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Thermodynamic Study of the Tautomerism Schiff Base derived from para-aminophenol by Catalyst

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Ortho-Methoxybenzylidene-para-hydroxyaniline, meta-Methoxybenzylidene-para-hydroxyaniline, para-Hydroxybenzylidene-para-hydroxyaniline as numbered 1,2,3 were synthesized by standard methods. The chemical structures of these compounds were confirmed previously by physical methods in addition to chemical tests. The tautomerism reactions of the above mentioned imine in this paper required the measurements of ultraviolet absorption spectra of imines under study. The tautomeric equilibrium constants of the Schiff bases under study were determined at five different temperatures ranging from 10°C to 50°C, facilitating the estimation of the equilibrium constants of the tautomerism reactions and the thermodynamic functions, namely ΔG, ΔH, and ΔS, of the Schiff base tautomers.

Introduction

Imine chemistry includes two main groups: schiff bases and oximes. The first are organic compounds formed by the union of the nitrogen atom in the primary amine with the carbonyl group in various aldehydes or ketones to form the azomethine group C=N-R R2, which is generally prepared by condensation reaction between the aldehyde or ketone with the primary amine. The azomethine bond is responsible for this biological activity that appears on Schiff bases[1]. Schiff bases are among the compounds that have recently received wide attention due to their diverse applications in various fields of daily life, including agriculture [2] and biological sciences [3,4]. They exhibit a range of biological activities such as antimicrobial [5], antifungal, antibacterial [6], anticancer, antitumor, and cytotoxic effects [7,8], as well as antifertility and enzymatic activities. Several Schiff bases also possess anti-inflammatory, anti-allergic, radical scavenging, analgesic, and antioxidant properties.

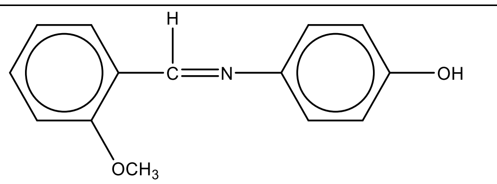
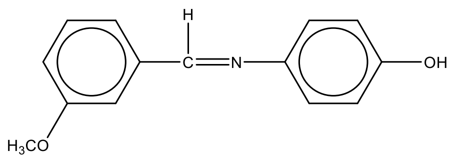
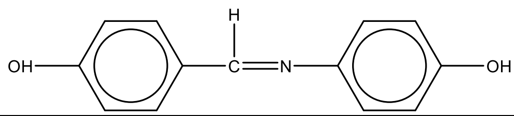
Transition metal complexes of Schiff bases with ligands such as 1,10-phenanthroline and 2,2'-bipyridine are utilized in petroleum refining. Popova and Berova reported that copper plays an important role in liver function, and its levels in blood and urine are associated with pregnancy disorders, nephritis, hepatitis, leprosy, anemia, and leukemia in children. Additionally, Schiff bases are used in various industrial applications as plant growth regulators, stimulants, dyes, and in polymer production [9,10]. Tautomerism was the presence of two or more chemical composition compounds that had the same chemical composition but were different (Combination) isomers and easily transformed between each other.The tautomerism phenomenon was well known in the pharmaceutical field as the presence of more than one tautomer for compounds such as ranitidine andomeprazole [11].

Tautomerism Keto enol is more common among other tautomerism in purine and pyrimidine nucleobases medicines and other types of tutumrier. The N-H tautomers of imidazole and pyrrole are good examples of prototropic tautomerism, wherein the proton moves within the ring. In medicinal chemistry, tautomerism plays a major role in understanding the mechanistic pathways of many life processes, including enzymes and proteins,DNA and RNA[12,13].

Experimental

In medicinal chemistry, tautomerism plays a major role in understanding the mechanistic pathways of many life processes, including enzymes and proteins. All amines (p-hydroxyaniline), aldehydes (O,M-methoxy benzylidene, p-hydroxybenzylidene) and Sodium carbonate used in this study were supplied from BDH and Fuka chemical companies. All the solutions were prepared by weighing the solid with a sensitive balance type using a GR-200, The Ultra.Violet (U.V)spectra of imines were measured by Schimdzo U.V-visible spectra photometer (U.V-1650 pc) water bath model. EyEL4. Type NTT-22opp was connected with the previously mentioned Spectrophotometer.

Table 1. Shows nomenclature and structures of Schiff bases prepared

Com. No.	Nomenclature	Structures
1	o-Methoxy benzylidene-p-hydroxy aniline	
2	m-Methoxy benzylidene-p-hydroxy aniline	
3	p-Hydroxy benzylidene-p-hydroxy aniline	

All Schiff bases under study were prepared by (standard method) [14].

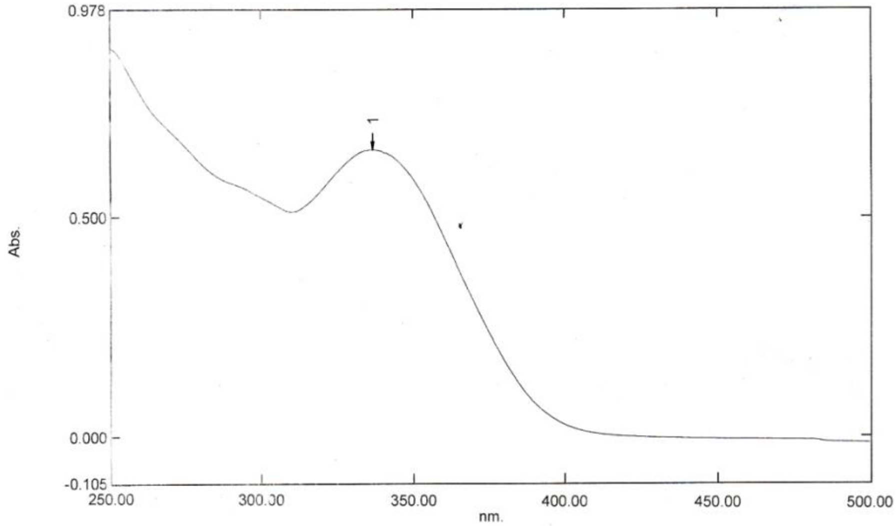


Figure 1. shows the U.v spectrum of Schiff base (2) in ethanol.

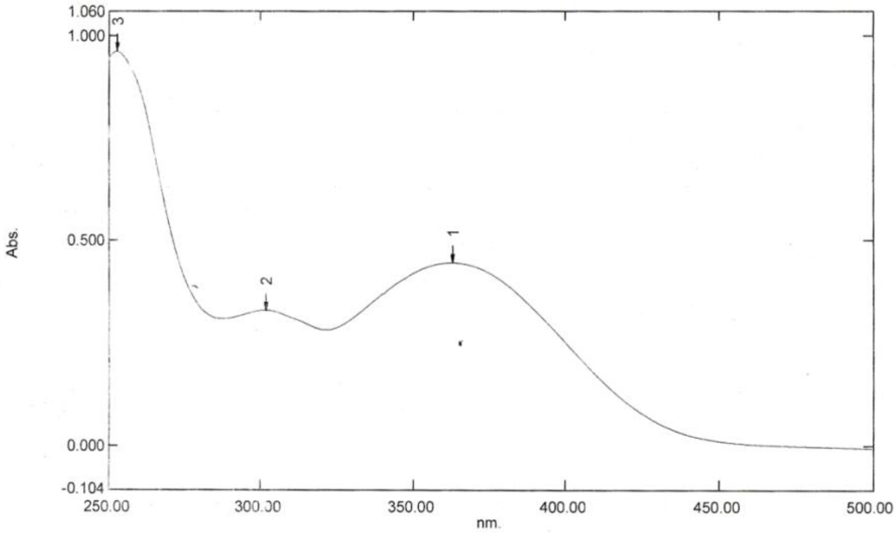


Figure 2. shows the Uv spectrum of Schiff base (2) after the addition (0.5) M of Na2CO3 at room temperature.

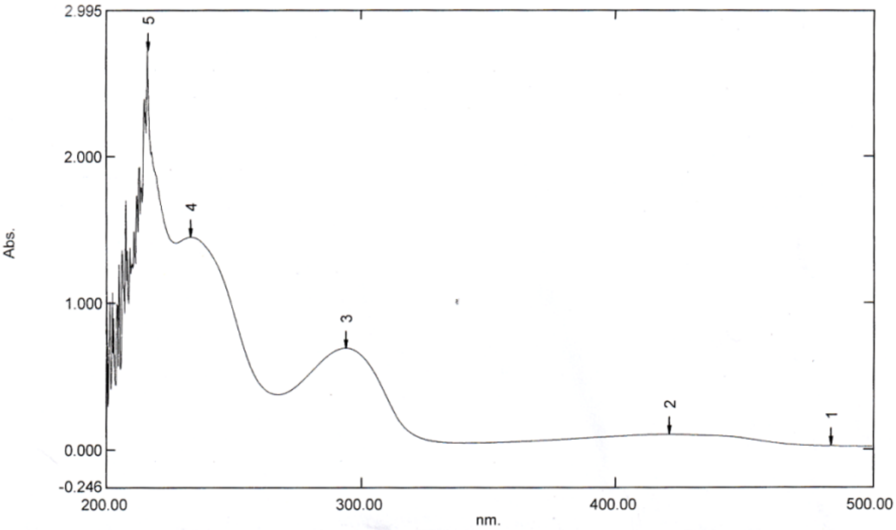


Figure 3. shows the Schiff base (1) after the addition Na2CO3 after the addition (0.5) M of Na2CO3.

Results and Discussion

At the beginning of the study, it was considered important to confirm the occurrence of a tautomeric reaction in the Schiff bases (1–3) under investigation. Therefore, the original electronic spectra of these compounds were recorded before and after the addition of a tautomerization agent (Na_2CO_3). The UV spectra of the prepared Schiff bases were measured in ethanol at room temperature. Schiff bases (1) and (3) each showed two absorption bands, which were attributed to the keto and enol tautomers at wavelengths of 285.8 & 232.4 nm and 252.6 & 215.8 nm, respectively [12]. However, Schiff base (2) displayed a single absorption band at 336.8 nm, which was attributed to the keto tautomer. After the addition of 0.5 mL of 0.5 M Na_2CO_3 to compound (1), its UV spectrum showed three distinct absorption bands at 294 nm, 323 nm, and 216 nm. These bands are attributed to the keto form at the longer wavelength and to the trans- and cis-enol forms at shorter wavelengths, as illustrated in Scheme (1) [15].

This observation confirms that two enol forms (cis and trans) appear at relatively shorter wavelengths alongside the keto tautomers, indicating the occurrence of two processes: a tautomerism reaction followed by an isomerism reaction. These findings are consistent with literature reports [16]. Similarly, the UV spectrum of imine (2), after the addition of 0.5 mL of 0.5 M Na_2CO_3 to a fixed volume (0.2 mL) of the Schiff base, exhibited three bands at 362.8 nm, 301.8 nm, and 252.6 nm. These bands are interpreted as corresponding to trans- and cis-keto forms at higher wavelengths, and the enol tautomer at 252.6 nm. The tautomerism of imine (3) was further investigated using different volumes of the base (Na_2CO_3) with a constant amount of imine (3), and the following results were obtained:

Table 2. Showed the ml. of Na_2CO_3 and wave length and absorbance of Schiff base (3)

ml. of base (Na2CO3)	λ (nm)	A
0.05	359.6	1.005
0.1	359.4	1.069
0.2	352.8	0.84

This means the conversion of enol tautomer was entirely to keto tautomer, which appears at a higher wave length than enol tautomer. The different results of tautomerism affect tautomerism reaction. Many researchers have been clear up for clear influence of equilibrium constant.

For tautomerism reaction of some imine by changing the temperature, standard thermodynamic variants of Schiff base tautomerism reaction were calculated depending on the Hartman method [17]. Therefore for any equilibrium reaction, the equilibrium constant is calculated from the relationship

$$K = \frac{A2}{A1} \cdot \frac{\propto 1}{\propto 2} \quad …….. (1)$$

These good results encourage the researcher to study the thermodynamic functions of keto enol tautomerism. The last was evaluated using standard equations (2-5) in the form:

$$\Delta G = - R\,T\,\ln K \quad ……... (2)$$

$$\ln K = \text{constant} = \frac{\Delta H}{RT} \quad ……... (3)$$

$$\Delta G = \Delta H - T\Delta S \quad ……... (4)$$

The thermodynamic study included electronic spectra at confirmed temperatures between (10 – 50) co

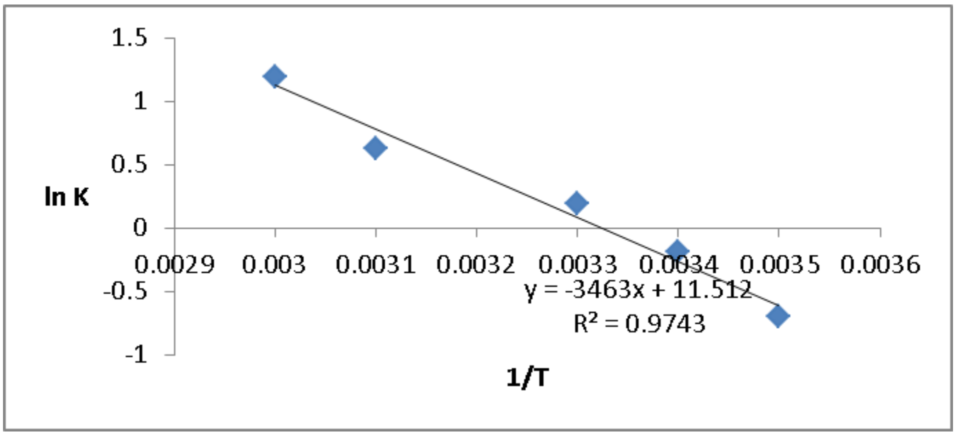


Figure 4. Showed the relationship between (T^{-1}) and lnK in comp. (1)

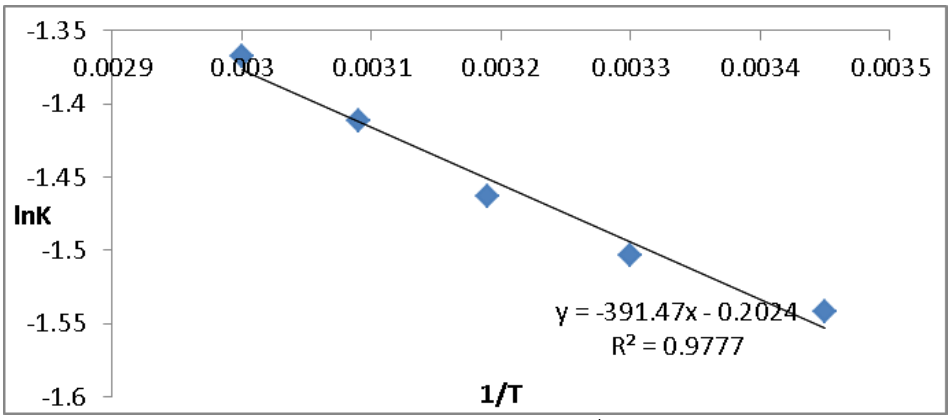


Figure 5. Showed the relationship between (T^{-1}) and lnK1 in comp. (2)

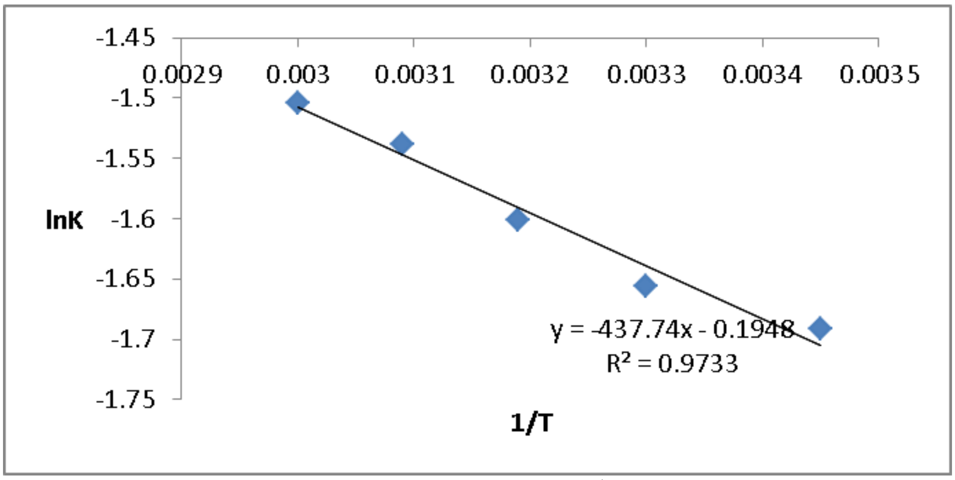


Figure 6. Showed the relationship between (T^{-1}) and lnK1 in comp. (3)

Table 3. Show the equilibrium constants and thermodynamic functions for Schiff bases with Na_2CO_3 1,2 at range (10 – 50) c°.

Com. Num.	T c°	$K = \frac{A2}{A1} \cdot \frac{\alpha 1}{\alpha 2}$	LnK	ΔG	$\Delta\bar{G}$	ΔH	$\Delta\bar{H}$	ΔS	$\Delta\bar{S}$
	10	0.21394	−1.5420	3628.11		3151.89		-1.682	
	20	0.22240	−1.5032	3661.79		3168.75		-1.682	
1	30	0.23146	−1.4633	3686.36	3664.11	3176.48	3154.24	-1.682	-1.682
	40	0.24388	−1.41107	3672.00		3145.30		-1.682	
	50	0.25472	−1.36759	3672.55		3128.78		-1.682	

Com. No.	T c^o	$K=\frac{A3}{A1}\cdot\frac{\propto1}{\propto3}$	lnK	ΔG	$\Delta\bar{G}$	ΔH	$\Delta\bar{H}$	ΔS	$\Delta\bar{S}$
	10	0.18422	−1.69160	3980.10		3521.76		-1.695	
	20	0.19092	−1.65590	4033.77		3559.24		-1.619	
1	30	0.20164	−1.60127	4033.82	4017.95	3543.09	3527.23	-1.619	-1.634
	40	0.21474	−1.53832	4003.14		3496.21		-1.619	
	50	0.22223	−1.50404	4033.98		3515.86		-1.619	

Com. Num.	T c^o	$K=\frac{A2}{A1}\cdot\frac{\propto1}{\propto2}$	lnK	ΔG	$\Delta\bar{G}$	ΔH	$\Delta\bar{H}$	ΔS	$\Delta\bar{S}$
	10	0.475	-0.7031	1654.29		28735.73		95.69	
	20	0.8283	-0.1883	458.29		28477.08		95.63	
	30	1.2133	0.1933	-486.95		28508.37		96.68	95.67
	40	1. 8627	0.6220	-1618.61	-636.38	28333.64	28355.11	95.69	
2	50	3.2791	1.1875	-3188.93		27720.76		95.69	

The positive value of ΔG for equilibrium constant of tautomerism and isomerization reactions in compound (1) indicates that the conversion of the enol form into the keto form is non-spontaneous. This difficulty in conversion suggests the relative stability of the enol tautomer, likely due to intramolecular hydrogen bonding of the H–O–H type and greater resonance aromatic structures [18,19].

For compound (2), the ΔG values for equilibrium constant were positive at temperatures between 10°C and 20°C [20], indicating a non-spontaneous tautomerism reaction within this temperature range. This suggests that the transformation from enol to keto tautomer requires an input of energy. However, at higher temperatures (30°C to 50°C), the ΔG values became negative, indicating that the reaction becomes spontaneous. This is because increased temperature promotes the conversion of enol to keto forms more efficiently.

The enthalpy change (ΔH) of the tautomerism reaction was evaluated using the integrated Van't Hoff equation (Equation 2). Plotting the equilibrium constant (K) against the inverse of temperature (1/T) produced straight lines with R2 range values (0.9777-0.9733) for all compounds studied [21]. The positive ΔH values for compounds (1) and (2) indicate that the tautomerism reaction is endothermic.

The ΔS = S2 - S1, S1 and S2 represent the entropy of enol and keto forms respectively The entropy change (ΔS) for compound (1) was positive [22,23], suggesting that the conversion from the enol to the keto form leads to increased randomness in the system. This may be due to greater opportunities for hydrogen bond formation among the reactant molecules compared to the products, increasing the system's disorder . In contrast, the ΔS values for compound (2) were negative, indicating that the keto tautomer is more ordered than the enol tautomer. This is likely due to the formation of strong hydrogen bonds in the keto form thus it leads to increase association property in it and decreases system randomness and as well as the interactions that occur in the polar solvent (the dipole interaction between donor and acceptor or solute solvent inter action [24,25].

From the above, there are three factors that affect the values of the thermodynamic variables for the tautomerism enol keto and isomerism cis trans reaction in imine 1, 2, which are temperature, the structural form of the imine (hydrogen bond, resonance aromatic structures) and polarity of the solvent[26,27,].

,In conclusion, the thermodynamic study of the tautomerism reactions under investigation is in good agreement with findings reported in similar studies in the literature [28,29].

Conclusion

The study contained effect of Na_2CO_3 and temperature on tautomerism reaction for Schiff base under study at (10-50) c^o. Tautomerism reaction was conducted by using Na_2CO_3 as a catalyst. U.V spectra were used to observed tautomerism phenomena Schiff base by Na_2CO_3, the keto tautomer in Schiff bases under study absorbed at higher wavelength than the enol tautomer of the same compound. The thermodynamic of tautomerism reaction of these Schiff base are estimated and showed the negative and positive value of ΔG and ΔS also ΔH value had a positive sign. These results were discussed in detail.

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