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**Oxidative Degradation Of Ortho Chloro Substituted Benzoic Acid Hydrazide  
By Vanadium (V). A Kinetic & Mechanistic Approach By Spectrophotometry**

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*The reactions between oxidant vanadium (V) and o-chloro benzoic acid hydrazide (o-Cl-BAH) was studied in sulphuric acid medium under pseudo first order condition. The mechanism involves the formation of complex between the reactants, which decomposes in the subsequent step to give products. The reaction proceeds by direct one electron transfer with intervention of free radical and found to be independent of concentration of hydrazide, concentration of oxidant, ionic strength and various salts. 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 entropy of activation. ( $-\Delta S^\ddagger = 153.60 \text{ K-1 mol-1 o-Cl-BAH}$ .)*

*Key Words: Hydrazide, Spectrophotometry, Kinetic, Mechanistic, Oxidation, Degradation.*

**Introduction:**

Hydrazides are derivatives of carboxylic acids with hydrazine<sup>1</sup>. They have been extensively used in various fields of chemistry<sup>2-8</sup>; therefore it is pertinent to understand the mechanism of their oxidation. The survey of kinetic and mechanistic studies on oxidation of hydrazides by different oxidants makes it very clear that, these studies are mainly on oxidation of aliphatic hydrazides. Although the kinetics of oxidation of hydrazides by variety of oxidants has been studied, their reactions with vanadium seem to have received much little attention. On the basis of literature survey and in the light of above fact, it is clear that enough information regarding the mechanism of oxidation of aromatic acid hydrazides is not known. Hence the study of kinetics of oxidation of chloro substituted benzoic acid hydrazides by vanadium(V) in aqueous acidic medium has been undertaken. The objective of the present study is not only to develop method for the oxidation of hydrazide to its corresponding carboxylic acids but also to determine the order of reactivity and to propose plausible mechanism of the reaction.

**Material and Method:**

o-Chloro substituted benzoic acid hydrazide was prepared by reported procedure<sup>11</sup> and characterized by its physical constant. The dry hydrazide was stored in amber coloured 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 stock solution of ammonium metavanadate was prepared by dissolving calculated quantity of ammonium metavanadate in hot double distilled water using standard 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 o-Chloro substituted benzoic acid hydrazide (o-Cl-BAH) solution was prepared by dissolving it in water..

**Experimental Technique :**

The reaction mixture was prepared by using requisite concentration of ammonium metavanadate, hydrazide, sulphuric acid and sodium perchlorate in solution, when and as required. The reaction is found to be proceed through formation of complex between vanadium(V) and hydrazide, as observed by the fact that when two reactants were mixed, there was change in colour from pale yellow to brown. The pseudo-first order rate constant  $k$  was obtained by plotting the log of absorbance at 415 nm against time for each hydrazide and was found to be fairly constant at different concentration of vanadium (V). The progress of the reaction was followed by measuring absorbance of the reaction mixture at 415 nm spectrophotometrically using UV-Vis spectrophotometer ELICO (INDIA) S.L.-169.

**Kinetic Studies:**

The reaction was studied under pseudo-first order condition in which, concentration of hydrazide under study was in excess as compared to that of ammonium metavanadate. Plot of  $\log(\text{Abs})$  against time was found to be linear in all the kinetic runs. The fact leads to conclude that the reaction is first order in oxidant concentration.

**Results And Discussion:**

**Table.1**

	Effect of	Unit Concentration	Multiples of Unit Concentration and respective rate Constants						
S	Substrate	[o-Cl-BAH] x 10 <sup>3</sup> M.	1.0	2.0	4.0	5.0	6.0	8.0	10
1	[hydrazide]	k x 10 <sup>4</sup> sec <sup>-1</sup>	1.27	1.27	1.50	1.46	1.57	1.61	1.69
2	Substrate in aqueous ethanol	[o-Cl-BAH] x 10 <sup>3</sup> M.	1.0	4.0	5.0	8.0	10	--	--
	60:40%Ethanol: Water	k x 10 <sup>4</sup> sec <sup>-1</sup>	5.53	3.76	3.26	2.76	2.15	--	--
3	Oxidant	[AMV] x 10 <sup>4</sup> M.	1.0	2.0	4.0	5.0	6.0	8.0	10.0
	[AMV]	k x 10 <sup>4</sup> sec <sup>-1</sup>	1.38	1.50	1.38	1.46	1.57	1.61	1.54
4	Medium	[H <sub>2</sub> SO <sub>4</sub> ] x 10 <sup>2</sup> M.	0.5	1.0	2.0	3.0	4.0	5.0	
	[H <sub>2</sub> SO <sub>4</sub> ]	k x 10 <sup>4</sup> sec <sup>-1</sup>	1.38	1.46	1.77	2.03	2.11	2.57	
5	Ionic Strength	[NaClO <sub>4</sub> ] x 10 <sup>1</sup> M.	0.5	1.0	2.0	3.0	4.0	5.0	
	[NaClO <sub>4</sub> ]	k x 10 <sup>4</sup> sec <sup>-1</sup>	1.57	1.46	1.61	1.65	1.73	1.80	
6	Effect of Temperature	Temperature I °C	3.0	35	40	45	50	55	
		k x 10 <sup>4</sup> sec <sup>-1</sup>	1.04	1.46	2.15	2.84	4.03	5.18	
7	Various Salts	[salt] <sub>0=1.0x10<sup>-1</sup>M</sub>	LiCl	NaCl	KCl	LiClO <sub>4</sub>	NaClO <sub>4</sub>	KClO <sub>4</sub>	MnCl <sub>2</sub>
		k x 10 <sup>4</sup> sec <sup>-1</sup>	1.96	1.69	1.42	1.80	1.46	1.96	1.57
8	Dielectric Constant	Dioxane	0	5	10	15	20	25	
		Dielectric Constant	78.54	77.57	77.01	75.72	74.72	73.51	
		k x 10 <sup>4</sup> sec <sup>-1</sup>	1.46	1.42	1.38	1.34	1.31	1.27	

**Table:2 Thermodynamic Parameters**

Hydrazide	Thermodynamic Parameters			
	Ea (KJ mol <sup>-1</sup> )	ΔH # (KJ mol <sup>-1</sup> )	ΔS # (J K <sup>-1</sup> mol <sup>-1</sup> )	ΔG # (KJ mol <sup>-1</sup> )
<b>o-Cl-BAH</b>	53.40	51.11	-153.60	99.58

### 1. Effect Of Reactant Concentration:

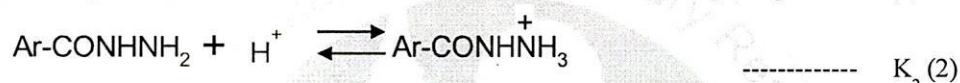
The reaction is found to proceed through formation of complex between vanadium (V) and hydrazide, as observed by the fact that when two reactants were mixed, there was change in color from pale yellow to brown. The linearity of the pseudo first order plots indicated that the order is unity in oxidant concentration. The specific rate of oxidation does not increase with increase in concentration of hydrazides and order with respect to hydrazide was found to be unity in aqueous medium..

### 2. Effect Of Sulphuric Acid Concentration:

The specific reaction rate increases as the concentration of acid is increased. This effect of sulphuric acid on the reaction may be due to the protonation prior equilibria. Oxidant vanadium (V) was reported to undergo variety of protonation reactions<sup>12</sup> and under the present experimental conditions protonated vanadate might be considered as a predominant species as shown by equilibrium (1).



The substrate, hydrazide is also known to undergo protonation<sup>13</sup> according to equilibrium (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 ( $5.0 \times 10^{-1}$  M to  $5.0 \times 10^{-2}$  M). Therefore, both protonated forms of the reactants may be active in the present investigation. The graph of  $\log k$  vs  $\log [\text{Acid}]$  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  $5.0 \times 10^{-2}$  to  $5.0 \times 10^{-1}$  M. It is investigated that rate of reaction is not influenced by increase in ionic strength.

Various percentage of 1-4 dioxane was used in order to investigate the effect of dielectric constant on specific rate of reaction.

The kinetics of oxidation of hydrazides under investigation was studied at different temperatures ranging from 30° to 55°C. The  $\log (\text{Abs})$  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 ( $E_a$ ), enthalpy of activation ( $\Delta H^\ddagger$ ), entropy of activation ( $\Delta S^\ddagger$ ) and free energy of activation ( $\Delta G^\ddagger$ ). (Table:1)

### 4. Reaction Intermediate, Stoichiometry And Product Analysis:

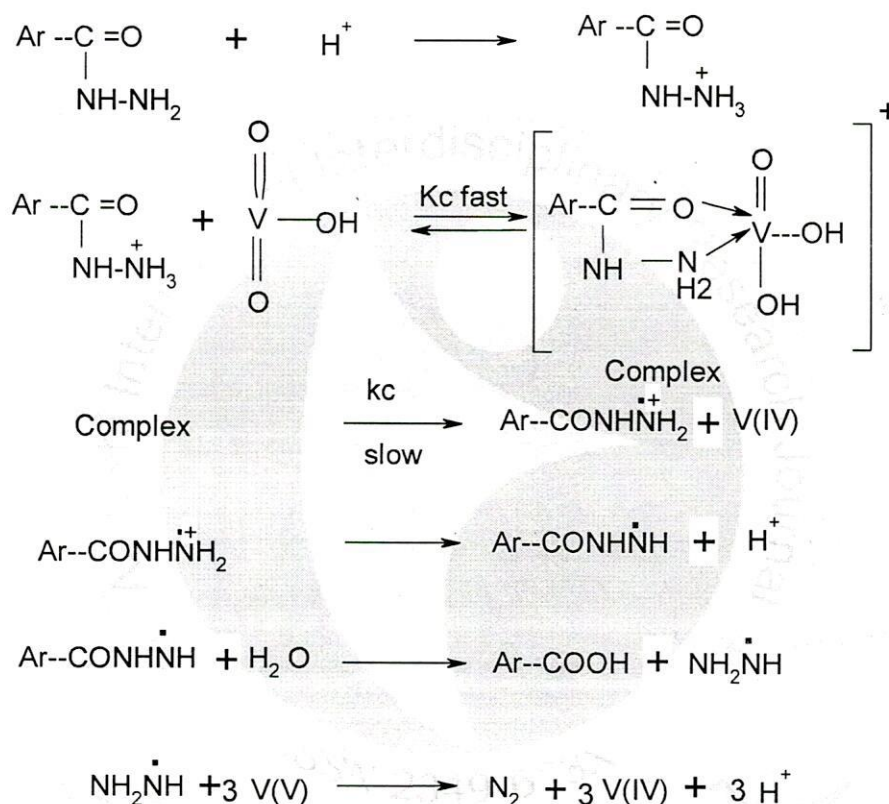
The formation of free radicals or radical ions during the course of reaction was confirmed from induced polymerisation of acrylonitrile<sup>15</sup>. The mole ratio of hydrazide: vanadium (V) is found to be 1:4 and it is independent of concentration of sulphuric acid that was used. The integral value 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).

The oxidation products identified in this reaction are as follows. Besides formation of corresponding carboxylic acids, the nitrogen gas is also evolved in each reaction.

The formation of carboxylic acids and  $N_2$  in the oxidation of aliphatic as well as aromatic acid hydrazides<sup>16</sup> is well documented in chemical literature. The study of oxidation of hydrazide by different oxidants indicated that, the formation of ammonia also takes place in addition to the formation of respective carboxylic acid and nitrogen<sup>17,18</sup>

The mechanism in terms of the active species of the oxidant  $HVO_3$  and substrate protonated hydrazide is shown in the scheme as follows.

**SCHEME**



where, Ar = o-Chloro substituted Benzoic acid

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,

$$\text{Rate} = k_c K_c [\text{HVO}_3] [\text{Ar}-\text{CONHNH}_3^+]$$

**5. Reactivity Of Substrate In Aqueous Medium :**

An examination of relative reactivities of hydrazides studied from literature, shows that o-Cl-BAH undergoes oxidation at slower rate. This lower reactivity of oxidation of o-Cl-BAH can be attributed to although chloro group can withdraw electron density by induction, it is also capable of supplying  $\pi$  electrons to the conjugated system, thus deactivating the carbonyl group of the



hydrazide<sup>19</sup>. There is possibility of steric hinderance between the complex and the bulky chlorine atom. As a result the extent of complexation will be less. This is again confirmed by the comparatively low initial absorbance in aqueous medium to similar systems in aqueous ethanol.

#### Reactivity Of Substrate In Aqueous Ethanol

The higher rate of o-Cl-BAH is due to strong electron withdrawing inductive effect<sup>20</sup> of chlorine, which outweighs it's weaker electron donating resonance effect because of distance; in this process of oxidation. It is proved that field effects can be affected by solvent<sup>21,22</sup>. There might be some such stabilization induced by solvation<sup>23</sup> by ethanol showing higher initial absorbance values for the complex in aqueous ethanol as compared to corresponding values in aqueous medium and may be probably rendering the electron withdrawing inductive effect more prominently<sup>23</sup>. The spectroscopic study for kinetic and mechanistic determination for oxidation of Benzoic acid hydrazide by ammonium metavanadate was done<sup>24</sup> and the entropy of activation was found to be  $(-\Delta S^\ddagger = 156.71 \text{ K}^{-1} \text{ mol}^{-1})$  Benzoic Acid Hydrazide.

#### Effect Of Solvents On Reactivity Of Substrate

The reactivity in aqueous ethanol is higher due to strong electron withdrawing inductive effect. The ethanol content in the reaction medium decreases the rate (Table;2) This can be attributed to the lower dielectric constant of medium. In other words this effect of solvent is due to stabilization of the complex formed between reactants<sup>13,21</sup> in a medium of low relative permittivity.

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