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Dr. Sanjay Vishnu Pore
Department of Chemistry
Bharati Vidyapeeth's
Matoshri Bayabai Shripatrao Kadam Kanya Mahavidyalaya Kadegaon.Dist- Sangli. (MS) India
E-Mail-poresanjay67@gmail.com Mob: 9881442429

Abstract: Redox-reaction of Pyridine, 2, carboxylic acid hydrazide by ammonium metavanadate for chemical kinetics and mechanistic determination was carried out under pseudo first order condition. The complex formed between the reactants gives picolinic acid, on its decomposition where Single electron transfer was observed during the course of this redox- reaction with intervention of free radical. The effect of different initial Concentration of reactants on the reaction rate was studied. The pseudo-first order kinetic behavior of the reaction is due to constancy in specific reaction rates at various amount of ammonium metavanadate.Increase in concentration of Pyridine, 2, carboxylic acid shows decreases in the specific rate of the reaction. The rate of reaction is directly proportional to the amount 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 reaction. The variation of ionic strength during reacton has negligible effect on specific rates of reacton. The temperature effect on rate of the reaction was studied from 30°C to 55°C and the rates of the reaction are found to be directly proportional to the increase in temperature of the reaction. The values of thermodynamic activation parameters support the mechanism proposed which is further supported by considerable decrease in entropy of activation.($-\Delta S^{\#} = -141.65$, J K^{-1} mol^{-1}). The investigation of the mechanism of the reaction was done by measuring the absorbance of the ammonium metavanadate at 390 nm.

Keywords: Redox reacton, Pyridine, 2, carboxylic acid hydrazide, ammonium metavanadate,

Introduction: The present study has been carried out with a view to postulate general mechanism for the oxidation of Pyridine, 2, carboxylic acid with ammonium metavanadate which is a versatile oxidizing agent., It is also used to oxidize many organic compounds like acetanildes, cyclohexanol, glycerol, hydrochloride, hydroxyl amine, L-Cysteine.[1-5].Hydrazides are the derivatives of carboxylic acids and hydrazines[6]. Due to its multiple use in various branches of chemistry[8,9,10,11,12,13] especially pharmaceutical Chemistry[7], needs to give special emphasis on the study of their mechanism of redox-

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reacton in detail. The formation of corresponding acids[14,15,16,17,18,19,20,21] is observed during the most of the redox reactions of hydrazine's. Literature survey showsthat, the chemical kinetic study of oxidative degradation of Pyridine,2, carboxylic acid hydrazide by ammonium metavanadate is not extensively studied.

Material and method: Ethyl ester of Picolinic acid was prepared by esterification[22] and converted to Pyridine, 2, carboxylic acid hydrazide by using the prescribed procedure[23].An equimolar mixture of ethyl ester of Pyridine 2 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 Pyridine, 2, carboxylic acid hydrazide recrystallised from ethanol and stored in amber colored bottles and kept in dark place. The anhydrous sodium bicarbonate, sulphuric acid, salt, ammonium metavanadate (AR grade), hydrazine hydrate (BDH 99%) and freshly distilled ethanol were used. 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 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 H_2O to maintain ionic strength. Standard Pyridine, 2, carboxylic acid hydrazide solution was prepared by dissolving it in aqueous alcoholic medium.

Determination of λmax of the redox reaction: The λmax of the reaction under study was determined at various wavelength. The maximum absorbance for both ammonium metavanadate and a mixture of Pyridine, 2, carboxylic acid hydrazide and ammonium metavanadate was obtained at 390 nm λmax.

Method of following the kinetics of the redox reaction: The ammonium metavanadate and Pyridine,2,carboxylic acid hydrazide 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^{O}C for 45 minutes. The redox reaction was studied kinetically 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 390 nm spectrophotometrically using UV-Vis. Spectrophotometer. Model no. 119 in sulphuric acid medium using water as a reference solvent. The reaction was studied under pseudo-first order condition in which, concentration of Pyridine,2,carboxylic acid hydrazide was in excess as compared to that of ammonium metavanadate.The reaction is found to proceed through formation of complex between ammonium metavanadate and Pyridine,2,carboxylic acid hydrazide. The rate constant K was obtained by plotting the log of absorbance at 390 nm against time for

Pyridine,2,carboxylic acid hydrazide and was found to be fairly constant at different concentrations of oxidant.

Reaction Intermediates: Intervention of free radical: The induced polymerization of acrylonitrile[24] and spontaneous reduction of $HgCl_2$[25] in reaction mixture itself indicates that, this reaction involves the formation of free radical.

Effect of sulphuric acid on Pyridine, 2, carboxylic acid hydrazide: A standard kinetic experiment was repeated by only changing the concentration ofsulphuric acid from0.0025 to 0.1 M containing equivalent quantities of Pyridine, 2, carboxylic acid hydrazide, 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, there is no significant hydrolysis of Pyridine, 2, carboxylic acid hydrazide in the presence of sulphuric acid up to 0.1 M.

Confirmation of status of acid (picolinic acid) content and to check hydrolysis of pyridine,2,carboxylic acid hydrazide under experimental condition: 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 Pyridine,2,carboxylic acid hydrazide under experimental conditions was observed. [26]

Stoichiometry of the redox reaction: A set of five reaction mixtures containing a known excess of sodium perchlorate over Pyridine,2,carboxylic acid hydrazide 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^{o}C for more than 48 hours. A blank experiment without Pyridine,2,carboxylic acid hydrazide was carried out concurrently using identical quantities of ammonium metavanadate, sulphuric and sodium perchlorate after volume correction with water for Pyridine,2,carboxylic acid hydrazide solution.

After completion of the reaction, concentration of ammonium metavanadate(IV) was determined at 765nm (ε =17.77). [27]from its absorbance and molar extinction coefficient (ε) by using the expressionC = Abs. / ε Finally, the moles of ammonium metavanadate(IV) formed in oxidation of one mole of Pyridine,2,carboxylic acid hydrazide were calculated in each case by using the relation. Mole ratio = - [V(IV)] / [Pyridine,2,carboxylic acid hydrazide]$_0$

The value of [V(IV)] / [Pyridine,2,carboxylic acid hydrazide]$_0$ 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 Pyridine,2,carboxylic acid hydrazide.

Identification of oxidation products:

The substrate, Pyridine, 2,carboxylic acid hydrazide and oxidant, ammonium metavanadate are mixed together in stoichiometric proportions with 1.0×10^{-2} M sulphuric acid medium and 1.0×10^{-1} M

sodium per chlorate. The reaction mixture was kept in a thermostated water bath at 35°C for 30 hours for its completion. Then, it was subjected to ether extraction and acid was separated.The presence of carboxylic acid group was detected by testing with 5% sodium bicarbonate solution. The amide derivative of the corresponding aromatic carboxylic acid was prepared[28]. The observed melting point of amide derivatives was in good agreement with those of benzamide. The formation of corresponding carboxylic acids in redox reaction of Pyridine, 2,carboxylic acid hydrazide was accompanied by evolution of N_2 gas which was detected by lime test.[29] A mixture of lime and MnO_2 in 10:1 proportion was ignited in a small hard glass tube. A test portion of concentrated reaction mixture was rendered neutral with NaOH 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 MnO_2 and $AgNO_3$ 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 indicates the formation of N_2 gas during the redox reaction. Finally considering the products of redox reaction, observed mole ratio and material balance, the oxidation of Pyridine,2,carboxylic acid hydrazide can be represented by the stoichiometric equation.

$$\text{Pyridine,2,carboxylic acid} + 4V(v) + H_2O \xrightarrow[NaClO_4]{H_2SO_4} \text{Picolinic acid} + N_2 + 4V(v) + 4H^+$$

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: The redox reaction proceeds with a measurable velocity using 1.5 x 10^{-3} M ammonium metavanadate, 1.5 x 10^{-2} M Pyridine,2,carboxylic acid hydrazide, 1.1 x10^{-1}M sodium perchlorate , 1.5 x 10^{-2} M sulphuric acid and 390 nm λmax 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 Concenteration	Multiples of Unit Concenteration and respective rate Constants						
1	Pyridine,2,carboxylic acid hydrazide]	[Pyridine,2,carboxylic acid hydrazide]x 10^3M	0.3	0.6	1.2	**1.5**	1.8	2.4	3.0
		k x 10^4sec^{-1}	3.71	3.66	3.21	2.89	2.68	2.37	2.16
2	[AMV]	[AMV] x 10^4M.	0.3	0.6	1.2	**1.5**	1.8	2.4	3.0
		k x 10^4sec^{-1}	3. 02	3.12	2.98	2.89	2.69	2.85	2.79
3	[H_2SO_4]	[H_2SO_4] x 10^2M.	0.5	1.0	1.5	2.0	3.0	4.0	5.0

		k x $10^4 sec^{-1}$	0.843	1.62	2.89	3.12	3.25	3.43	3.58
4	$[NaClO_4]$	$[NaClO_4]$ x 10^1M.	0.3	0.6	1.0	1.5	2.0	2.5	3.0
		k x $10^4 sec^{-1}$	3.00	3.02	2.89	2.97	2.98	2.97	2.87
5	various Salts	$[SALT]_o$ =1.0 x10^{-1}M	LiCl	NaCl	KCl	$MnCl_2$	$LiClO_4$	$NaClO_4$	$KClO_4$
		k x $10^4 sec^{-1}$	2.87	2.85	2.98	3.00	2.95	2.89	2.98
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 $10^4 sec^{-1}$	3.50	3.21	2.89	1.93	1.33	--	--
7	Temperature	Temperature in °C	25	30	35	40	45	50	55
		k x10^4 sec^{-1}	1.51	2.18	2.89	4.29	5.63	8.34	10.97

The various Energy parameters calculated are:

Sr	Energy parameters	Value	Sr	Energy parameters	Value
1	Temperature Coefficient	1.95	4	Entropy of activation $\Delta S^{\#}$ (J $K^{-1}mol^{-1}$)	-141.65
2	Energy of activation Ea (KJ mol^{-1})	54.21	5	Free energy of activation $\Delta G^{\#}$ (KJ mol^{-1})	96.93
3	Enthalpy of activation $\Delta H^{\#}$ (KJ mol^{-1})	52.55			

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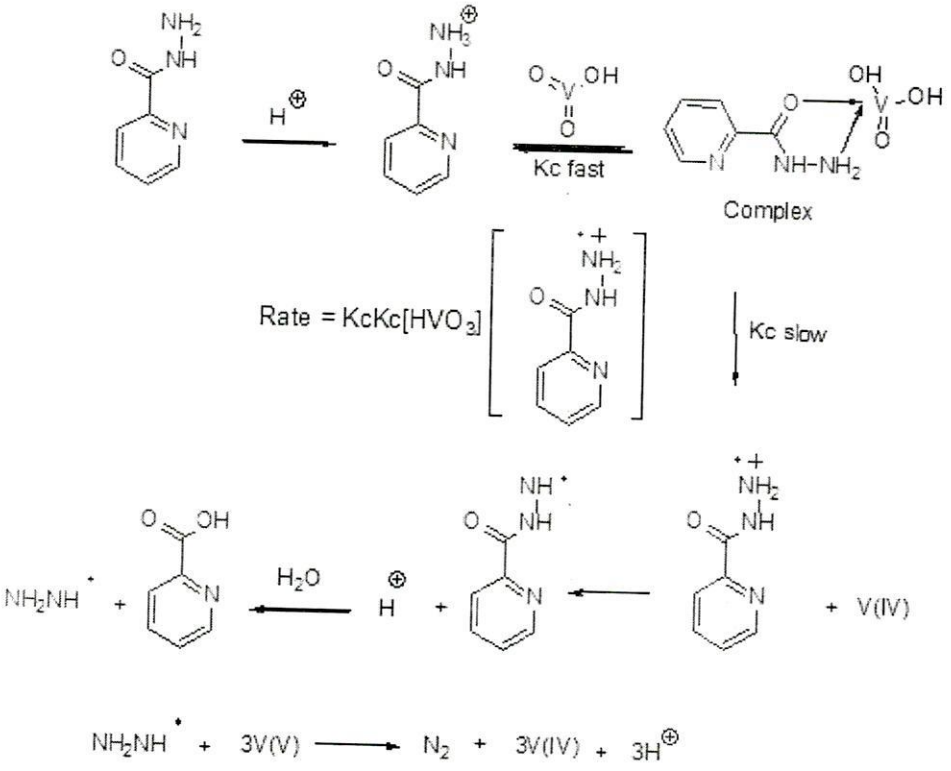
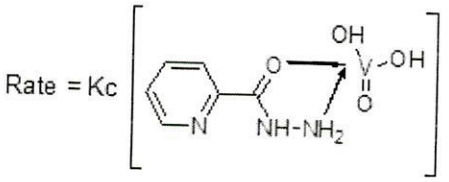
Mechanism of the reaction:

SCHEME



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



Substituting the value of [Complex] from the equilibrium, Rate = $k_c K_c$ [HVO_3] [Ar-$CONHNH_3$] .

CONCLUSION: The pseudo-first order rate constant decreases with increase in concentration of Pyridine,2,carboxylic acid hydrazide. It can be attributed to greater stability of the complex in alcoholic medium probably due to solvation[30].

The rates of oxidation of Pyridine,2,carboxylic acid hydrazide are almost constant with increase in concentration of ammonium metavanadate and the order of the reaction with respect to

oxidant remains one throughout the used amount of ammonium metavanadate as a oxidant. The reaction follows the first order chemical kinetics as the log (Abs) / time plot in each case is linear with positive slope and intercept on log (Abs) axis. The constancy of k values at different initial amount of ammonium metavanadate indicates the pseudo-first order kinetic behavior of reaction.

The specific reaction rate increases with increase in medium of the reaction that is concentration of sulphuric acid.

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

The specific rate of reactions is decreasing with decrease in dielectric constant[31] of the reaction medium. The rate of reaction increases with increase in temperature. The values of rate constants observed were used to calculate thermodynamic parameters like temperature coefficient (195), energy of activation (Ea) 54.21 KJ mol^{-1} , enthalpy of activation ($\Delta H^{\#}$) 52.55 KJ mol^{-1}, entropy of activation ($\Delta S^{\#}$)-141.65 J K^{-1} mol^{-1} and free energy of activation ($\Delta G^{\#}$)96.93 KJ mol^{-1}. The log (Abs) against time plots at different temperatures are linear which indicates pseudo-first order kinetic behavior of the reaction which is not affected by change in temperature of the redox reactoion. The formation of free radicals or radical ions during the redox reaction was confirmed from induced polymerisation of acrylonitrile[24, 25]. The formation of carboxylic acids and elimination of nitrogen gas in the oxidation of aliphatic as well as aromatic acid hydrazides[32] is well documented in literature. The mole ratio of Pyridine,2,carboxylic acid hydrazide:ammonium metavanadate is to be 1:4 and it is independent of concentration of sulphuric acid..

The integer value of observed mole ratio, its independence on medium of the reaction means sulphuric acid concentration and formation of only carboxylic acid along with N_2 gas as redox reaction products deduces that, the two rate determining steps occurring simultaneously results in the formation of same intermediate. Although the observed mole ratio (Pyridine,2,carboxylic acid hydrazide : 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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