

INVESTIGATION OF MECHANISM OF OXIDATIVE DEGRADATION OF NIAZID BY AMMONIUM METAVANADATE FOLLOWED BY KINETICS

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ABSTRACT: Investigation of mechanism of oxidative degradation of Niazip by ammonium metavanadate followed by kinetics of the reaction was carried out under pseudo first order condition. The complex is formed between the reactants, which on decomposition gives Pyridine 3 carboxylic acid. Single electron transfer was observed during the course of this oxidation reaction with intervention of free radical. The effect of different initial Concentration of reactants on oxidation was studied. The pseudo-first order kinetic behavior of the reaction is due to constancy in specific reaction rates at various concentrations of Oxidant. Increase in concentration of substrate shows decreases in the specific rate of the Oxidation. The rate of reaction is directly proportional to the concentration of the acid as well as dielectric constant of the medium of the reaction. There is no effect of change in concentration of salt as well as various salts of the same concentration under the experimental conditions on the specific rate of the oxidation. The variation of ionic strength during oxidation has negligible effect on specific rates of oxidation. The effect of temperature on rate of the oxidation was studied from 30°C to 55°C and the reaction rates are found to be directly proportional to the increase in temperature. The values of thermodynamic activation parameters support the mechanism investigated which is further supported by considerable decrease in entropy of activation. ($-\Delta S^\ddagger = 134.83, \text{J K}^{-1} \text{mol}^{-1}$). The investigation of the mechanism of the oxidation was followed by measuring the absorbance (A) of the oxidant at 390 nm.

Keywords: Niazip, Ammonium metavanadate, Oxidation, degradation, Kinetics etc.

INTRODUCTION: Ammonium metavanadate, a versatile oxidizing agent, has also been used to oxidize many organic compounds like hydroxyl amine hydrochloride, acetaniides, L-Cysteine, glycerol and cyclohexanol¹⁻⁵. Hydrazides are obtained by preparing derivatives of Carboxylic acids and hydrazines⁶. It's multiple use in various branches of chemistry^{8,9,10,11,12,13} especially pharmaceutical Chemistry⁷, needs to study the mechanism of their oxidation in detail. The formation of corresponding acids^{14,15,16,17,18,19,20,21} is observed during the most of the oxidation reactions of hydrazine's. Literature survey shows that, the chemical kinetic study of oxidative degradation of Niazip by ammonium metavanadate is not extensively studied. The present study has been carried out with a view to postulate general mechanism for the oxidation of Niazip with ammonium metavanadate.

MATERIAL AND METHOD: The anhydrous sodium bicarbonate, sulphuric acid, salt, ammonium metavanadate (AR grade), hydrazine hydrate (BDH 99%) and freshly distilled ethanol was used. Ethyl ester of pyridine 3 carboxylic acid was prepared by esterification²² and converted to Niazip by using the prescribed procedure²³. An equimolar mixture of ethyl ester of Pyridine 3 Carboxylic acid and hydrazine hydrate (B.D.H. 99%) was refluxed for more than fifteen minutes. Then enough absolute ethanol was added through the condenser to get clear solution and further refluxed for more than six hours. The excess of hydrazine hydrate, solvent ethanol and other unreacted material was removed by distilling the solution under reduced pressure. The resulting Niazip recrystallised from ethanol and stored in amber colored bottles and kept in dark place. The distilled water obtained by redistillation of distilled water in the presence of a few crystals of potassium permanganate and a few pellets of potassium hydroxide using borosil glass distillation assembly was used throughout the experiment. The 0.01 M solution of oxidant ammonium metavanadate was prepared by dissolving accurately calculated and weighed quantity of ammonium metavanadate in hot double distilled water using Pyrex glass measuring flask. The standardization of ammonium metavanadate (v) solution was done by titrating it against standard ferrous ammonium sulphate solution by using diphenylamine as an indicator. Similarly the stock solution of sodium perchlorate was prepared by dissolving equivalent quantities of Sodium carbonate and perchloric acid (70% E.Merck) in H₂O to maintain ionic strength. Standard Niazip solution was prepared by dissolving it in aqueous alcoholic medium.

DETERMINATION OF ABSORPTION MAXIMA (λ MAX) OF THE REACTION: The absorption maxima i.e. λ max of the reaction under study was determined by varying wavelength. it was observed that maximum absorbance for both ammonium metavanadate and a mixture of Niazip and ammonium metavanadate was obtained at 390 nm λ max.

METHOD OF FOLLOWING THE KINETIC REACTION: The oxidant and Niazip are taken in separate conical flasks along with required quantities of sulphuric acid and sodium perchlorate and are kept in a thermostat at 35±0.1°C for more than half an hour. The kinetic study was followed by mixing thermally equilibrated solution of reactants and transferring the reaction mixture to 1cm³ cuvette. The progress of reaction was followed by measuring absorbance of the reaction mixture at 390 nm spectrophotometrically using UV-Vis. Spectrophotometer in sulphuric acid medium using water as a reference solvent. The reaction was studied under pseudo-first order condition in which, concentration of Niazip was in excess as compared to that of ammonium metavanadate. The reaction is found to proceed through formation of complex between ammonium metavanadate and Niazip. The

pseudo-first order rate constant K was obtained by plotting the log of absorbance at 390 nm against time for Niazyd and was found to be fairly constant at different concentrations of ammonium metavanadate.

REACTION INTERMEDIATES: INTERVENTION OF FREE RADICAL: The induced polymerization of acrylonitrile²⁴ and spontaneous reduction of mercuric chloride²⁵ in reaction mixture itself indicates that, the present reaction involves the formation of free radical.

EFFECT OF SULPHURIC ACID ON SUBSTRATE (HYDRAZIDE): A standard kinetic experiment was repeated by only changing the concentration of sulphuric acid from 0.0025 to 0.1 M containing equivalent quantities of Niazyd, oxidant, salt and temperature. The mixtures in each flask were made alkaline and tested for detection of hydrazine after three hours. It was seen that, the resultant solution in various flasks didn't give any response to ammonical silver nitrate and Fehling's solution, indicating absence of hydrazine. Hence it can be concluded that, there is no significant hydrolysis of Niazyd in the presence of sulphuric acid up to 0.1 M.

CONFIRMATION OF STATUS OF ACID CONTENT AND TO CHECK HYDROLYSIS OF NIAZID UNDER EXPERIMENTAL CONDITIONS: The confirmation of hydrolysis of substrate under experimental conditions was done by conducting similar set of experiments. It was subjected to alkalimetric estimation of acid content in the beginning and at the end. When it was found that there was no perceptible change in acid content of any mixture after a period of minimum three hours. This invariance of acid concentration can be attributed to the fact that, there was no hydrolysis of Niazyd under experimental conditions was observed. Similar observations are already reported.²⁶

STOICHIOMETRY OF THE REACTION: The number of moles of ammonium metavanadate consumed by one mole of Niazyd in reaction under investigation means the stoichiometry of the reaction was investigated by spectrophotometric method. A set of five reaction mixtures containing a known excess of sodium perchlorate over Niazyd in the presence of 1.0×10^{-2} M sulphuric acid and 5.0×10^{-2} M sodium perchlorate was kept in a thermostat at 35°C for more than 48 hours. A blank experiment without Niazyd was carried out concurrently using identical quantities of ammonium metavanadate, sulphuric and sodium perchlorate after volume correction with water for Niazyd solution.

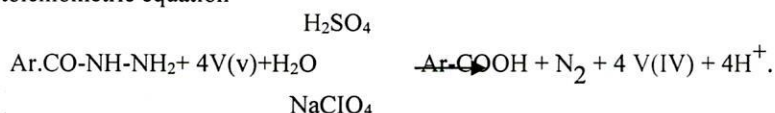
After completion of the reaction, concentration of ammonium metavanadate (IV) was determined at 765nm ($\epsilon = 17.77$).²⁷ from its absorbance and molar extinction coefficient (ϵ) by using the expression $C = \text{Abs.} / \epsilon$

Finally, the moles of ammonium metavanadate (IV) formed in oxidation of one mole of Niazyd were calculated in each case by using the relation. Mole ratio = $- [V(IV)] / [Niazyd]_0$

The value of $[V(IV)] / [Niazyd]_0$ for different experiments was found to be nearly equal to 4. Therefore it is concluded that 4 moles of ammonium metavanadate were required for oxidation of one mole of Niazyd.

IDENTIFICATION OF OXIDATION PRODUCTS:

For the identification of oxidation products, the reaction was studied by using Niazyd and ammonium metavanadate in stoichiometric proportions in presence of 1.0×10^{-2} M sulphuric acid and 1.0×10^{-1} M sodium perchlorate. The flask containing reaction mixture was kept in a thermostated water bath maintained at 35°C for 26 hours to complete the reaction. After the completion of the reaction, the reaction mixture was subjected to ether extraction and acid was separated. The presence of carboxylic acid group was detected by testing with five percent bicarbonate solution. The amide derivative of the corresponding aromatic carboxylic acid was prepared²⁸. The observed physical constant of amide derivatives was found to be in good agreement with those of benzamide. The formation of corresponding carboxylic acids in oxidation of Niazyd was accompanied by evolution of nitrogen gas. Nitrogen was detected by lime test.²⁹ A mixture of lime and manganese dioxide in 10:1 proportion was ignited in a small hard glass tube. A test portion of concentrated reaction mixture was rendered neutral with sodium hydroxide solution and it was added to the ignited mixture. The tube was heated slowly and the liberated gas was tested with filter paper moistened with manganese nitrate and silver nitrate solutions. This indicator paper held at the mouth of the tube shows grey fleck, which turns blue immediately on treatment with a drop of benzidine solution which, indicates the formation of nitrogen gas during the oxidation. Finally considering the products of oxidation, observed mole ratio and material balance, the oxidation of Niazyd can be represented by the stoichiometric equation



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

RESULTS AND DISCUSSION: It was found that, the reaction proceeds with a measurable velocity using 1.5×10^{-3} M ammonium metavanadate, 1.5×10^{-2} M Niiazid, 1.1×10^{-1} M sodium perchlorate, 1.5×10^{-2} M sulphuric acid and 390 nm λ_{max} at 35°C . The observed rate constant (k) of the reaction goes on slightly decreasing with time, the order of reaction with respect to ammonium metavanadate (v) is one.

The specific reaction rate constants determined by graphical method are:

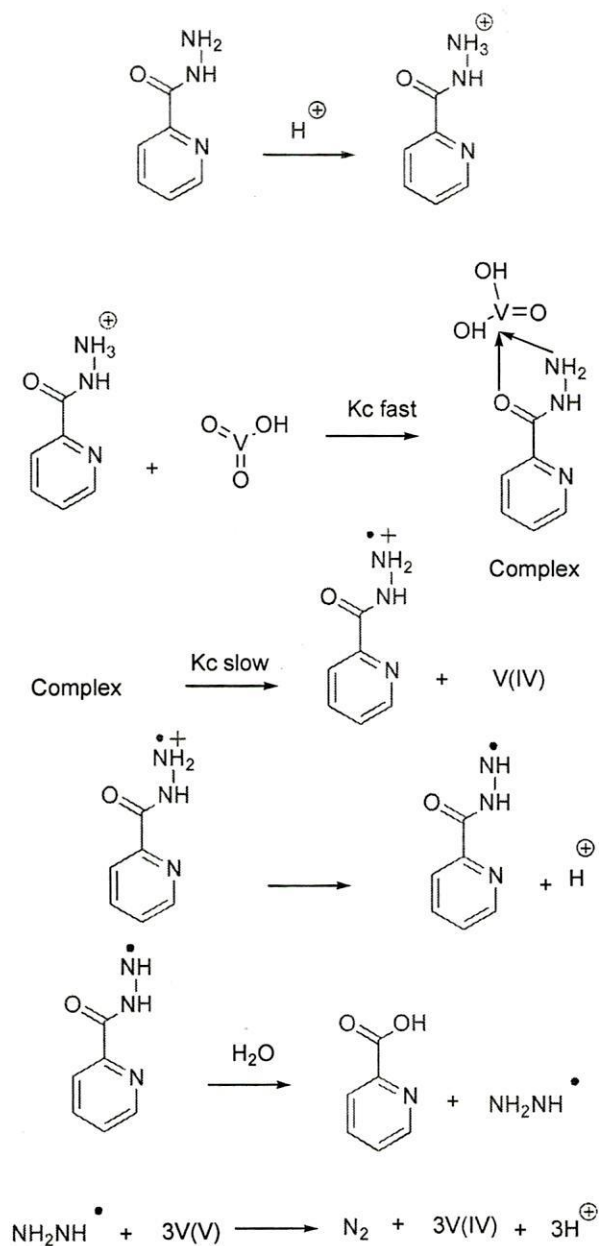
Effect of	Unit Concentration	Multiples of Unit Concentration and respective rate Constants						
		0.3	0.6	1.2	1.5	1.8	2.4	3.0
1 [Niiazid]	[Niiazid] x 10^3 M	4.85	4.40	3.96	3.66	3.25	3.04	2.56
	k x 10^4sec^{-1}	3.77	3.83	3.73	3.66	3.67	3.54	3.59
2 [AMV]	[AMV] x 10^4 M.	0.3	0.6	1.2	1.5	1.8	2.4	3.0
	k x 10^4sec^{-1}	1.035	2.24	3.66	3.79	4.04	4.17	4.42
3 [H ₂ SO ₄]	[H ₂ SO ₄] x 10^2 M.	0.3	0.6	1.0	1.5	2.0	2.5	3.0
	k x 10^4sec^{-1}	3.62	3.67	3.66	3.58	3.60	3.73	3.60
4 [NaClO ₄]	[NaClO ₄] x 10^1 M.	0.3	0.6	1.0	1.5	2.0	2.5	3.0
	k x 10^4sec^{-1}	3.60	3.67	3.66	3.58	3.60	3.73	3.60
5 various Salts	[SALT] ₀ = 1.0×10^{-1} M	LiCl	NaCl	KCl	MnCl ₂	LiClO ₄	NaClO ₄	KClO ₄
	k x 10^4sec^{-1}	3.60	3.58	3.60	3.73	3.67	3.66	3.52
6 Dielectric Constant	Ethanol %	40	50	60	70	80	--	--
	Water %	60	50	40	30	20	--	--
	Dielectric constant	69.23	65.18	61.29	55.74	48.48	--	--
	k x 10^4sec^{-1}	4.35	3.98	3.66	2.47	1.76	--	--
7 Temperature	Temperature in $^{\circ}\text{C}$	25	30	35	40	45	50	55
	k x 10^4sec^{-1}	1.85	2.75	3.66	5.46	7.21	10.76	14.31

The various Energy parameters calculated are:

Sr	Energy parameters	Value	Sr	Energy parameters	Value
1	Temperature Coefficient	1.99	4	Entropy of activation $\Delta S^{\#}$ ($\text{J K}^{-1} \text{mol}^{-1}$)	-134.83
2	Energy of activation E_a (KJ mol^{-1})	55.60	5	Free energy of activation $\Delta G^{\#}$ (KJ mol^{-1})	96.26
3	Enthalpy of activation $\Delta H^{\#}$ (KJ mol^{-1})	54.04			

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

SCHEME



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,

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

CONCLUSION: The investigation of the effect of Niiazid concentration on the reaction rate shows that, The pseudo-first order rate constant decreases with increase in Niiazid concentration. It can be attributed to greater stability of the complex in alcoholic medium probably due to solvation³⁰.

The effect of oxidant concentration on the reaction shows that, the rates of oxidation of Niiazid are almost constant with increase in concentration of ammonium metavanadate and the order of the reaction with respect to ammonium metavanadate

remains one throughout the used concentrations of ammonium metavanadate. In other words, Oxidation follows the first order kinetics because the log (Abs) versus time plot in each case is linear with positive slope and intercept on log (Abs) axis. The constancy of k values at different initial [ammonium metavanadate] indicates the pseudo-first order kinetic behavior of reaction.

The effect of concentration of sulphuric acid on the rates of oxidation of Niiazid shows that, the specific reaction rate increases as the concentration of sulphuric acid increases.

The reaction rates are not influenced by increase in ionic strength similarly the reactions rates are not influenced by using various salts, under the experimental conditions .

The specific rate of reactions is decreasing with decrease in dielectric constant³¹ of the reaction medium. The study of effect of temperature on oxidation of Niiazid clearly shows that, the rate of reaction depends on temperature and it increases with increase in temperature. The values of observed rate constants were used to determine various thermodynamic parameters like temperature coefficient(199), energy of activation (Ea) 55.60 KJ mol⁻¹, enthalpy of activation (ΔH^\ddagger) 54.04 KJ mol⁻¹, entropy of activation (ΔS^\ddagger)-134.83 J K⁻¹ mol⁻¹ and free energy of activation (ΔG^\ddagger) 96. 26 KJ mol⁻¹. The log (Abs) against time plots at different temperatures are linear which reveals that, the pseudo-first order kinetic behavior of the reaction is not affected by change in temperature. The

formation of free radicals or radical ions during the course of reaction was confirmed from induced polymerisation of acrylonitrile²⁴.
²⁵ The formation of carboxylic acids and N₂ in the oxidation of aliphatic as well as aromatic acid hydrazides³² is well documented in chemical literature. The mole ratio of Niiazid:ammonium metavanadate is found to be 1:4 and it is independent of concentration of sulphuric acid..

The integer value of observed mole ratio, its independence on sulphuric acid concentration and formation of only carboxylic acid along with nitrogen gas as oxidation products leads to deduce that, the two rate determining steps occurring simultaneously results in the formation of one and the same intermediate. Although the observed mole ratio (Niiazid : ammonium metavanadate) of the reaction is 1:4, as is pointed out earlier, the order of reaction with respect to ammonium metavanadate is one.

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