.

2. Effect of Sulphuric Acid Concentration:

The specific reaction rate increases as the concentration of acid increases. This effect of sulphuric acid on the reaction rate may be due to the protonation prior equilibria. Oxidant vanadium (V) was reported to undergo variety of protonation reactions[2] and under the present experimental conditions protonated vanadate might be considered as a predominant species as shown by equilibrium (1).

$$VO_3^- + H^+ \rightleftharpoons HVO_3 \qquad \text{---------- } K_1 \text{ (1)}$$

The substrate, hydrazide is also known to undergo protonation[19] according to equilibrium (2)

$$Ar\text{-}CONHNH_2 + H^+ \rightleftharpoons Ar\text{-}CONHNH_3^+ \qquad \text{---------- } K_2 \text{ (2)}$$

The protonation constants of both oxidant and substrate, K_1 and K_2, are very high, thus converting both the reactants almost completely into their protonated forms in the hydrogen ion concentration range used in the present study (5.0×10^{-1} M to 5.0×10^{-2} M). Therefore, both protonated forms of the reactants may be active in the present investigation. The graph of log k vs log [Acid] is linear and the order of reaction is found to be fractional.

3. Effect of Ionic Strength, Dielectric Constant and Temperature:

The effect of ionic strength was studied by varying the concentration of sodium perchlorate in the reaction mixture from 0.3×10^{-1} to 3.0×10^{-1} M. It is investigated that rate of reaction is not influenced by increase in ionic strength.

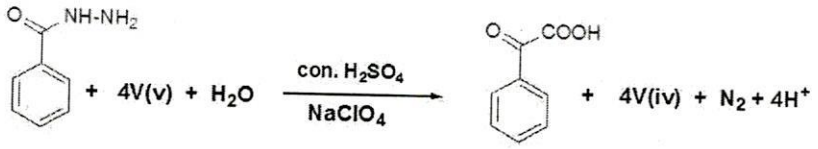
To investigate the effect of dielectric constant on specific rate of reaction, various percentage of aqueous ethanol were used. The specific rate of reactions decreases with decrease in dielectric constant. Such decrease in rate with decrease in dielectric constant is reported[11]. The graphs of log k vs 1 /Dielectric Constant are plotted, which are linear.

The kinetics of oxidation of hydrazides was studied at different temperatures ranging from 25° to 55°C. The log (Abs) against time plots at different temperatures are linear which reveals that, the pseudo-first order kinetic behaviour of the reaction is not affected by change in temperature. The values of observed rate constants were used to determine various thermodynamic parameters like temperature coefficient, energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta G^{\#}$).

4. Reaction Intermediate, Stoichiomerty and Product Analysis:

The formation of free radicals or radical ions during the course of the reaction was confirmed from induced polymerisation of acrylonitrile[8]. The mole ratio of hydrazide: vanadium (V) is found to be 1:4 and it is independent

of concentration of sulphuric acid that was used during course of the reaction under study. The integral value of observed mole ratio, its independence on sulphuric acid concentration and formation of only carboxylic acid along with nitrogen gas, as oxidation product leads to deduce that, the two rate determining steps occurring simultaneously result in the formation of one and the same intermediate. Although the observed mole ratio (substrate: oxidant) of the reaction is 1:4, as is pointed out earlier, the order of reaction with respect to vanadium (V) is one. This fact makes it clear that 3 moles of vanadium (V) are consumed in fast step(s) taking place after rate determining step(s).



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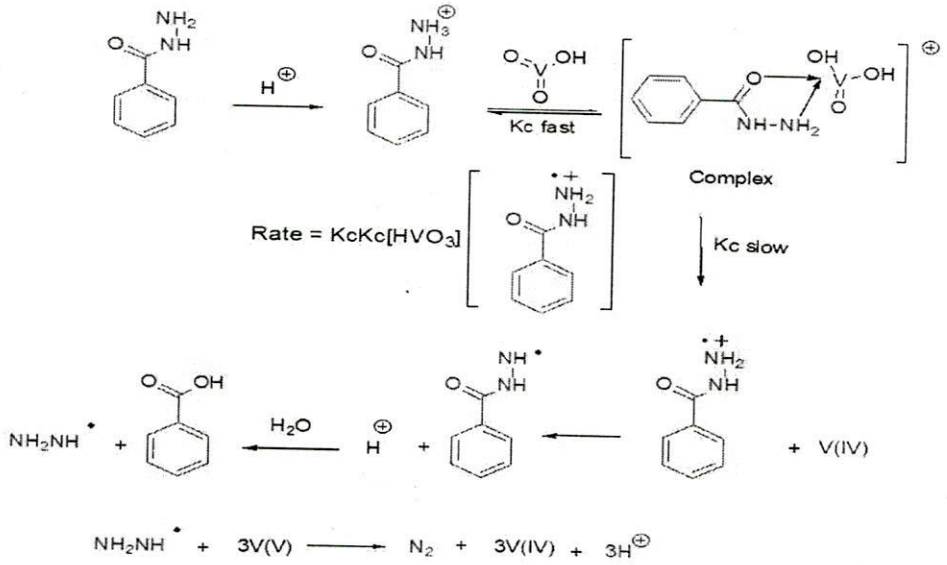
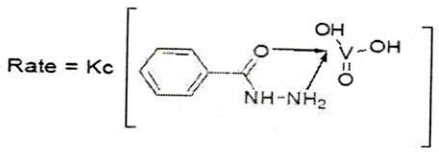


According to the above scheme the rate of the reaction is given by



where, Ar = substituted Aromatic moiety (C_6H_5O-CO-)
According to the above scheme the rate of the reaction is given by Rate = k_c [Complex]
Substituting the value of [Complex] from the equilibrium,
Rate = $k_c K_c$ [HVO_3] [Ar-$CONHNH_3$]

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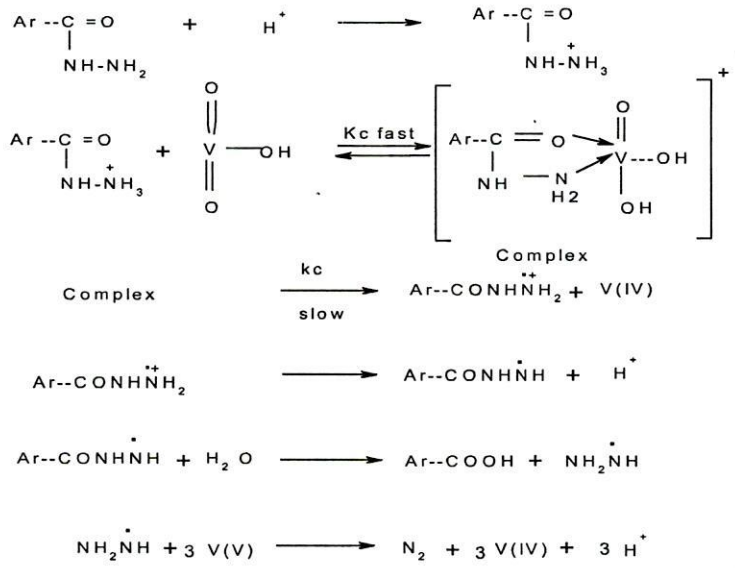
Mechanism of the reaction: The mechanism in terms of the active species of the HVO_3 and substrate protonated hydrazide is shown in the scheme as mentioned follows.

SCHEME



where, Ar = C_6H_5

According to the above scheme the rate of the reaction is given by

$$\text{Rate} = k_c\,[\text{Complex}]$$

Substituting the value of [Complex] from the equilibrium,

$$\text{Rate} = k_c K_c\,[HVO_3]\,[\text{Ar-CONHNH}_3]\,.$$