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Influence of buffers and temperatures in tautomerism reactions of p-aminobenzylidene o-hydroxyaniline

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ABSTRACT

As an answer of unsuccessful dye formation by reaction of p-aminobenzylidene-o-hydroxyaniline (I) with diazotied sulphanilic acid mixture, the tautomerism reactions in such molecule were found to be the correct reason. Molecule I was prepared by a standard method, its structure was confirmed by the measurements of melting point, beside UV and IR spectra.

The main aim of this investigation was deal with tautomerism study in I by the aid of U.V spectrum. Some factors affecting on equilibrium constants K_1 and K_2 of tautomerism reactions happen in I were discussed. These included influence of different buffers in the range of pH 4-10 and different temperatures were studied.

Finally, the thermodynamic parameters of tautomerism reactions ΔG° , ΔH° and ΔS° were calculated and discussed.

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KEYWORDS

Schiff base;
Tautomerism;
Buffers;
Thermodynamic;
UV spectroscopy.

INTRODUCTION

Schiff bases derived from sulphdrug and salicylaldehyde had been found to be good fungicides^[1], bacteriocides^[2] as well as chelating^[3] agents.

Tautomerism interconversion^[4] had been investigated during last decade. The keto enol equilibria for varieties of Schiff bases^[5-7] others studied the influence of temperature^[8] and solvent^[9] on tautomerism of imines derived from 2-hydroxy-1-naphthaldehyde. The process of tautomerism and isomerization reactions were proved by the evaluation of thermodynamic parameters. The enthalpies values for both reactions indicate an exothermic reactions type. Also three different empirical parameters for solvent polarity were used as E_T^N , $\mu 10$

³⁰ cm and $E_t(30)$ kcal.mole⁻¹.

The present investigation is an extension of the previous studies. It deals with effect of pH and temperature on tautomerism reactions happen in p-aminobenzylidene-o-hydroxy aniline. The study accomplished by measuring the thermodynamic parameters for tautomerism reactions, namely the ΔH° , ΔG° and ΔS° in this imine as given and discussed.

EXPERIMENTAL

All chemicals used throughout this work were of Fluka or molecula origins.

Molecule (1) was prepared^[10] by mixing equimolar amounts i.e 10^{-2} mole of p-aminobenzaldehyde with o-

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aminophenol in 20ml absolute ethanol. The mixture was refluxed for about 1.5 hour, cooling and separation of product by filtration. Pure molecule (1) was obtained after hot recrystallization of sample in absolute ethanol, having a melting point value of (121-123)C°.

Solution prepared

- 1 0.5M sodium carbonate as catalyst for tautomerism reaction.
- 2 The following buffer solutions also for tautomerism reaction, as in TABLE 1.

TABLE 1 : Composition of buffers having pH range value 4-10

pH	Composition
4	0.2 M CH ₃ COONa (9ml) + 0.2 M CH ₃ COOH (41 ml)
5	0.2 M CH ₃ COONa (35.25ml) + 0.2 M CH ₃ COOH (14.75 ml)
6	0.2 M CH ₃ COONa (191 ml) + 0.2 M CH ₃ COOH (9 ml)
7	0.05 M Borax (12 ml) +(12.4 gm Boric acid + 2.93 gm NaCl) inliter (188ml)
8	0.05 M Borax (11 ml) +(12.4 gm Boric acid + 2.93 gm NaCl) inliter (29ml)
9	0.05 M Borax (40 ml) + (12.4 gm Boric acid + 2.93 gm NaCl) inliter (10ml)
10	Equal volume from 0.025M(Na ₂ CO ₃ +NaHCO ₃)

Eye14 type NTT-2200P, manufactured by Rikakikai Co. LTD.

Instrumentations

- 1 The IR spectrum of I was measured by FTIR spectrophotometer Tensor-27 manufactured by Bruker, using KBr disk method.
- 2 UV spectrum was measured by using 1×1×3cm³ quartz cell, UV+
- 3 The pH of any solution was measured by using WTW pH₇₂₀ Weilheim 82362.
- 4 The temperature of any solution during UV measurements were controlled by connecting the spectrophotometer mentioned with thermostat model

surement of UV spectrum of 10⁻³M in ethanol showed the following absorption bands :-

RESULTS AND DISCUSSION

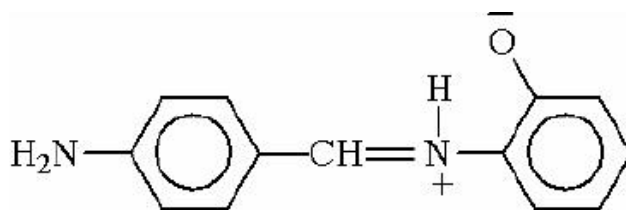
At the beginning of this investigation it was though of importance to measure the IR spectrum of I to confirm its chemical structure. This showed the following absorption bands :-

- 1 Two weak absorptions at wavenumbers 3432.63cm⁻¹ and 3402.98cm⁻¹ related to asymmetric vibration of NH₂ group.
- 2 A broad absorption at wavenumber 3355.58cm⁻¹ belong to vibration of phenolic group.
- 3 A medium absorption at wavenumber 1670.72cm⁻¹ belong to vibration of azomethine linkage.
- 4 A strong absorption at wavenumber 1589.52cm⁻¹ related to aromaticity.
- 5 A weak absorption at wavenumber 1749cm⁻¹ related to carbonyl group. The last could only happen by tautomerism^[14] reaction type enol ⇌ keto, resulted to conversion of phenol group to carbonyl linkage.

The tautomerism reaction of I was started by mea-

λ ₁ (nm)	Σ ₁	λ ₂	Σ ₂	λ ₃	Σ ₃
436.4	151	322.6	1300	231.8	1273

Band λ₁ was observed at longer wavelength. This indicated the occurrence of Schiff base in its zwitter^[12] ion formation as follows :-



Other bands λ₂ and λ₃ were related to the presence of I in enol and keto forms with molar extension values of 1300 and 1273 in units of Liter.mole⁻¹.cm⁻¹ respectively. The near values of Σ_{max} mean the near abundances of these two tautomers in ethanol, which agreed with previous studies^[13,14].

The influence of buffers in the pH range 4-10 were studied by preparing 10⁻³M solution I in ethanol, mixed in buffers of pH stated. These showed some precipitates due to the insolubility of solute in the mixed etha-

nol-water medium. In order to overcome on the solubility problem, this encourage the work to exchange ethanol by a mixture composed from 40%-acetone-60% ethanol. The UV spectrum of 10^{-4} M of I in mixed solvent illustrated in Figure 1.

Figure 1 illustrated four bands in the U.V spectrum of I as follows :-

λ_1 (nm)	Σ_1	λ_2	Σ_2	λ_3	Σ_3	λ_4	Σ_4
416.4	4990	331.2	5870	283.2	6050	237	10140

Accordance to the increase in wavelength λ_1 , λ_2 , λ_3 and λ_4 were related to trans keto, cis keto, cis enol and tran enol tautomers respectively. This illustrated in tautomerism^[14] and isomerism^[14] in Schiff base mol-

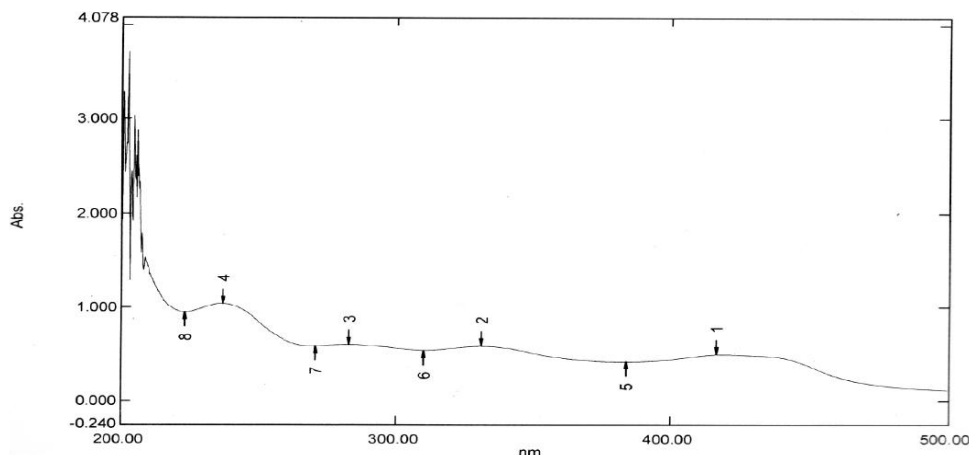
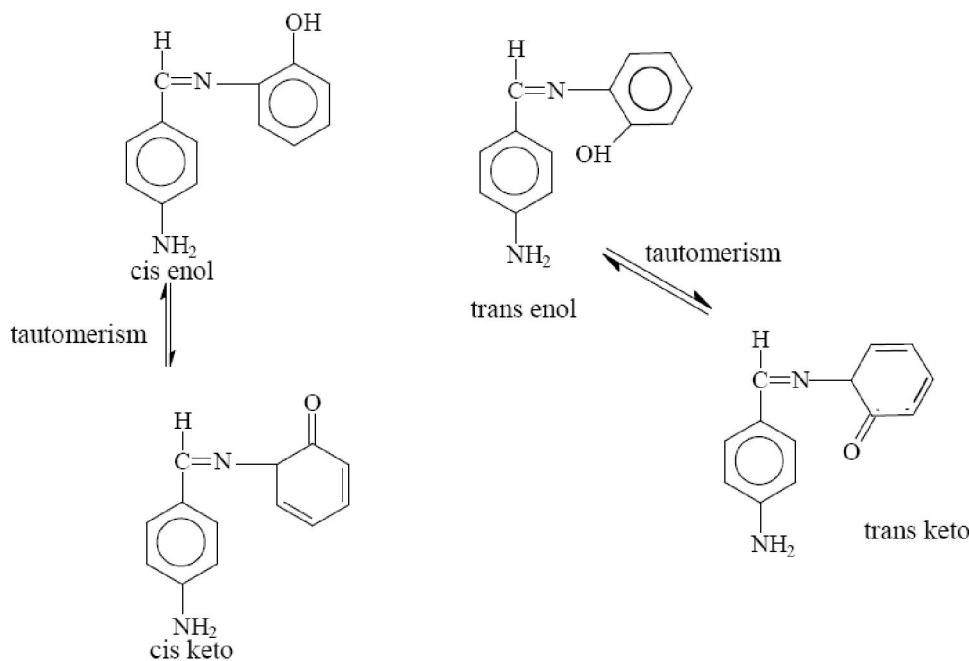


Figure 1 : UV spectrum of 10^{-4} M of I in 40%-acetone-60% ethanol mixed solvents



Scheme 1 : Cis-trans keto-enol tautomers in molecule 1

ecule as in Scheme 1.

Scheme 1 showed four different cis-trans keto-enol tautomers which was expected and agreed with literature^[15].

TABLE 2 showed the influence of different buffers having pH range 4-10 on UV spectra of molecule (1).

TABLE 2 illustrated the following results :-

- At pH₄ the spectrum of I showed three bands at wavelength λ_1 , λ_2 and λ_3 with molar extinction values greater than 1000 unit, which correspond to nitrilium ion $\text{CH}=\overset{\text{H}}{\underset{\oplus}{\text{N}}}-\text{H}$, trans and cis enol forms :-
- At pH₆ the spectrum of I showed four bands which

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TABLE 2 : Influence of buffers on UV spectra of I in 40%-acetone-60% ethanol mixed solvent

pH	λ_1	Σ_1	λ_2	Σ_2	λ_3	Σ_3	λ_4	Σ_4
4	424.2	3030	319.2	3330	223.6	6500	---	---
6	430.0	2640	318.4	3460	276.0	3530	229.4	6200
8	434.2	2790	318.4	4000	301.6	4020	296.0	4020
9	340.4	2820	319.6	3880	228.4	7050	---	---
10	435	2240	340.6	2410	306.0	2780	232.8	4740

$\lambda = \text{nm}$, $\Sigma = \text{Liter.mole}^{-1}.\text{cm}^{-1}$

TABLE 3 : Absorbances A1, A2 and A3 of molecule 1 at pH₉ with different temperatures

tc ⁰	A ₁	$\lambda_1(\text{nm})$	A ₂	$\lambda_2(\text{nm})$	A ₃	$\lambda_3(\text{nm})$
10	0.282	430.4	0.290	319.6	0.590	228.4
20	0.278	430.6	0.320	318.6	0.665	230.4
30	0.274	430.4	0.360	319.2	0.705	228.4
40	0.271	431.2	0.376	319.2	0.790	229.6
50	0.267	428.2	0.415	318.8	0.850	229.0

were related to nitrilium ion, trans-enol, cis-enol and trans keto totomers.

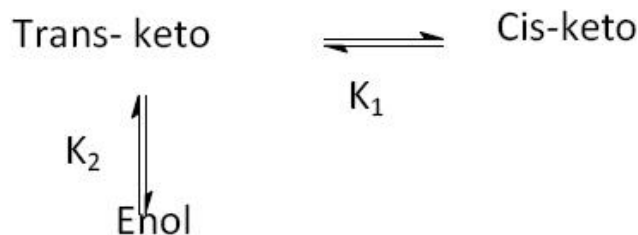
- At pH₈ the spectrum of I appeared four bands at wavelengths λ_1 , λ_2 and λ_3 and λ_4 . These related into trans keto, cis keto, trans and cis enol tautomers. This mean both tautomerism^[13,14,16] enol \rightleftharpoons keto and isomerism^[14] cis \rightleftharpoons trans reactions were happened in compound under investigation at this basic medium.
- At pH₉ the spectrum of I appeared three peaks or bands at wavelengths λ_1 , λ_2 and λ_3 . They were related to trans-keto, cis-keto and trans enol tautomers respectively, or the occurrence of enol keto tautomerism reaction.
- At pH₁₀ the UV spectrum of I showed similar result to that obtained at pH₈.

This tautomerism study come in agreement with other imine compound derived from 2-hydroxy-1-naphthylaldehyde^[8] and other studies^[16,17].

Then after the study was extended to the influence of temperatures in the range (10-50)C° on equilibrium constants of tautomerism reactions. Particular attention was given to pH values 9 and 10. These were for tautomerism reactions happened at such pH values. Hence the following division of results were necessary :-

1 At pH₉

The UV spectrum of 10⁻⁴M of I dissolved in pH₉ showed λ_1 , λ_2 and λ_3 wavelengths as in TABLE 3. These wavelengths were related in to tautomers^[18-19] trans

Scheme 2 : Tautomerism of I at pH₉

keto, cis keto and enol respectively. When the same spectrum of I repeated at temperature range stated, the following results as in TABLE 3 were tabulated.

Now when absorbances A₁, A₂ and A₃ were plotted versus t C°, this led to Figure 2 which illustrated three lines of R² range (0.977-0.988).

This showed an inverse relationship between A₁ for reactant versus t C°. A₁ represent the trans keto tautomer, because it absorbed at longer wavelength. Also an direct relationships between A₂ and A₃ versus t C° were obtained. A₂ and A₃ absorbances were related to cis keto and enol tautomers respectively. Hence these λ_1 , λ_2 and λ_3 wavelengths were agreed with similar study⁸ on imines derived from 2-hydroxy-1-naphthylaldehyde.

The tautomerism reactions of I at pH₉ was illustrated in Scheme 2.

Now when A₁ were plotted versus A₂, this showed a straight line of R² = 0.995 with a slope = 0.12 will equivalent to $\frac{\alpha_1}{\alpha_2}$ when Hartman^[20] etal was used for estimation of equilibrium constant of tautomerism reac-

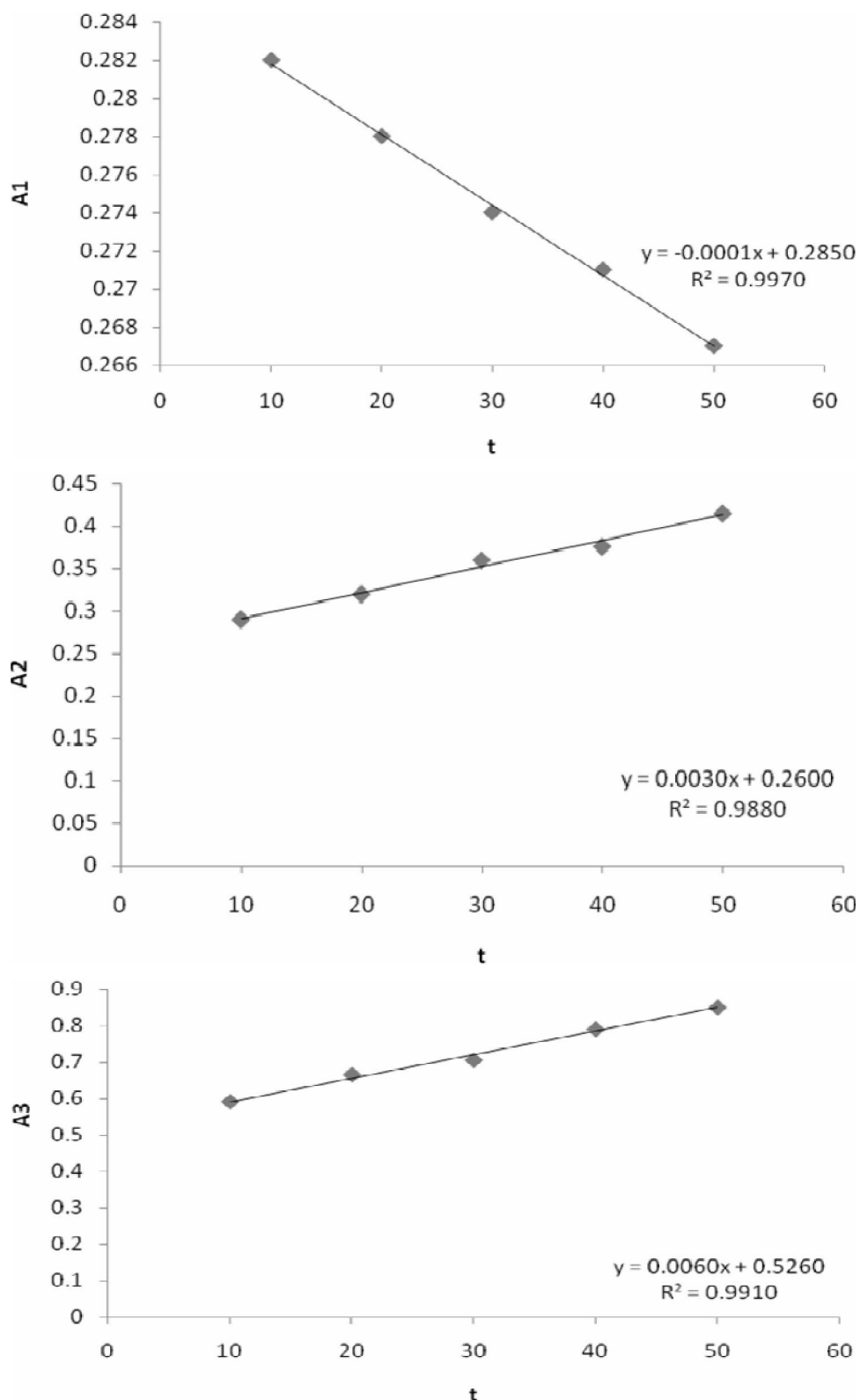


Figure 2 : The relationships between absorbances versus t C° in I

tion. Similarly when A_1 were plotted versus A_3 , this gives Figure 3.

straight line of $R^2 = 0.984$ with slope $\frac{\alpha_1}{\alpha_2} = 0.056$ as in

The thermodynamic parameters ΔG° , ΔH° and ΔS° for tautomerism reactions of I were shown in TABLE

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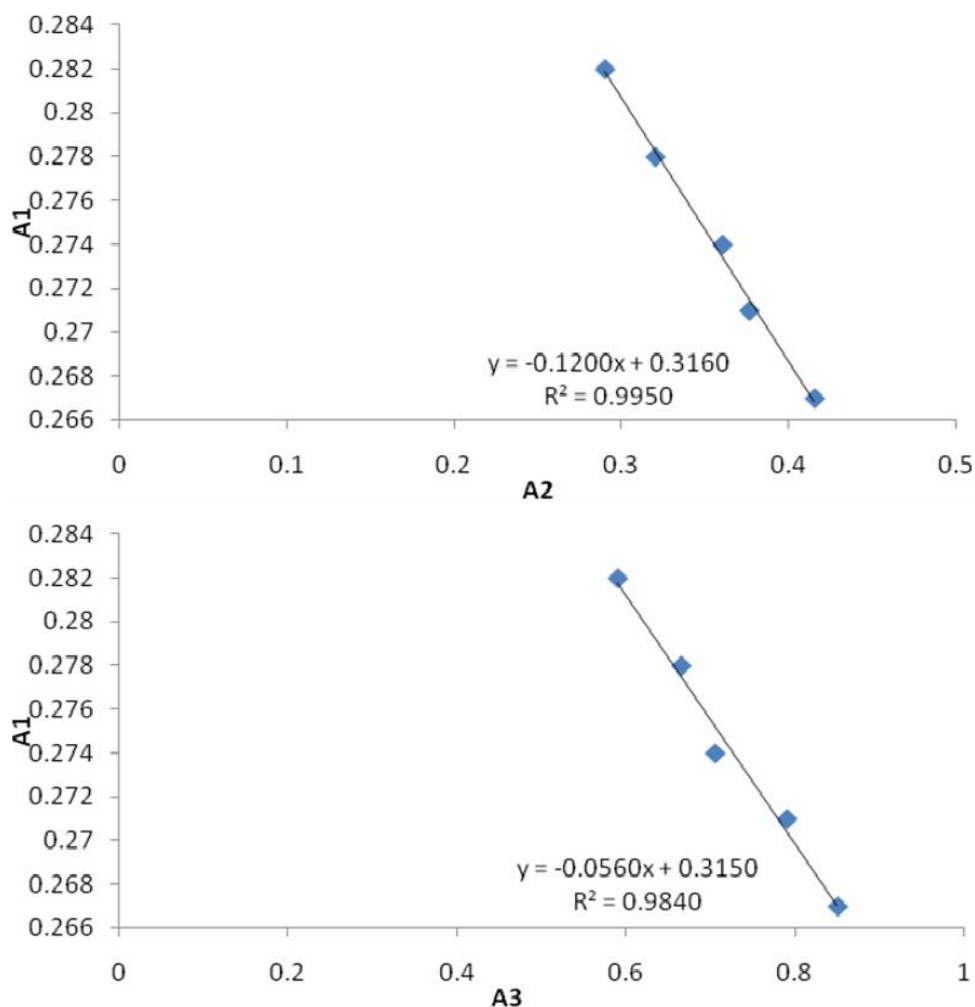


Figure 3 : The relationships for tautomerism of I at pH₉ (a) A1 versus A2 (b) A1 versus A3

4. ΔH° was estimated from plot of $\ln K$ versus T^{-1} as in Figure 4.

This led to the following conclusions :-

- (1) The positive value of $\Delta \bar{G}_1^\circ$ for K_1 equilibrium constant was non spontaneous. Also the positive values of $\Delta \bar{H}_1^\circ$ and $\Delta \bar{S}_1^\circ$ mean that tautomerism reaction was endothermic and accompanied by an increase of random respectively.
- (2) Similarly $\Delta \bar{G}_2^\circ$ negative value for K_2 equilibrium constant was non spontaneous. Also the positive signs of $\Delta \bar{H}_2^\circ$ and $\Delta \bar{S}_2^\circ$ mean than tautomerism reaction stated was endothermic and accompanied by an increase of random.

2. At pH₁₀

The UV spectra of I at pH₁₀ and at temperature

range (10-50)C° showed four bands at wavelength λ_1 , λ_2 , λ_3 and λ_4 .

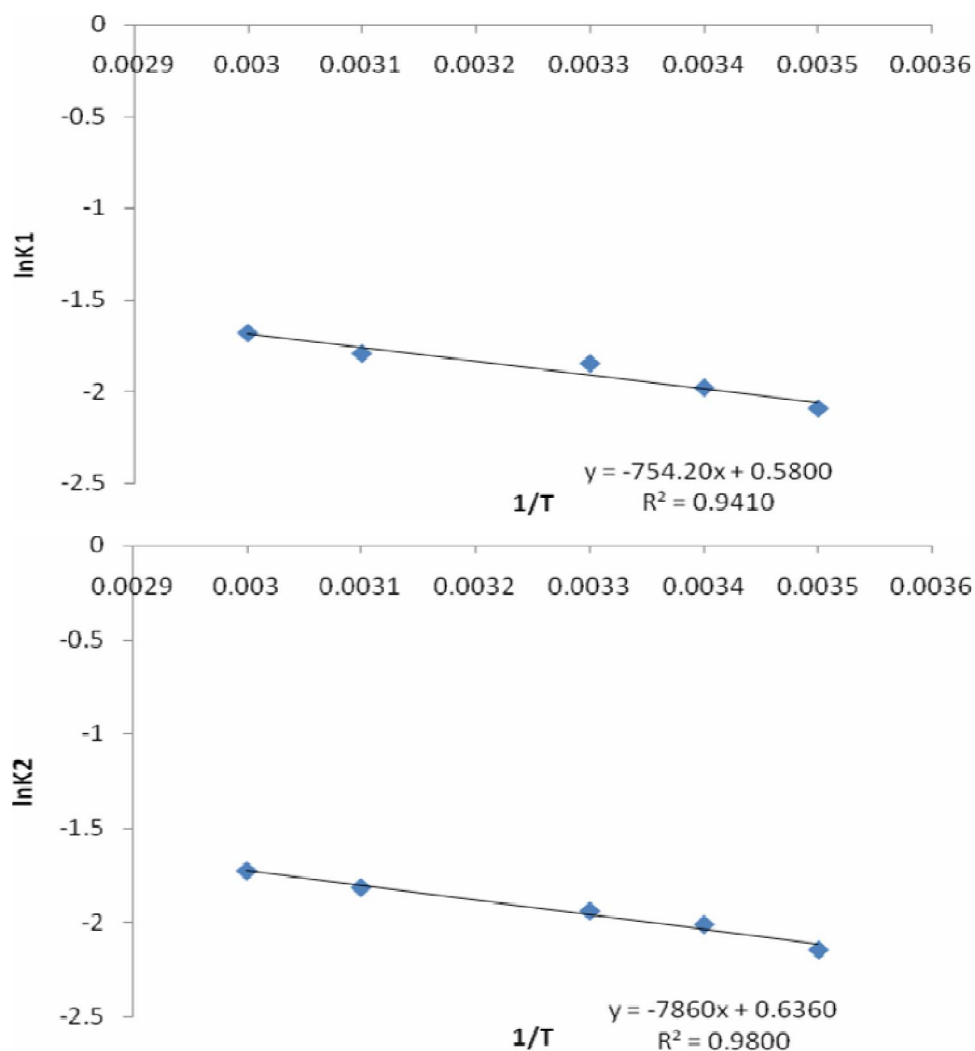
λ_4 bands was some times appeared or not appeared. This mean it was unstable. Hence in this study it was focused on these three original bands as shown in TABLE 5.

Now when A_1 was plotted versus t C°, resulted into an inverse straight line of $R^2 = 0.994$, or when A_2 and A_3 were plotted versus t C° resulted to direct plots of R^2 values 0.9928 and 0.9983 respectively.

These λ_1 , λ_2 and λ_3 wavelengths were related to tautomers enol, cis keto and trans keto respectively as agreed with similar study⁸.

The tautomerism reactions happened in I were illustrated in Scheme 2

When a straight lines were plotted between A_1 versus A_2 and A_1 versus A_3 resulted to slopes $\frac{\alpha_1}{\alpha_2}$ and $\frac{\alpha_1}{\alpha_3}$ of

Figure 4 : Relationship between $\ln K_1$ or $\ln K_2$ versus T^{-1} TABLE 4 : Thermodynamic parameters of tautomerism reactions K_1 and K_2 of I at pH_9

$\frac{1}{T}$	$K_1 = \frac{A_2}{A_1} \cdot \frac{\alpha_1}{\alpha_2}$	$\ln K_1$	ΔG_1^0 KJ.mole ⁻¹	$\Delta G_1^{\bar{0}}$ KJ.mole ⁻¹	ΔH_1^0 KJ.mole ⁻¹	$\Delta H_1^{\bar{0}}$ KJ.mole ⁻¹	ΔS_1^0 J.mole ⁻¹ . K ⁻¹	$\Delta S_1^{\bar{0}}$ J.mole ⁻¹ . K ⁻¹
0.0035	0.1234	-2.0923	4.92289		6.28755		4.82	
0.0034	0.1381	-1.9797	4.82255		6.23543		4.82	
0.0033	0.1576	-1.8476	4.65436	4.71521	6.11546	6.17632	4.82	4.82
0.0031	0.1664	-1.7933	4.66667		6.17599		4.82	
0.0030	0.1865	-1.6793	4.50962		6.06717		4.82	
$\frac{1}{T}$	$K_2 = \frac{A_3}{A_1} \cdot \frac{\alpha_1}{\alpha_3}$	$\ln K_2$	ΔG_2^0 KJ.mole ⁻¹	$\Delta G_2^{\bar{0}}$ KJ.mole ⁻¹	ΔH_2^0 KJ.mole ⁻¹	$\Delta H_2^{\bar{0}}$ KJ.mole ⁻¹	ΔS_2^0 J.mole ⁻¹ . K ⁻¹	$\Delta S_2^{\bar{0}}$ J.mole ⁻¹ . K ⁻¹
0.0035	0.1171	-2.1447	5.04618		6.54260		5.28	
0.0034	0.1339	-2.0106	4.89782		6.44712		5.28	
0.0033	0.1440	-1.9379	4.88184	4.83496	6.48401	6.43713	5.28	5.28
0.0031	0.1632	-1.8127	4.71715		6.37220		5.28	
0.003	0.1782	-1.7248	4.63181		6.33974		5.28	

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TABLE 5 : Influence of temperatures on tautomerism reactions of I at pH₁₀

tc ⁰	A ₁	λ ₁ (nm)	A ₂	λ ₂ (nm)	A ₃	λ ₃ (nm)
10	0.590	234	0.278	316.0	0.15	428.0
20	0.550	235	0.280	319.0	0.20	435.8
30	0.503	240	0.284	317.0	0.25	433.8
40	0.477	241	0.287	319.6	0.30	427.6
50	0.435	240	0.290	319.4	0.34	433.6

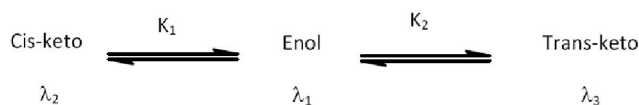
TABLE 6 : Equilibrium constants K₁ and K₂ and their thermodynamic parameters of tautomerism reactions of I at pH₁₀

$\frac{1}{T}$	$K_1 = \frac{A_2 \cdot \alpha_1}{A_1 \cdot \alpha_2}$	lnK ₁	ΔG_1^0 KJ.mole ⁻¹	$\Delta G_1^{\bar{0}}$ KJ.mole ⁻¹	ΔH_1^0 KJ.mole ⁻¹	$\Delta H_1^{\bar{0}}$ KJ.mole ⁻¹	ΔS_1^0 J.mole ⁻¹ . K ⁻¹	$\Delta S_1^{\bar{0}}$ J.mole ⁻¹ . K ⁻¹
0.0035	5.7828	1.7548	-4.128.80		5.36029		33.53	
0.0034	6.2480	1.8322	-4.463.24		5.36115		33.53	
0.0033	6.9294	1.9357	-4.876.30	-4.86311	5.28339	5.29658	33.53	33.53
0.0031	7.3843	1.9993	-5.202.74		5.29226		33.53	
0.003	8.1820	2.1019	-5.644.48		5.18581		33.53	
$\frac{1}{T}$	$K_2 = \frac{A_3 \cdot \alpha_1}{A_1 \cdot \alpha_3}$	lnK ₂	ΔG_2^0 KJ.mole ⁻¹	$\Delta G_2^{\bar{0}}$ KJ.mole ⁻¹	ΔH_2^0 KJ.mole ⁻¹	$\Delta H_2^{\bar{0}}$ KJ.mole ⁻¹	ΔS_2^0 J.mole ⁻¹ . K ⁻¹	$\Delta S_2^{\bar{0}}$ J.mole ⁻¹ . K ⁻¹
0.0035	0.2023	-1.5980	3.75987		1.741823		48.26	
0.0034	0.2894	-1.2399	3.02039		1.716139		48.26	
0.0033	0.3956	-0.9273	2.33600	2.43825	1.695961	1.706187	48.26	48.26
0.0031	0.5006	-0.6919	1.80051		1.690676		48.26	
0.003	0.6221	-0.4746	1.27450		1.686337		48.26	

values 12.273 and 0.796 respectively. TABLE 6 showed the thermodynamic parameters for K₁ and K₂ equilibrium constants for tautomerism reactions.

This concluded the following points :-

- The negative signs of $\Delta \bar{G}_1^{\bar{0}}$ means tautomerism reaction as expressed by K₁ equilibrium constant occurred spontaneously. Mean while $\Delta \bar{H}_1^{\bar{0}}$ and $\Delta \bar{S}_1^{\bar{0}}$ of positive signs mean that reaction happened in an endothermic process and accompanied by an increase of random.
- The positive sign of $\Delta \bar{G}_2^{\bar{0}}$ of K₂ equilibrium constant means that reaction occurred in non spontaneous process. The positive signs of $\Delta \bar{H}_2^{\bar{0}}$ and $\Delta \bar{S}_2^{\bar{0}}$ were similarly explained as in the previous paragraph.



Scheme 2

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