

Electron Transfer Reaction of Pyridine with 12-Tungstocobaltate (III) in Acidic Buffer Medium

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ABSTRACT

The electron transfer reaction of pyridine with 12-tungstocobaltate (III) was studied spectrophotometrically over the range $3.8 \leq 10^4[\text{Co}^{\text{III}}\text{W}^{5-}]_{\text{T}} \leq 4.2$, $4.2 \leq 10^2 [\text{PyN}]_{\text{T}} \leq 12.6$, $3.8 \leq \text{pH} \leq 5.4$ and $313\text{K} \leq T \leq 328\text{K}$. The reaction shows zero order dependence in $[\text{Co}^{\text{III}}\text{W}^{5-}]_{\text{T}}$ and first order in $[\text{PyN}]_{\text{T}}$ and inverse dependence in $[\text{H}^+]_{\text{T}}$. k_{obs} and second order rate constant, k_2 were found to increase with the increase in temperature. The activation parameters, ΔH^\ddagger (kJ/mol) and ΔS^\ddagger ($\text{JK}^{-1}\text{mol}^{-1}$) were found to be 53.16 and -34.22. Negative value of ΔS^\ddagger indicates ordered transition state for the electron transfer reaction.

Keywords : Pyridine, Tungstocobaltate(III), Spectrophotometer, Kinetics, Product Analysis, Activation Parameters.

I. INTRODUCTION

The oxidant Keggin type 12-tungsto cobaltate (III), ($\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}^{5-}$ or $\text{Co}^{\text{III}}\text{W}^{5-}$) Cluster has a reduction potential of 1.0V^1 . Hence it can accept electrons from pyridine. The above cluster is known for photochemical hydrogen generation and is involved in multielectron reduction process²⁻⁴. The redox behaviour of above cobalt cluster with few biomolecules like ascorbic acid⁵, glutathione⁶, citric acid⁷, DL-methionine⁸ and cystine⁹ have been investigated., In order to examine the redox behavior of 12-tungstocobaltate(III), its reaction with pyridine has been undertaken.

II. METHODS AND MATERIAL

A. Experimental

$[\text{Co}^{\text{III}}\text{W}_{12}\text{O}_{40}]^{5-}$ was prepared by the reported method¹⁰ and was characterized spectro photometrically¹¹ and by elemental analysis. All chemicals used were of AnalaR grade. Pyridine (Merck) was used as such. Ionic strength was maintained with NaClO_4 (Merck). Electron transfer reaction was studied at $3.8 \leq \text{pH} \leq 5.4$ using a pre-standardised Elico (India) digital pH meter equipped with glass electrode. The pH of solution was maintained by using potassium hydrogen phthalate, sodium acetate and acetic acid buffer solution. The solutions were

prepared in freshly prepared doubly distilled water using an all quartz distillation apparatus containing little amount of KMnO_4 crystals.

Kinetics Measurement

Kinetics measurements were performed using systronic 2202 UV-vis spectrophotometer. The kinetics was followed under pseudo first order conditions keeping large excess of [pyridine] over [oxidant]. The reaction was initiated by mixing previously thermostated solution of [pyridine] and $[\text{CoW}_{12}\text{O}_{40}]^{5-}$ which contained required amount of acidic buffer and double distilled water. The progress of the reaction was followed spectrophotometrically at 388 nm (spectral scan) by monitoring decrease of absorbance of oxidant with time. The pseudo-first order rate constant (k_{obs}) were determined from the slope of linear plot of $\ln(A_t - A_\infty)$ vs t (s) using EXCEL programme.

$$\ln(A_t - A_\infty) = \ln(A_o - A_\infty) - k_{\text{obs}}t \quad (1)$$

where A_t and A_∞ are the absorbance of the reaction mixture at time 't' and at equilibrium respectively. The reported data represents an average of duplicate runs. The rate constant were reproducible within $\pm 5\%$ and the reaction was studied upto 80% completion. The co-

relation coefficients of plots used to determine k_{obs} were found to be 0.99 in most of the cases.

Stoichiometry and Identification of the product

The stoichiometry of the electron transfer reaction was determined in the following way. The pH of the mixture containing tungstocobaltate (III) and pyridine in a mole ratio (1:5) was maintained at pH = 5.4 and the temperature of mixture was maintained at 50°C and kept about 6 hours. After the reaction was completed, the solution was analysed by determining the unreacted tungstocobaltate spectrophotometrically. It was found that 2 moles of oxidant reacted with 1 mole of pyridine. Therefore the stoichiometry of reaction can written as

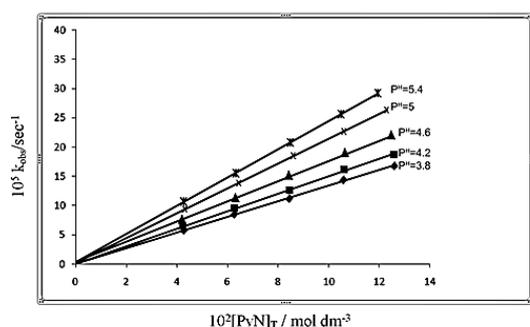
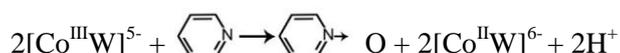


Figure - 1 The Plot of $10^2[\text{PyN}]_T / \text{mol dm}^{-3}$ vs $10^5 k_{\text{obs}}/\text{sec}^{-1}$

Conditions : $[\text{Co}^{\text{III}}\text{W}^5]_T = 4.2 \times 10^{-4}\text{M}$

Temp = 50°C

$\lambda = 388.5 \text{ nm}$

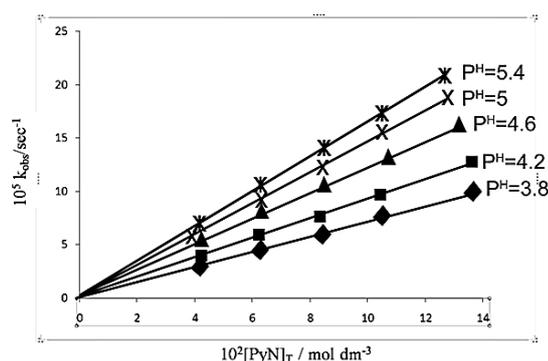


Figure - 2 The Plot of $10^2[\text{PyN}]_T / \text{mol dm}^{-3}$ vs $10^5 k_{\text{obs}}/\text{sec}^{-1}$

Conditions : $[\text{Co}^{\text{III}}\text{W}^5]_T = 4.2 \times 10^{-4}\text{M}$

Temp = 40°C

$\lambda = 388.5 \text{ nm}$

At the end of the redox reaction, the solution was treated with Dowex 50 x 8 (Na^+ form) resin to remove metal ion. A part of the solution shows the presence of Cobalt(II)

by Kitson method. The remaining solution was evaporated at low temperature till the volume was reduced to 1/3rd of the initial volume of the solution. It was kept in refrigerator overnight. The crystalline product was isolated and it was filtered and dried in desiccator. FTIR spectra of the product were determined. Fig. 2.(a) is the FTIR spectra of the reactant which is compared with the FTIR spectra of the product Fig.2(b). Most of the peaks showing very slight shift and one new peak appeared at 1315cm^{-1} in Fig.2(b), due to $\text{N}=\text{O}$ stretching frequency without disturbing the molecular frame of pyridine. Hence the isolated product was identified as pyridine N-oxide.

III. RESULT AND DISCUSSION

Rate dependence on $[\text{Co}^{\text{III}}\text{W}^5]_T$

Keeping all conditions constant, $[\text{Pyridine}] = 12.6 \times 10^{-2} \text{ mol dm}^{-3}$, pH= 5.4, temperature = 50°C, $[\text{Co}^{\text{III}}\text{W}^5]_T$ was varied from 3.8×10^{-4} to $4.2 \times 10^{-4} \text{ mol dm}^{-3}$. The average k_{obs} value did not change appreciably and was found to be $(3.48 \pm 0.5)10^{-5} \text{ sec}^{-1}$. This fact indicates that the reaction is showing zero order dependence in $[\text{Co}^{\text{III}}\text{W}^5]_T$.

Rate dependence on pH

Keeping all the conditions constant, $[\text{Pyridine}] = 12.6 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{Co}^{\text{III}}\text{W}^5]_T = 4.2 \times 10^{-4} \text{ mol dm}^{-3}$, temperature = 50°C, when pH changes from 3.8 to 5.4, rate constant increases from $16.8 \times 10^{-5} \text{ sec}^{-1}$ to $34.8 \times 10^{-5} \text{ sec}^{-1}$. The rate of reaction was found to increase with the increase in pH. $\text{P}K_b$ of pyridine = 8.77 at 25°C. So it indicates that at pH= 8.77, there will be 50% protonated form of pyridine. As pH increased from 3.8 to 5.4, the percentage of neutral form was increased. Hence, the rate of reaction was increased, because the protonated form of pyridine could not participate in electron transfer reaction.

Rate dependence on [pyridine]

With increasing $[\text{pyridine}]$ at a given pH and at a given temperature with constant $[\text{oxidant}]$, the rate of the reaction is found to increase (Table-1&2). Keeping $[\text{Co}^{\text{III}}\text{W}^5]_T = 4.2 \times 10^{-4} \text{ mol dm}^{-3}$, temp = 50°C when

[Pyridine] were varied from $4.2 \times 10^{-2} \text{ mol dm}^{-3}$ to $12.6 \times 10^{-2} \text{ mol dm}^{-3}$, $10^5 k_{\text{obs}}$ increased from 12.5 to 34.8 sec^{-1} at $\text{pH} = 5.4$. This shows that as the [pyridine] is increased at a given pH, the concentration of neutral form was increased and hence the rate of reaction was increased.

Table 1. Pseudo- first order rate constants for electron transfer reaction of 12-tungstocobaltate(III) with pyridine
 $[\text{Co}^{\text{III}}\text{W}^5]_{\text{T}} = 4.2 \times 10^{-4} \text{ mol dm}^{-3}$, $\text{temp} = 50^{\circ}\text{C}$, $\lambda = 388\text{nm}$

$10^2[\text{PyN}]_{\text{T}} \text{ mold m}^{-3}$	pH	$10^5 k_{\text{obs}}$
12.6	5.4	34.8
	5.0	24.8
	4.6	22.0
	4.2	18.5
	3.8	16.8
10.5	5.4	25.7
	5.0	23.5
	4.6	21.8
	4.2	19.2
	3.8	16.2
8.4	5.4	21.0
	5.0	19.2
	4.6	18.2
	4.2	15.7
	3.8	14.5
6.3	5.4	16.3
	5	14.7
	4.6	10.3
	7.2	9.83
	3.8	7.66
4.2	5.4	12.5
	5.0	10.66
	4.6	8.66
	4.2	7.50
	3.8	6.83

$10^2[\text{PyN}]_{\text{T}} \text{ mold m}^{-3}$	pH	$10^5 k_{\text{obs}}$
12.6	5.4	19.5
	5.0	15.2
	4.6	11.5
	4.2	9.66
	3.8	7.83
10.5	5.4	17.0
	5.0	13.3
	4.6	10.7
	4.2	8.50
	3.8	6.85
8.4	5.4	14.2
	5.0	12.4
	4.6	9.4
	4.2	7.6
	3.8	5.9
6.3	5.4	10.5
	5.0	9.4
	4.6	8.6
	7.2	6.3
	3.8	5.8
4.2	5.4	5.0
	5.0	4.3
	4.6	3.8
	4.2	3.2
	3.8	2.98

Table -2. Pseudo- first order rate constants for electron transfer reaction of 12-tungstocobaltate(III) with pyridine

$[\text{Co}^{\text{III}}\text{W}^5]_{\text{T}} = 4.2 \times 10^{-4} \text{ mol dm}^{-3}$, $\text{temp} = 40^{\circ}\text{C}$, $\lambda = 388\text{nm}$

Table 3. Electron transfer rate constant, activation parameters and thermodynamic parameters for redox reaction of 12-tungstocobaltate (III) with pyridine.

Condition : pH=5.4, [PyN] = 12.6 x 10⁻² mol dm⁻³,
[Co(III)] = 4.2 x 10⁻³ mol dm⁻³

Temp p (t) (°C)	10 ³ k _{ob} s	10 ⁵ k _{ob} s (sec ⁻¹)	k ₂ = $\frac{k_{obs}}{[PyN]}$ (mol ⁻¹ lit sec ⁻¹)	k ₂ /T	Log (k ₂ /T)
55	3.0	45.3	3.6 x 10 ⁻³	1.179	0.0715
50	3.1	34.8	2.8 x 10 ⁻³	0.892	7
45	3.1	22.5	1.8 x 10 ⁻³	0.568	-
40	3.2	19.5	1.5 x 10 ⁻³	0.484	0.0495
				5	8
					-
					0.2456
					-
					0.3147

$\Delta H^\ddagger = 53.16 \text{ kJ mol}^{-1}$ $\Delta S^\ddagger = -34.22 \text{ JK}^{-1} \text{ mol}^{-1}$
 $\Delta G^\ddagger (298\text{K}) = 63.3 \text{ kJ mol}^{-1}$

Rate dependence on temperature

Keeping all the conditions constant, the rate of the redox reaction was increased when temperature was increased. This can be explained on the basis of Arrhenius equation. Basing on the above facts, the mechanism of reaction can be delineated and rate law can be derived.

Mechanism



$$K_b = \frac{[PyNH^+]}{[PyN][H^+]}$$

$$[PyNH^+] = K_b [PyN][H^+]$$



$$Rate = k_{et} [PyN]_e [Co(III)]$$

$$[PyN]_T = [PyN]_e + [PyNH^+]_e$$

$$= [PyN]_e + K_b [PyN][H^+]$$

$$= [PyN]_e \{1 + K_b [H^+]\}$$

$$[PyN]_e = [PyN]_T / \{1 + K_b [H^+]\}$$

$$Rate = \frac{k_{et} [PyN]_T [Co(III)]}{1 + K_b [H^+]} \quad (5)$$

$$Rate = k_{obs} [Co(III)] \quad (6)$$

$$k_{obs} = \frac{k_{et} [PyN]_T}{1 + K_b [H^+]} \quad (7)$$

$$k_{obs} (1 + K_b [H^+]) = k_{et} [PyN]_T \quad (8)$$

The plot of L.H.S. = k_{obs} (1+K_b[H⁺]) vs [PyN]_T, is linear. Slope of the plot is equal to k_{et}. The value of k_{et} at temperature range 313K to 328K are collected in Table 3. The ΔH^\ddagger (kJ/mol) = 53.16 and ΔS^\ddagger (JK⁻¹ mole⁻¹) = -34.22 has been calculated using Eyring equation. since K_b(PyN) = 1.7 x 10⁻⁹ (25°C), the product K_b[H⁺] (in the pH range 3.8 to 5.4) will be small in comparison to 1.0. Hence plot of k_{obs} vs [PyN]_T is linear (fig 4 & 5). Negative activation entropy indicates that the reaction is passing through an ordered transition state.

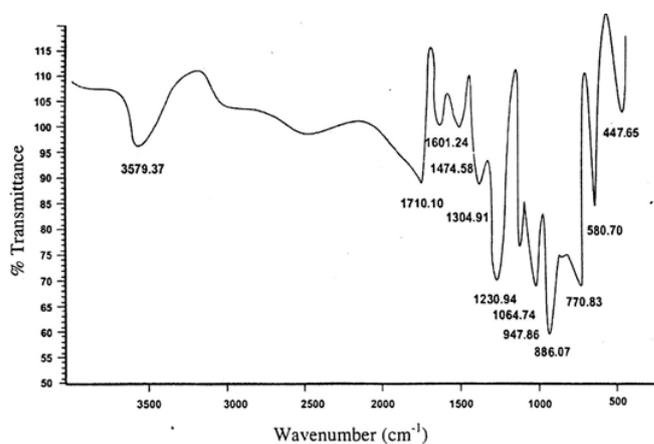


Figure-3 FTIR spectra of 12- tungstocobaltate

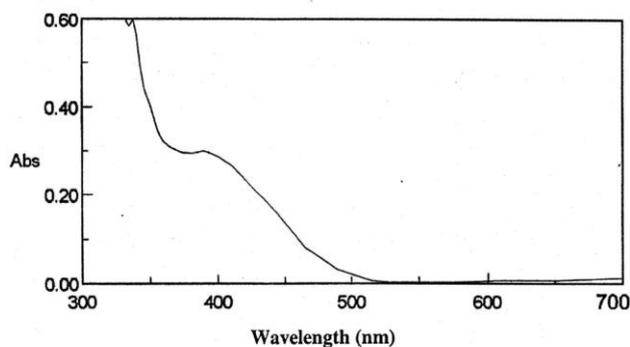


Figure-4 UV-Vis spectra of the 12- tungstocobalate

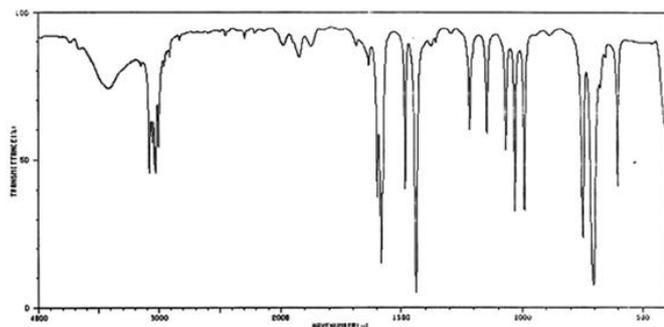


Figure 5. FTIR spectra of Pyridine Oxide

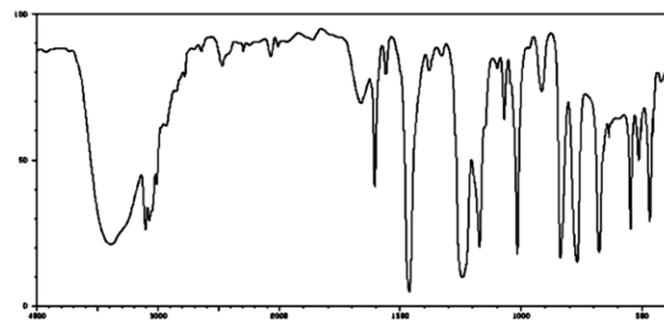


Figure 6. FTIR spectra of Pyridine Oxide

IV. CONCLUSION

The Kinetics of redox reaction between 12-tungstocobalate (III) and pyridine under varying pH, temperature, concentration of pyridine shows first order dependence in [PyN], inverse dependence in $[H^+]$, Zero order in 12-tungstocobalate (III). The overall stoichiometry found to be 2:1 corresponding to oxidant and reductant. Second order electron transfer rate was found to increase with increase in temperature. Moderate activation parameters favour the electron transfer process.

V. ACKNOWLEDGEMENT

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