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Title of Research Project : Kinetics and Mechanistic Study of Single Electron Transfer Oxidation Reactions of Structurally Related Heterocyclic Acid Hydrazides by Vanadium”
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EXCUTIVE SUMMARY OF THE FINDINGS

A detailed kinetic study of oxidation of Picolinic, Isonicotinic and Nicotinic acid hydrazide by ammonium metavanadate in acidic medium is presented in this project. To study the oxidation of hydrazide, the reaction mixture was prepared by using requisite concentrations of ammonium metavanadate i.e. Vanadium (V), hydrazide, sulphuric 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. The λmax 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.

1. STANDARD KINETIC RUN: At the beginning preliminary experiments were performed in order to decide, the range of temperature and appropriate concentrations of ammonium metavanadate, hydrazide, sulphuric acid and sodium perchlorate. It was found that the reaction proceeds with a measurable velocity at 35^0C using 1.5×10^{-3} M ammonium metavanadate , 1.5×10^{-2} M hydrazide, 1.5×10^{-2} M sulphuric acid and 1.1×10^{-1} M sodium perchlorate. The table 5:1: A embodies the kinetic data of these experiments.

The observed rate constant (k) of the reaction was evaluated by graphical and integration method and further confirmed by least square method.

Table: 1

[PAH, INAH, NAH]$_o$=1.5x10^{-2} M, [H$_2$SO$_4$]$_o$=1.5 x 10^{-2} M

[AMV]$_o$ = 1.5 x 10^{-3} M,Temp = 35^{0}C, λmax = 390 nm [NaClO$_4$]$_o$ = 1.1 x 10^{-1} M

Sr.no	Substrate (hydrazide)	K x 10^4 sec^{-1}
1	Picolinic acid hydrazide	2.89
2	Isonicotinic acid hydrazide	3.51
3	Nicotinic acid hydrazide	3.66

Thus rates of oxidation of hydrazides are in the order PAH < INAH < NAH

2. EFFECT OF VANADIUM (V) CONCENTRATION:

Oxidation of hydrazide at different initial concentrations of Vanadium (V) follows the first order kinetics.The constancy of K values at different initial concentrations of Vanadium (V) indicates the pseudo-first order kinetic behavior of the reaction.

Table: 2

[PAH, INAH, NAH,]$_o$ = 1.5 x 10^{-2} M [H$_2$SO$_4$]$_o$ = 1.5 x 10^{-2} M

Temp = 35^{0}C, λmax = 390 nm [NaClO$_4$]$_o$ = 1.1 x 10^{-1} M

	[AMV]$_o$ X 10^3 M	0.3	0.6	1.2	1.5	1.8	2.4	3.0
PAH	k x 10^4 sec^{-1}	3.02	3.12	2.98	2.89	2.69	2.85	2.79
INAH	k x 10^4 sec^{-1}	3.66	3.67	3.62	3.51	3.58	3.41	3.50
NAH	k x 10^4 sec^{-1}	3.77	3.84	3.72	3.66	3.68	3.53	3.60

3. EFFECT OF HYDRAZIDE CONCENTRATION:

In order to investigate the effect of concentration of hydrazide on the rate of reaction, it was necessary to study the reaction at different initial concentrations of substrate (hydrazide). It is seen that the value of pseudo-first order rate constant (k) depends on initial concentrations of hydrazides and it decreases with increase in [Hydrazide]$_{0.}$

Table: 3

[AMV]$_o$ = 1.5 x 10^{-3} M [H$_2$SO$_4$]$_o$ = 1.5 x 10^{-2} M

Temp = 35^{0}C λmax = 390 nm [NaClO$_4$]$_o$ = 1.1 x 10^{-1} M

	[HZ]$_o$ x10^{2}M	0.3	0.6	1.2	1.5	1.8	2.4	3.0
PAH	k x 10^4 sec^{-1}	3.71	3.66	3.21	2.89	2.68	2.37	2.16
INAH	k x 10^4 sec^{-1}	3.79	3.69	3.60	3.51	3.08	2.68	2.39
NAH	k x 10^4 sec^{-1}	4.85	4.40	3.96	3.66	3.25	3.04	2.56

4. EFFECT OF SULPHURIC ACID CONCENTRATION:

The effect of varying sulphuric acid concentration on the rate of oxidation of hydrazide was studied over a range of sulphuric acid concentration.The values of rate constants increases with increase in hydrogen ion concentration studied.

Table: 4

$[PAH]_o$= 1.5 x 10^{-2} M $[AMV]_o$ = 1.5 x 10^{-3} M

Temp = 35^0C λmax = 390 nm $[NaClO_4]_o$ = 1.1 x 10^{-1} M

	$[H_2SO_4]_o$ x 10^2 M	0.5	1.0	1.5	2.0	3.0	4.0	5.0
PAH	k x 10^4 sec^{-1}	0.843	1.62	2.89	3.12	3.25	3.43	3.58
INAH	k x 10^4 sec^{-1}	0.961	2.06	3.51	3.71	3.93	4.10	4.31
NAH	k x 10^4 sec^{-1}	1.035	2.24	3.66	3.79	4.04	4.17	4.42

5. EFFECT OF SODIUM PERCHLORATE CONCENTRATION:

In order to investigate the effect of ionic strength on specific rate of reaction, the reaction was studied by varying the concentration of sodium perchlorate.The specific rate of reaction is not influenced by increase in ionic strength. It was almost constant during this variation of ionic strength.

Table: 5

$[PAH]_o$= 1.5 x 10^{-2} M $[AMV]_o$ = 1.5 x 10^{-3} M

Temp = 35^0C λmax = 390 nm $[H_2SO_4]_o$ = 1.5 x 10^{-2} M

	$[NaClO_4]_o$ x 10^1M	0.3	0.6	1.0	1.5	2.0	2.5	3.0
PAH	k x 10^4 sec^{-1}	3.00	3.02	2.89	2.97	2.98	2.97	2.87
INAH	k x 10^4 sec^{-1}	3.52	3.44	3.51	3.41	3.54	3.44	3.50
NAH	k x 10^4 sec^{-1}	3.62	3.67	3.66	3.58	3.60	3.73	3.60

6. EFFECT OF SPECIFIC IONS:

To observe the effect of foreign ions on the rate of reaction, the reaction was carried out using different neutral salts like LiCl, NaCl, KCl, $MnCl_2$, $LiClO_4$, $KClO_4$ in place of $NaClO_4$ keeping all the parameters as in standard kinetic run.

The non–influence of the added salts on rate constant clearly indicates that, at constant ionic strength, the rate of the reaction is independent of the kind of the anion or cation present in the reaction medium. This insensitivity of rate of reaction to the kind of added ions gains further support from the constancy of k values observed at different concentrations of ammonium metavanadate where proportion of cations and anions present in the reaction medium varies from experiment to experiment.

The lack of specific ion effect observed in the present oxidation reaction clearly indicates the absence of catalytic as well as inhibitory effect of added ions.

Table: 6

$[PAH]_o = 1.5 \times 10^{-2}$ M $[AMV]_o = 1.5 \times 10^{-3}$ M

Temp = 35^0C λmax = 390 nm $[H_2SO_4]_o = 1.5 \times 10^{-2}$ M

	1.1×10^{-1}M	LiCl	NaCl	KCl	$MnCl_2$	$LiClO_4$	$NaClO_4$	$KClO_4$
PAH	$k \times 10^4 sec^{-1}$	2.87	2.85	2.98	3.00	2.95	2.89	2.98
INAH	$k \times 10^4 sec^{-1}$	3.45	3.42	3.49	3.57	3.53	3.51	3.38
NAH	$k \times 10^4 sec^{-1}$	3.60	3.58	3.60	3.73	3.67	3.66	3.52

7. 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 different temperatures ranging from 25 to 55 ^{0}C

The result clearly shows that, the rate of reaction depends on temperature and it increases with increase in temperature. The values of rate constants by graphical method at different temperatures were used to determine various thermodynamic activation parameters, energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$) and free energy of activation ($\Delta G^{\#}$) are calculated by using the graphical as well as formula

Table: 7: A

$[PAH]_o = 1.5 \times 10^{-2}$ M $[H_2SO_4]_o = 1.5 \times 10^{-2}$ M
$[AMV]_o = 1.5 \times 10^{-3}$ M , λmax = 390 nm $[NaClO_4]_o = 1.1 \times 10^{-1}$ M

	Temp ^{0}C	25	30	35	40	45	50	55
PAH	$k \times 10^4 sec^{-1}$	1.51	2.18	2.89	4.29	5.63	8.34	10.97
INAH	$k \times 10^4 sec^{-1}$	1.76	2.65	3.51	5.17	6.84	10.12	13.41
NAH	$k \times 10^4 sec^{-1}$	1.85	2.75	3.66	5.46	7.21	10.76	14.31

Table 7: B

Hydrazide	Temp. Coeff	Ea KJ mol^{-1}	$\Delta H^{\#}$ KJ mol^{-1}	$\Delta S^{\#}$ J K^{-1} mol^{-1}	$\Delta G^{\#}$ KJ mol^{-1}
PAH	1.94	55.22	52.58	-141.68	96.96
INAH	1.96	56.60	53.38	-135.78	95.87
NAH	1.98	56.73	54.07	-134.86	96.29

The rates of oxidation of these hydrazides, mentioned earlier are found to be in the order. PAH < INAH < NAH

The high negative value of entropy of activation $\Delta S^{\#}$in each case indicates the formation of highly ordered transition state.

8. EFFECT OF DIELECTRIC CONSTANT OF SOLVENT:

The effect of dielectric constant (D) of the solvent on the rate of oxidation of hydrazide was studied in binary solvent containing varying proportions (V/V) of ethanol and water under identical conditions as in standard run.

The pseudo-first order kinetic behavior of the reaction is retained in various proportions of ethanol and water also. The specific rate of reaction decreases with decrease in dielectric constant of the solvent, i.e. the reaction is favored in the solvent having high dielectric constant.

Table: 8

$[\text{Hydrazide}]_o = 1.5 \times 10^{-2}$ M, λmax = 390 nm $[\text{AMV}]_o = 1.5 \times 10^{-3}$ M

$[\text{NaClO}_4]_o = 1.1 \times 10^{-1}$ M, Temp = 35^0C $[\text{H}_2\text{SO}_4]_o = 1.5 \times 10^{-2}$ M

%Ethanol & %Water(V/V)	D	k x 10^4 sec^{-1}		
		PAH	INAH	NAH
40: 60	69.23	3.49	4.11	4.34
50 :50	65.18	3.22	3.88	3.99
60 :40	61.29	2.92	3.49	3.65
70 :30	55.74	1.92	2.34	2.46
80 :20	48.48	1.34	1.65	1.77

9. EFFECTS OF VARIOUS SOLVENTS: In order to investigate the effect of solvent polarity (alcohols) on the rate of reaction, the reaction was also carried out using methanol as a solvent instead of ethanol maintaining 60 % alcohol and 40 % water ratio at 35 ^{0}C and at constant ionic strength keeping the concentration of hydrazide, sulphuric acid and sodium perchlorate as in standard run..

An examination of data in Table: 9 make it clear that specific rate of the reaction decreases with decrease in dielectric constant of the solvent.

Table:9

60% alcohol + 40% water	D in mixture	$k \times 10^4 sec^{-1}$		
		PAH	INAH	NAH
Ethanol	61.29	2.89	3.51	3.66
Methanol	59.95	2.81	3.40	3.54

10. DETECTION OF REACTION INTERMEDIATES / TEST FOR INTERVENTION OF FREE RADICAL:

The induced polymerization 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 the course of the reaction.

11. EFFECT OF SULPHURIC ACID CONCEN ON SUBSTRATE:

To check the possibility of hydrolysis of hydrazides in the presence of sulphuric acid under experimental conditions, blank experiments were carried out in the absence of Vanadium (V) .

A series of mixtures containing 1.5 X 10^{-2} M hydrazide and different quantities of H_2SO_4 (0.0025 – 0.1 M) were kept in thermo stated water bath (35^0C) after adjusting ionic strength and volume as in the standard kinetic run for oxidation of the same hydrazide.

After three hours, the mixtures in different flasks were made alkaline and analyzed for detection of hydrazine. It was observed that, the resultant solutions in various flasks did not 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 hydrazide in the presence of H_2SO_4 up to 0.1M.

In addition to the above qualitative aspect, similar set of experiments was subjected to alkalimetric estimation of acid content at 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 three hours. This invariance of acid concentration can be attributed to lack of formation of carboxylic acid, which confirms that, there is no considerable hydrolysis of hydrazide under experimental conditions. he lack of hydrolysis of hydrazide in the present study is a good signal to state that, substrate hydrazide might be getting oxidized directly and it is not a process of hydrolysis followed by oxidation.

12. DETERMINATION OF STOICHIOMETRY OF THE REACTION: 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.

A fractional stoichiometry of the reaction is reported in oxidation of nicotinic and iso-nicotinic acid hydrazides by iron (III) in acid medium. This fact was attributed by, suggesting two simultaneous paths resulting in formation of N_2 and NH_3. In this respect results obtained in present investigation are different.

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 result in the formation of one and the same intermediate.

Although the observed mole ratio (substrate: oxidant) of the reaction is 1:4, as it 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).

13. IDENTIFICATION OF OXIDATION PRODUCTS:

The oxidation products identified in these reactions are as follows.

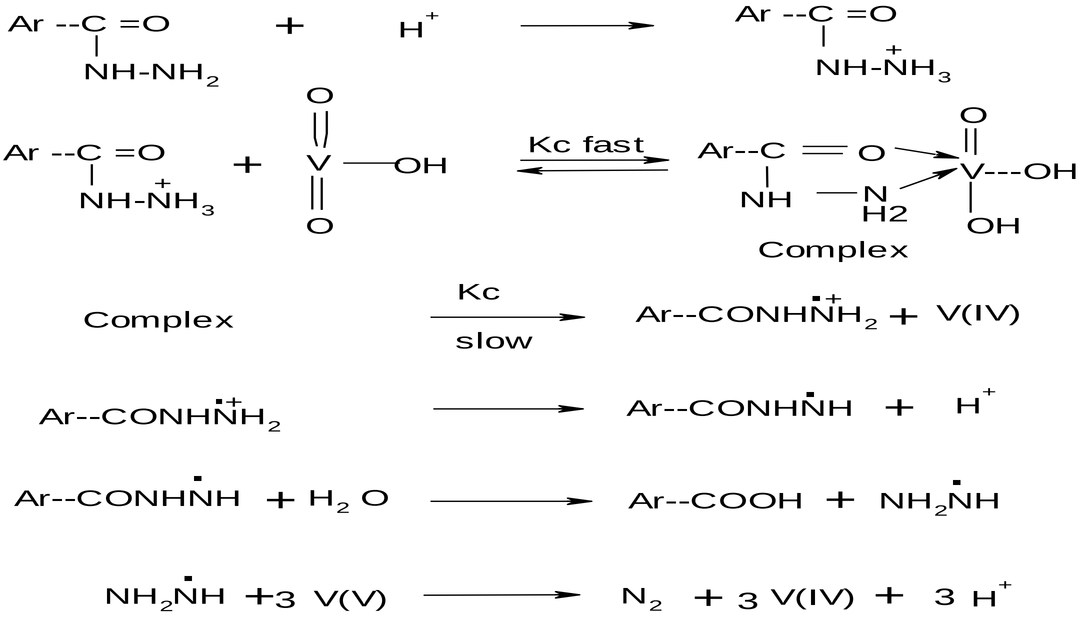
Sr	Hydrazide	Oxidation Product
1	Picolinic acid hydrazide	Picolinic acid, /Pyridine 2 carboxylic acid
2	Nicotinic acid hydrazide	Nicotinic acid, /Pyridine 3 carboxylic acid
3	Isonicotinic acid hydrazide	Isonicotinic acid /Pyridine 4 carboxylic

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.

14. MECHANISM OF THE REACTION:

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

Scheme



Where, Ar = C_5H_4N -

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 = $k_c K_c [HVO_3] [Ar\text{-}CONHNH_3]$.

15. RELATIVE REACTIVITIES OF HYDRAZIDES: The objective of the present study is not only to develop method for oxidation of hydrazides to their corresponding acids but also, to study the effect of the position of nitrogen in aromatic ring; on the rate of reaction as well as on mechanism.The order of reactivities of the hydrazides under investigation is PAH < INAH < NAH

The observed sequence can be attributed to various possibilities and factors. The variation in the rates of oxidation in these hydrazides may be explained on the basis of molecular orbital calculations which shows that the **π electrons** density at position **β** or 3 (1.052) of the pyridine ring is higher than that of position **α** or 2(0.881) and **γ** or 4 (0.941) with respect to the nitrogen in the heterocyclic ring of the corresponding hydrazides.. This is a consequence of nitrogen being more electronegative than carbon. The nitrogen atom therefore causes a drift of electrons in its direction. The drift denudes the **α** or 2 (Picolinic acid hydrazide) and **γ** or 4 (Isonicotinic acid hydrazide) positions of electrons by a resonance interaction in the Nicotinic acid hydrazide and the effect is found to be very strong.

The **π** electron densities at the various positions of the pyridine ring have been calculated by a self consistent field method and are reported here in above figure

The rates of oxidation of pyridine 2 0r **α**, 3 0r **β** and 4 0r γ hydrazides correlate well with the electron densities at position 2 0r **α** (0.881), 3 0r **β** (1.052) and 4 or γ (0.941) positions of pyridine. The variation in electron densities at **α** (0.881),, **β** (1.052) and γ (0.941) position of pyridine may affect the rate of formation of free radical ion by hydride obstruction to a some extent. Thus causing oxidation of nicotinic acid hydrazide faster than Isonicotinic acid hydrazide and subsequently the Picolinic acid hydrazide has lowest rate of oxidation in series of the compounds under study. .

This effect is more powerful in the case of **β** isomer than **α** and subsequently γ. Since, carbonyl carbon withdraws electron density from the adjacent ring carbon by induction, thus makes the resonance stronger and therefore increases the rate of formation of radical ion. The Picolinic acid hydrazide has lowest rate in series of compounds under consideration.

The comparative lowest reactivity of oxidation of Picolinic acid hydrazide than the Isonicotinic acid hydrazide and Nicotinic acid hydrazide can be due to low **π** electron density at **α** or 2 position in the pyridine ring[210] with respect to the position of the nitrogen in the heterocyclic ring of the Picolinic acid hydrazide. However, In case of Picolinic acid hydrazide , the carbonyl carbon is at **α position which is very** nearer to reaction site with respect to the nitrogen from the pyridine ring and being more bulky and due to steric hindrance there is a very weak electron withdrawing inductive effect might be operating which has neglible effect on its reactivity, alternatively in case of Nicotinic acid hydrazide the carbonyl carbon is at **β position which is not** nearer to reaction site as compared with the **α** position with respect to the nitrogen from the pyridine ring and there is a somewhat strong electron withdrawing inductive effect might be operating which has considerable effect on its reactivity. Similarly, In case of Isonicotinic acid hydrazide, the carbonyl carbon is at **γ position which is not so** nearer to reaction site as in Picolinic acid hydrazide and Nicotinic acid hydrazide, with respect to the nitrogen from the pyridine ring and due to this there is a weak electron withdrawing inductive effect might be operating which has moderate effect on its reactivity.

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