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Original Article

Kinetic Study of Beckmann Rearrangement Reactions of Methyl 3 and 4-Pyridyl Ketoximes by UV-Spectra

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Abstract

This work deals with kinetic data of Beckmann rearrangement reaction of methyl 3 and 4- pyridyl ketoximes (No.1and 2) to the corresponding 3- pyridine and 4-pyridine carboxylic acid and methyl amine by action of perchloric acid as a catalyst. A spectrometric method was used in this investigation by following the decay of absorbances of ketoximes at optimal wavelengths. These reactions were obey pseudo first order kinetic with respect to ketoximes. Rate constants for these ketoximes were evaluated in the temperature range (298-338) k and found to depend on temperature, structure of ketoxime and the concentration of acid catalyst employed. Finally, the activation parameters for Beckmann rearrangement reaction of ketoximes were calculated, interpreted and discussed.

Keywords: Ketoxime, Beckmann, Rearrangement, Kinetic, Activation parameter

Introduction

The rearrangement of ketoximes to the corresponding amid, known [1] as the Beckmann reaction, was a topic of current interest. This reaction is known [2] a typical rearrangement catalyzed by Bronsted and Lewis acids.

The Beckmann rearrangement of cyclohexanone oxime is catalysed [3] by oleum producing caprolactam. This last chemical is important in petrochemicals for producing synthetic fiber and engineering plastic. The kinetic study of caprolactam oxidation had received attention by Romero et al [4]. Very little was known [2] about Beckmann rearrangement of cyclohexanone oxime in vapor phase by means of pulse reactor unit directly coupled to a gas chromatograph. Several kinetic studies on Beckmann rearrangement reaction of ketoximes [5] and other oximes [6,7] had been done in various media to conclude that rate constants depend on temperature, solvent, substituent and type catalyst.

In 201, Azzouz etal [8] compared the rate constants for the Beckmann rearrangement reactions of syn. and anti-substituted benzaldoximes in perchloric acid. Results collected showed that K_{syn} / K_{anti} had relative values greater than unity in all aldoximes with exception of 3- nitrobenzaldoxime.

The lack of kinetic study for Beckmann rearrangement reactions of heterocyclic ketoxime as methyl 3 and 4 - pyridyl ketoximes at a range of temperature (298-338) k prompted this work.

Experimental

All chemicals used throughout this work were of Fluka and BDH origins. 60% perchloric acid was supplied from Fluka. All ketoximes were synthesized by the standard method [9], i.e by reactions of equimolar amounts of 3 or 4- acetyl pyridine with hydroxyamine hydrochloride.

Synthesis of syn methyl 3 or 4- pyridyl ketoxime:

In 1oo ml round bottom flask attached with reflux condenser, 0.7 gm from hydroxylamine hydrochloride was mized with 1.1 ml of 3 acetyl pyridine or 4- acetyl pyridine and added 5 ml of absolute ethanol with (0.5-1.0) ml of pyridine. The final mixtures were refluxed for 1.5 hours. The contents of round bottom were poured in 1oo ml beaker while cooling until a complete separation of solid oximes. Finally, the solid was collected by filtration and recrystallized from absolut ethanol. Melting points of syn. methyl -3- pyridyl ketoxime and syn. methyl- 4 - pyridyl ketoxime had values (100-102) $^{\circ}$C and (117-119) $^{\circ}$C respectively. These were carried out by mixing 1 ml each of each ketoximes separately, of 10^{-4} M in ethanol with 0.6328 M $HClO_4$. The final mixtures were diluted with distilled water in a final 10 ml volume. The decay of absorbance for oxime mixtures wasfollowed at optimal wavelengths λ_{max} versus time against a blank sample until more than 85% completion of reaction. These measurements were performed at a range of temperature (298-338) K°.

The same initial concentrations of ketoximes and $HClO_4$ were used in this study. One milliliter of any ketoxime was mixed with various volumes of $HClO_4$ in the range (1-5) ml. The final mixtures were diluted with distilled water to 10 ml. Decay curves for reactants versus time were measured versus blank at optimum wavelengths as above.

Instrumentations:

- The FTIR spectra of solids ketoximes were measured by KBr disc method using FTIR spectrophotometer model Tensor - 27 manufactured by German Bruker company.
- All UV spectra of 10^{-4} M ketoximes in ethanol solvent were measured by Shimadzu model UV-1601.
- The temperature during UV spectra was controlled by connecting UV-spectrophotometer with a water thermostat EyEL4 type NTT- 2200, manufactured by Rikakikai Co. LTD Tokyo.

Results and Discussion

At the beginning of this investigation, it was thought of great importance to confirm the structures of oximes (1-2) by the physical method. This leads to the measurements of IR and UV- spectra, in addition to melting points mentioned previously. Table 1 showed the IR and UV -spectra for ketoximes.

Table 1. Solid IR spectra (cm^{-1}) with UV- spectra of 10^{-3} M ketoximes

Comp. NO	$V_{C=N}$	V_{C-H}	$V_{Py.}$	V_{OH}	V_{N-O}	λ_{max} *(nm)*	*A*	$_{max}{}^{*}\Sigma$
1	1634.88 (m)	3063.54 (m)	1601.30 (m)	3161.99 (m)	926.86 (s)	246.8	2.041	2041
2	1645.13 (m)	3071.61 (w)	1601.36 (s)	3446.21 (m)	940.54 (s)	254.8	1.219	1219

* Unit: Litter. $mole^{-1}.cm^{-1}$

Table 1: Illustrates the following:

1- A medium stretching bands for ketoximes in the range (1635.88 – 1645.13) cm^{-1}.

2- A medium or weak absorption stretching bands for C-H linkages.

3- A medium or strong absorption stretching bands for Pyridine rings.

4- A medium absorption stretching bands for hydroxy groups of oximes.

5- A strong absorption for stretching vibration of N-O linkage of oxime groups.

The UV-spectra of ketoximes (1-2) showed one main band for each ketoximes with $\pi \rightarrow \pi^*$ transitions as confirmed from Σ_{max} values which were greater than 1000 units. These indicated a planar [10] structure for these ketoximes.

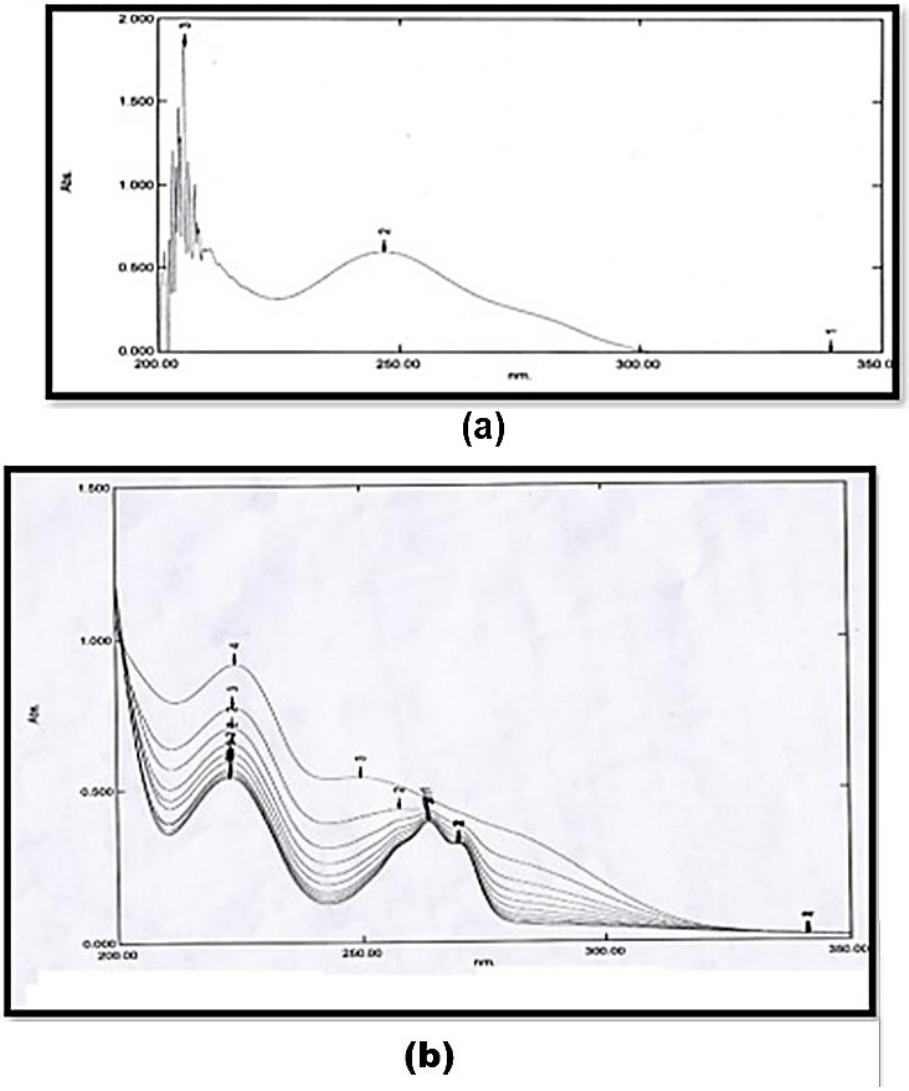
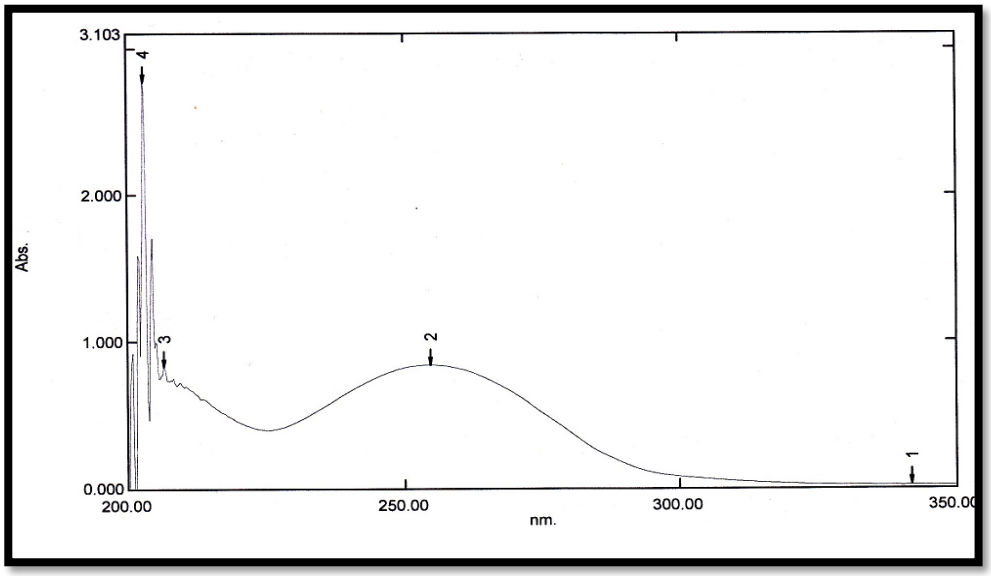
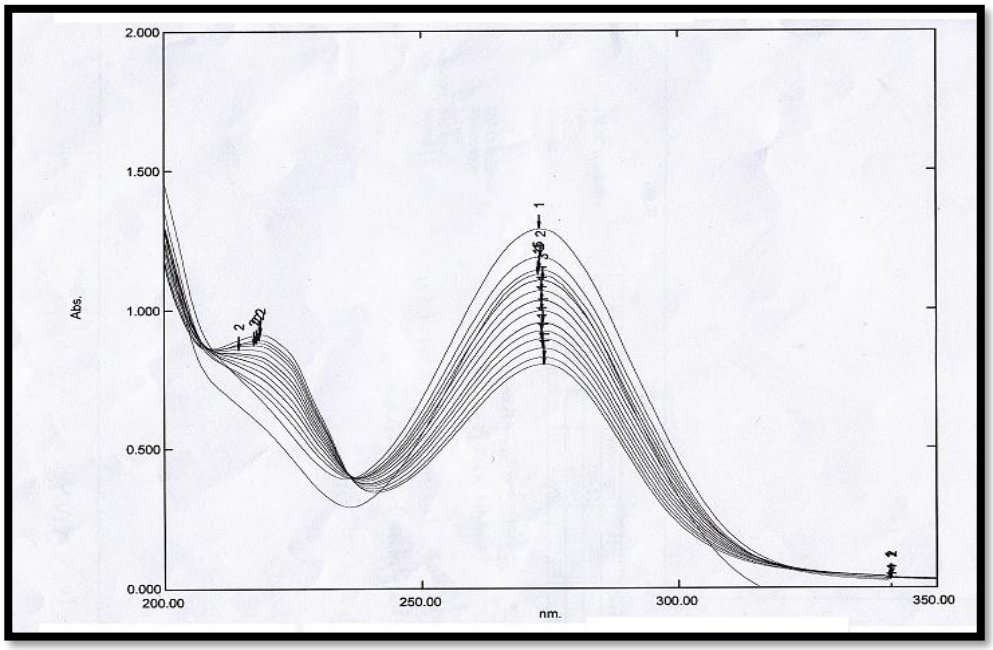


Figure 1. (a) UV Spectrum of 10-3M of ketoxime (1) in ethanol. (b) Kinetic spectrum of ketoxime (1) after addition of catalysed HClO4.



(c)



(d)

Figure 2. (c) UV spectrum of 10^{-3}M of ketoxime 2 in ethanol. (d) Kinetic spectrum of ketoxime 2 after addition of catalysed $HClO_4$.

Catalysed HClO4., the second band in the spectrum was observed at wavelength 223.6 nm. Its intensity increased by increasing time for product formed. The difference in wavelengths between these two bands was $\Delta\lambda = 40$ nm. This means no spectrum interference between reactant and product for ketoxime (1). The last encourages the workers in this investigation to deal with kinetic study. The kinetic study started by measurement of 10-3M solutions of ketoximes (1-2) in absolute ethanol. These showed single absorption bands for each ketoxime at wavelength 246.8 nm and 254.8 nm respectively. Then after a mixture of ketoxime (1) with catalysed perchloric acid was prepared as shown in the experimental section. This showed two bands for ketoxime (1) at wavelengths 263.6 nm and 223.6 nm in the spectrum. The intensity of first band was observed to be decreased by increasing time of reaction. This represents a protonated oxime after combination of oxime with protons liberated from similar spectrum for ketoxime (2) was obtained after addition of perchloric acid to ketoxime (2) with bands 55.2 and two at wavelengths 273.8 nm and 218.6 nm with $\Delta\lambda = 55.2$ nm. Typical kinetic spectra of ketoximes (1-2) were shown in Fig (1-2).

Now when absorbances values versus times for ketoximes (1-2) at temperature range (298-338) K° were plotted by using a pseudo first order kinetic equation, the results were collected as shown in Fig. (3-4). These showedvery good straight lines of correlation range. R^2 values (0.868-0.984 and 0.906-0.999) for ketoximes (1-2) respectively.

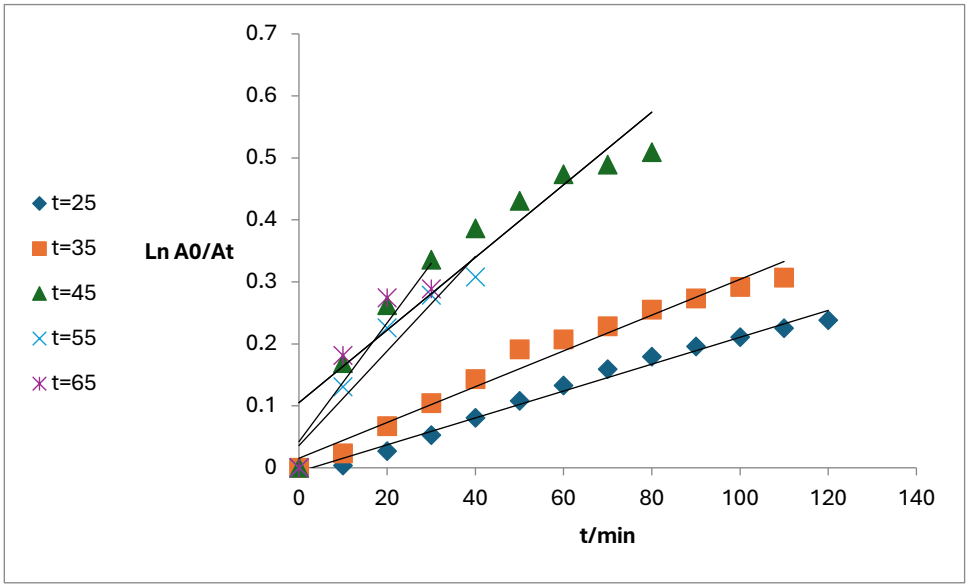


Figure 3. Kinetic plots for ketoxime (1).

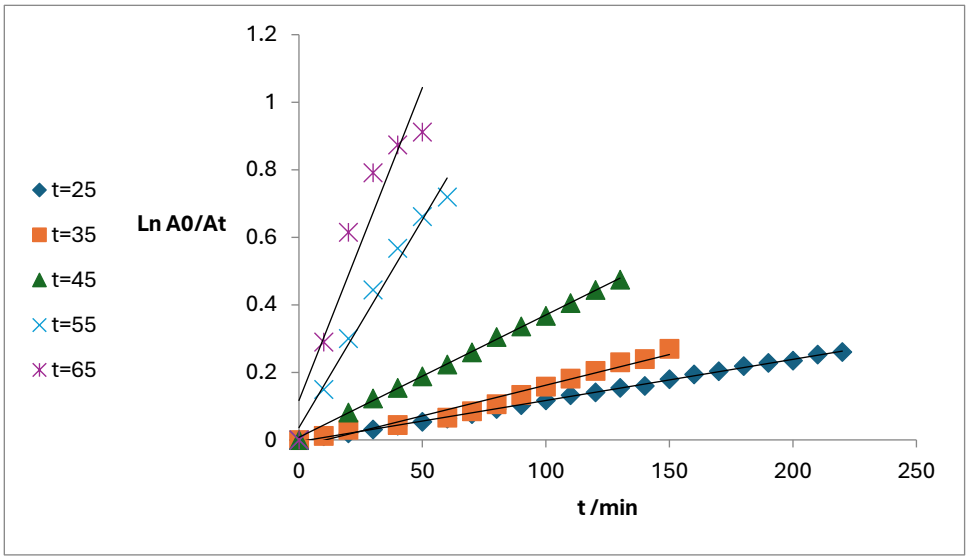


Figure 4. Kinetic plots for ketoxime (2).

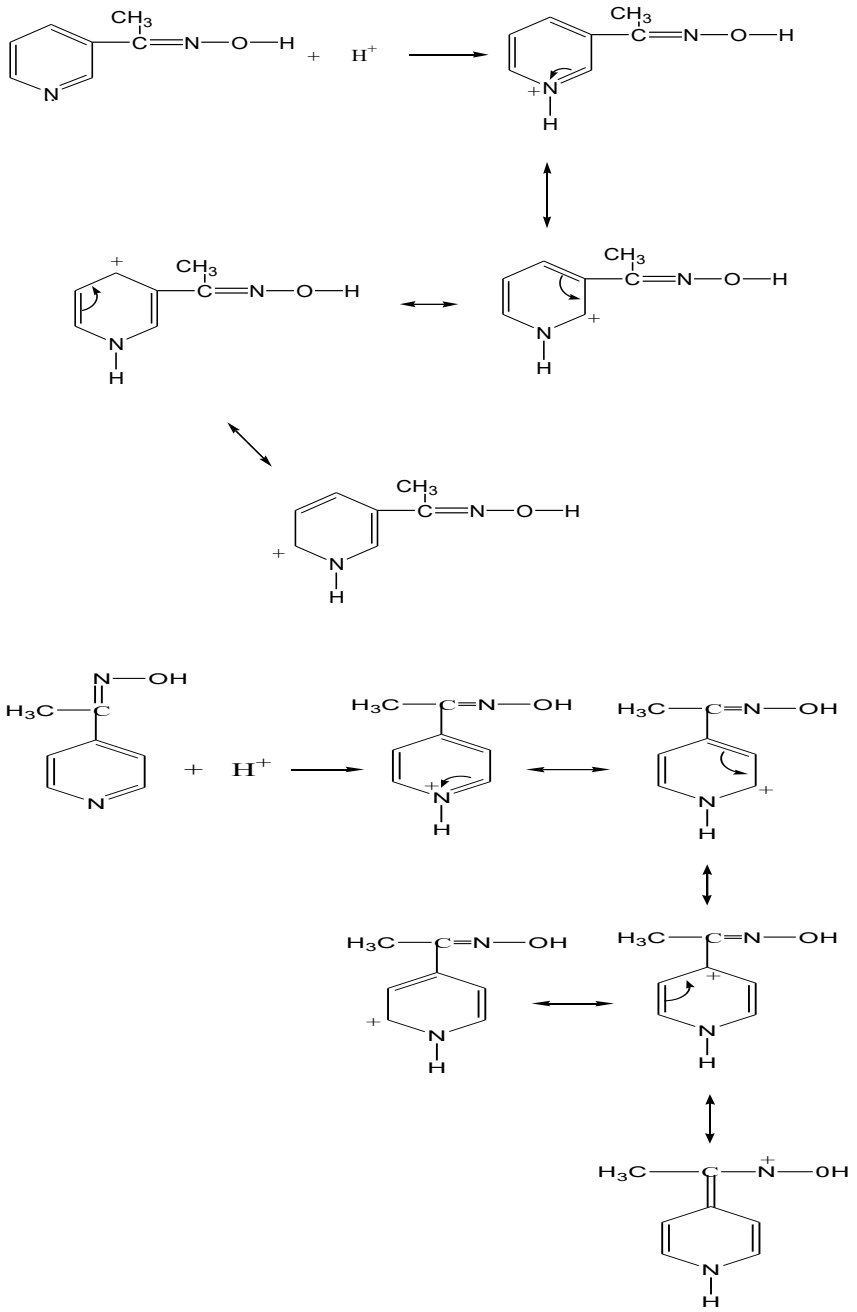
These kinetic plots for ketoximes (1-2) agreed well with pseudo kinetic data collected in this study, since the ratio of concentrations of catalysed $HClO_4$ to ketoximes of a value was 6328:1. In other words, these reactions rates grow depending on concentrations of ketoximes only.

The activation energies E_a for ketoximes (1-2) were calculated from Arrhenius plots as in Fig. (5) using the following equation.

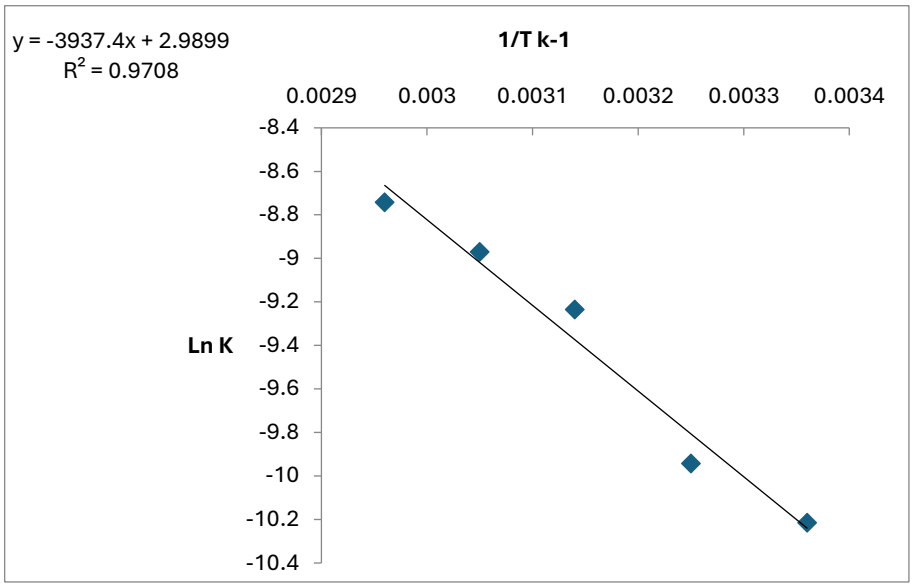
$$\ln k_1 = A\, e^{-Ea/RT} \quad \text{------} \quad (1)$$

The activation energies for ketoximes (1-2) had a value of 32.73 KJ. mole^{-1} and 60.73 KJ. mole^{-1} respectively. {omparison of these values showed that ketoxime (1) proceed faster with greater rate constants K_1 if compared with ketoxime(2). The reason for such variation can be understood by the following: -

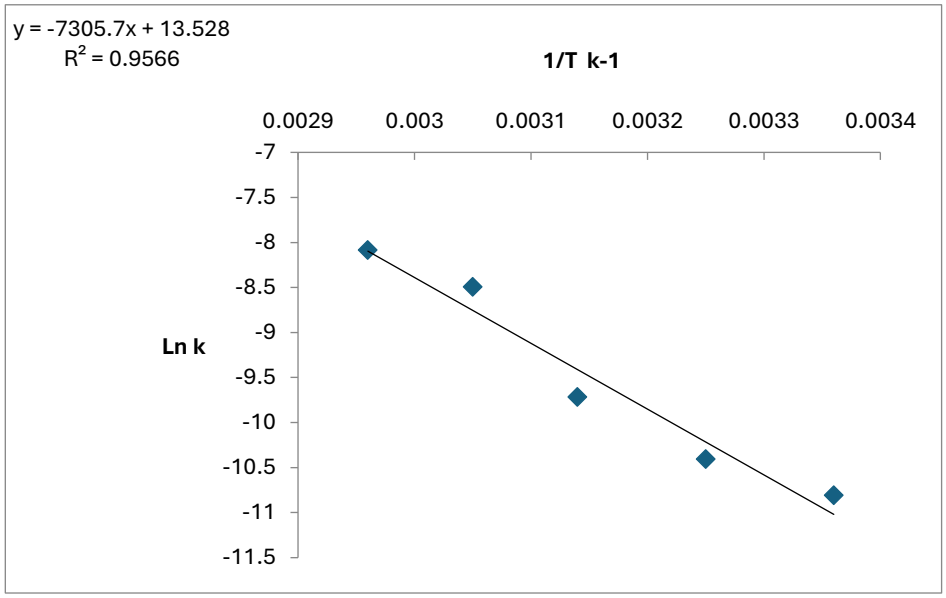
It is known in literature [11] that pyridine nucleus can form salt with acids forming a pyridinium ion. The resonance structures formed ketoximes (1-2) were expected and shown in Scheme (1).



Scheme 1. Resonance structures of protonated oxime (1-2).



(a)



(b)

Figure 5. Arrhenius plots for reaction of (a) Ketoxime 1 (b) Ketoxime 2.

Scheme (1) showed resonance structures of ketoximes (1-2) that had four and five resonance hybridis . The lower value of resonance structures of ketoxime (1) means that it is a pyridinium ion that was less stable compared with pyridinium ion of oxime (2). These results were in full agreement with faster reaction rate constant K1 for ketoxime (1) if compared with ketoxime (2).

The activation parameters namely for these kinetic reactionsΔG^*, ΔH^* and ΔS^* were calculated from equations (2-4) of the forms: -

$$\ln k_1 = \ln kT/h + \Delta S^*/R - Ea/RT \text{ -------(2)}$$

$$\Delta H^* = Ea - RT \text{ ----------(3)}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \text{----------(4)}$$

The results of activation parameters were tabulated in Table (2).

Table 2. Activation parameters for ketoximes (1-2)

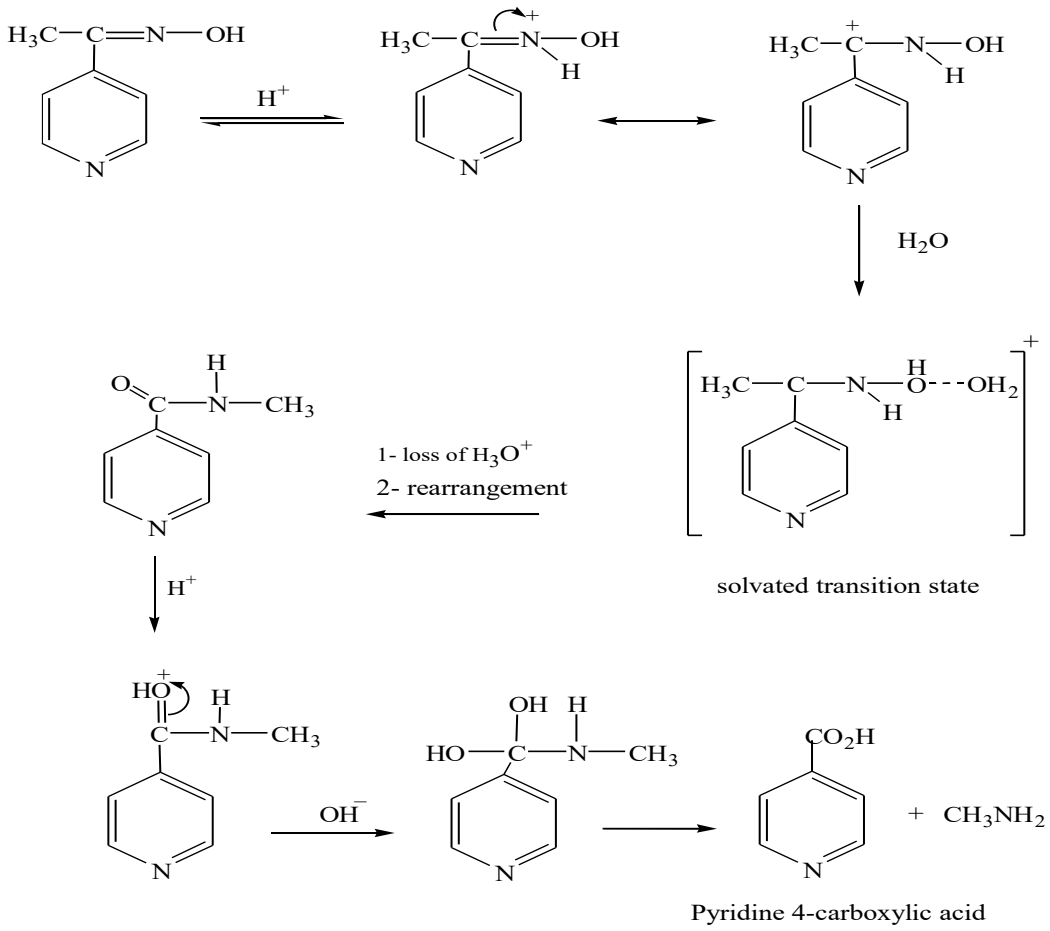
Ketoxime NO	*T(K)*	ΔH^* *KJ.mole^{-1}*	ΔS^* *J.mole^{-1}.K^{-1}*	ΔG^* *K J .mole^{-1}*	E_a *K J . mole^{-1}*
1	298	30.25	-26.46	38.14	32.73
	308	30.17	-26.65	38.38	
	318	30.09	-26.38	38.48	
	328	30.01	-26.52	38.70	
	338	29.92	-26.68	38.94	
2	298	58.26	-15.75	62.95	60.73
	308	58.17	-16.18	63.16	
	318	58.09	-16.26	63.26	
	328	58.01	-15.77	63.18	
	338	57.92	-16.05	63.35	

The ΔH* and ΔG* activation parameters for ketoxime (2) were greater than ketoxime (1) and molecules of ketoxime (2) need more energy to reach the activated complex in the energy profile diagram. The signs of ΔS* activation parameters in ketoximes (1-2) were negative. These mean that activated complex molecules were more ordered as compared with reactant molecules. These happen by either solvation [12,13] of activated complex molecules or by passing the mechanism of rearrangement reactions through cyclic intermediates.

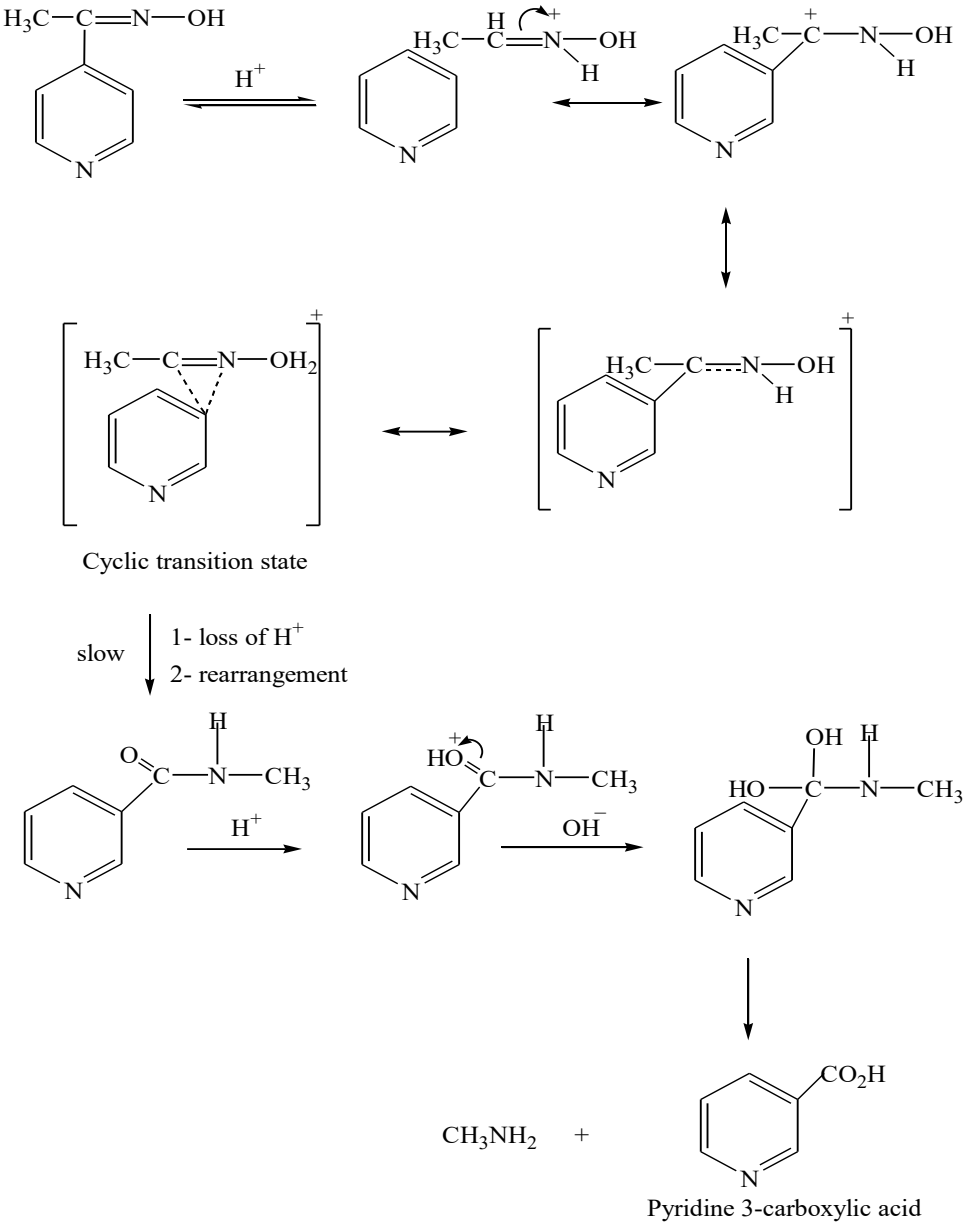
In order to confirm which of these assumption mechanisms had a greater weight in determining the structures of intermediates during mechanisms, this encourages the workers here to study the influence of various concentration of catalysed HClO4 or their pH values on rate constants of reactions, as shown in Fig. (6)[14]. So when log K plotted versus pH, these showed straight lines of slopes 1.142 and 1.769 for ketoximes 1 and 2 respectively. These numbers agreed well with specific and general acid catalysed [15], reactions in these molecules.

This means that ketoxime 1 is catalysed by hydrogen ion alone, while ketoxime 2 by both hydrogen ion and water molecule. These come as a support of negative ΔS* values mentioned above.

The proposed mechanisms for cyclic and salvation rearrangement reactions of ketoximes (1-2) were as follows:


H+
H2O
1- loss of H3O+
2- rearrangement
solvated transition state
OH−
+ CH3NH2
Pyridine 4-carboxylic acid

Ketoxime (1)



Ketoxime (2)

Conclusion

1- The Beckmann rearrangement reactions of ketoximes (1-2) were studied kinetically by using the decay of reactants absorbance with time at optimal wavelengths.

2- The rate constants K1 for these rearrangement reactions of ketoximes were calculated from pseudo first order plots.

3- The favoured form of activated complexes during kinetic study of ketoxime 1 and 2, were through cyclic intermediate and solvated one respectively.

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