The Influence of pH and Temperature on Tautomerism Reactions of Some Aromatic Mono and Bi Schiff Bases

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Abstract

The aims at investigation the tautomerism reaction of mono and bi aromatic Schiff bases by actions of different values of pH's and temperatures. The pH under study was chosen in a range between 4-10.

Experiments prove the existence of Schiff bases under study, as tautomeric equilibrium mixture of different ratios of keto and enol forms , as well as , the formations of nitrilium and phenoxonium ions in acidic and basic media respectively. Equilibrium constants K for the tautomerism reaction are evaluated at a temperature range between 298-338k. the last shows an inverse relationship between K and T which facilitates the evaluation of thermodynamic parameters. Finally evidence for supporting the tautomerism reaction is mentioned and disussed.

الخلاصة

الهدف من البحث دراسة التفاعلات التوتومرية في قواعد شيف الاروماتية الأحادية والثنائية وذالك بفعل الدوال الحامضية ودرجات الحرارة المختلفة.

تضمنت الدراسة اختيار دوال حامضية بمدى يتراوح بين 4-10. لقد أكدت التجارب تواجد قواعد شيف تحت الدراسة على هيئة مخاليط توتومرية من اشكال الكيتو و الاينول وبنسب مختلفة ، هذا بالإضافة الى تكوين ايونات النتريليوم و الفينوكسونيوم في الاوساط الحامضية و القاعدية على الترتيب . لقد حسبت ثوابت التوازن K بعدة درجات حرارية و في مدى محصور بين 298-338 مطلقة ، و أن القيم لـ K كانت علاقتها عكسية مع درجات الحرارة المطلقة و التي سهلت استخراج المتغيرات الثرموديناميكية . و أخيراً فأن تفاعلات التوتومرية في المركبات تحت الدراسة قد اثبتت و نوقشت.

Introduction

The concept of tautomerism of carbonyl[1,2] , analide[3] and Schiff base[4] had been extensively studied.

The enolization reaction is probably the most discussed type of prototropic tautomerism. The method [1]used for the determination of keto $\rightleftharpoons$ enol equilibrium constants can be classified as chemical and physical , particularly spectroscopic method. In 2004 a new spectrophotometric method [5] had been developed for the determination of trace amounts of Schiff base benzylidene o-hydoxyaniline via coupling with suphanilic acid salt at pH 7.

A few publications[1] concerning the tautomerism of carbonyl compounds in the gas phase are observed in literature. This is due to experimental difficulties. The last encourage Azzouz[6] to deal with tautomerism and thermodynamic study of deoxybenzoin and some related compounds by using the integrated ion current (IIC) curve by mass spectrometry.

Recently , and in our laborotary we have synthesized[7] some Schiff bases derived from salicyladehyde and o-methoxy benzaldehyde with an appropriate primary amines, forming mono and bi base linkages. A prelimenary UV and IR spectral study on these Schiff bases revealed their tautomeric existence in 1,2-dichloro ethane solvent.

As a continuation for the last work , this paper describes the influence of pH and temperature on tautomerism reactions of Schiff bases mentioned.

Experimental

All chemicals used throughoul this work , the synthesis of Schiff bases and their characterization by melting points , UV and IR spectra have been mentioned[7].

Apparatus:

All UV absorption measurements were made by using pye Unicam sp 8000 spectrophotometer using a matched silica cell. It is connected to julabo paratherm pt 40 ps water thermostat. A fixed temperature is obtained through cell compartment by water circulation.

Results and discussion

This investigation deals with studying the experimental factors Affecting the tautomerism reactions in Schiff bases under study , namely the pH and temperature. Table (1) show the nomenclatures , structures and melting points of all mono and bi Schiff bases linkages used in this work. The following division of results are thought to be necessary :-

I. Influence of pH on tautomerism reaction.

It is confirmed from UV and IR spectra in our pervious study[7] that Schiff bases(1,4-6) are able to from a double folds intramolecular hydrogen bondings of the type O-H···N alone or a mixture of O-H···N and N-H···N. In the meantime Schiff bases 2 and 3 can from the mono intramolecular hydrogen bonding of the type O-H···N. These bondings can give additional stabilities[8-10] to such Schiff bases or they are kinetically stable or don't susceptible by hydrolysis[11] cleavage in water- ethanol mixture as known[11] on Schiff basess , especially the aliphatic ones. This encourage the workers to study the influence of pH in arrange 4-10 on tautomerism reactions in Schiff bases summarized as follow :-

1. salicylidene –o-aminoanilin (1).

This compound show three bands in its UV spectra at pH range 4-5. They attributed to nitrilum[12] ion at such acidic range , the keto and enol forms respectively. The wavelengths of these bands are in order of nitrilium ion >keto > enol. At pH 6-7, the nitrilium band is completely disappeared. Finally , when the pH is raised to a range 8-10 , also other three bands are generated.

They are assigned to the formation[12] of phenoxide ion , the keto and enol forms.

2. salicylidene m-amioanline

At pH range 4-7 a three UV bands are also observed. They are reffered to the keto form , the nilrium ion and the enol form and in order of increasing wavelenghths. The intensity of nitrilium ion band is founded to be decreased by elevation of pH. This observation is used here as a confirmation method for assigning the nitrilium ion band.At pH range between 8-10 , only two bands are observed for the keto and enol forms only.

3. salicylidene-p-aminoaniline(3).

This compounds shows only one band in its UV spectra at acidic range as assigned to enol form only. The tautomerism reaction are started at pH range 7-10 and resulted to the formation of enol and keto forms , at shorter and longer wavelengths respectively.

4. Disalicylidene –o-aminoanline.(4)

At pH range between 4-7 , it shows one UV band , with wavelength directly proportional to the pH of the medium as assigned to enol tautomer. Elevation of pH in a range 8-10 , resulted to the appearance of two UV bands as assigned to keto and enol forms.

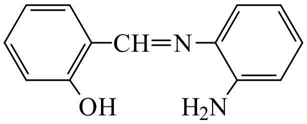
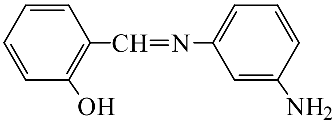
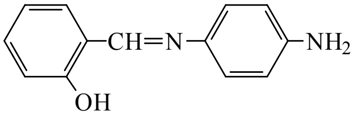
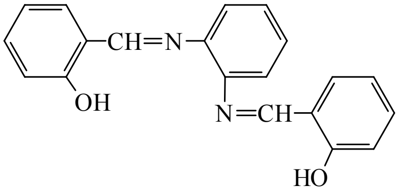
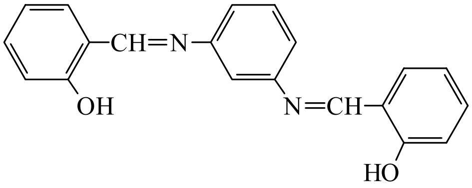
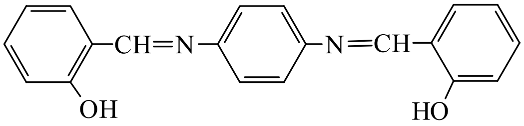
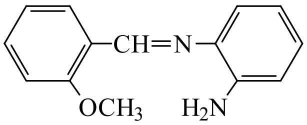
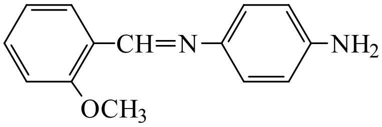
5. Disalicylidene –m-aminoaniline (5).

This molecule shows one UV band at pH range 4-9. The wavelength of the band is increased by increasing pH and assigned to enol form only. Similarly , at pH 10, the molecule shows two UV bands for keto and enol forms.

6. Disalicylidene –p-aminoaniline (6).

At pH range 4-8 the comound shows one UV band for the enol form. The wavelength of the band is directly proportional to pH. An exclusion to the last case is observed at pH 6 and resulted to the formation of two bands as assigned nitrilium ion and enol forms. When the pH is raised 9-10, the compound shows two UV bands for enol and keto forms at lower and longer wavelengths respectively.

Tabel (1) Nomenclatures structures and melting points of imines

No.	Nomenclature	Structure	Melting point (°C)
1	Salicylidene-o-aminoaniline		62-63
2	Salicylidene-m-aminoaniline		84-85
3	Salicylidene-p-aminoaniline		199-200
4	Disalicylidene-o-aminoaniline		165-166
5	Disalicylidene-m-aminoaniline		208-209
6	Disalicylidene-p-aminoaniline		218-219
7	o-Methoxybenzylidene-o-aminoaniline		90-92
8	o-Methoxybenzylidene-p-aminoaniline		105-107

II. Influence of temperature.

Surely , the temperature as known has a great influence on many chemical reactions , as tautomerism[6], formation of hydrogen bonds[13-15] pK_a of benzaldoxime and other[17].

The thermodynamic of tautomerism represents the various energies forms associated with enol keto reversible reaction. These required the evaluation of thermodynamic parameters , namely ΔG,ΔH and ΔS.The last required the evaluation of equilibrium constant for the reaction outlined above from the relation $K=A_{keto}/A_{enol}$,where A_{keto} and A_{enol} are absorbances of keto and enol respectively.The thermodynamic parameters of tautomerism are evaluated from standard equations(1-3) of forms :-

$$\Delta G=-RT \ln K \quad \ldots(1)$$

$$\ln K=\text{const.} - \frac{\Delta H}{RT} \quad \ldots(2)$$

$$\Delta G=\Delta H-T\Delta S \quad \ldots(3)$$

Tables (2) and (3) show the equilibrium constants thermodynamic parameters calculated for the tautomerism reactions of Schiff bases at different temperatures and in 1,2-dichloroethane (1,2-DCE) and ethanol respectively. The plot of lnK versus the inverse of absolute temperature show a straight lines with correlation coefficients range 0.995792-0.999151 and standard error of estimation range 0.005376-0.009947 as evident from statagraph computer programme. A typical plots for the last are show in Fig. (1) for the tautomerism reaction in disalicylidene -o-aminoaniline in solvents 1,2DCE and ethanol..

Tables (2-3) show the thermodynamic parameters calculated and clearly indicate that the sign of ΔG are varied i.e plus or minus or depending on the structure or stability of Schiff base tautomer and the temperature and are highly expected. The positive sign of $\overline{\Delta G}$ as in Tables (2-3) means the nonspontaneous conversion of enol tautomer to keto tautomer. In other words greater stability of enol in Schiff bases compared to their keto forms , possibly by their strong hydrogen bonding ability with solvents mentioned. On the contrary to that the negative sign of ΔG can be interpreted by the greater stability of keto tautomers and the ease of tautomerism process.

The enthalpy ΔH of tautomerism process as calculated from equation (2) by plotting lnK versus T^{-1} with typical plot shown in Fig (1) for the disalicylidene –o-aminoaniline in 1,2-DCE and ethanol solvents. All average $\overline{\Delta H}$ values calculated have a negative signs which means that the tautomerism reaction are exothermic. An exception to that is Schiff (6) which gives a positive ΔH values in 1,2-DCE and ethanol. These abnormalities can be interpreted by assuming two processes happening in a consecutive steps. The first is the deassociation of Schiff base (6) to its monomer which required an absorption of heat ΔH_1 to overcome on hydrogen bondings between reactants stated previously as a main step. The second minor step is the tautomersim reaction which is accompanied evolution of heat $-\Delta H_2$. when ΔH_1 > ΔH_2 so , net $\overline{\Delta H}$ $=\Delta H_1-\Delta H_2$ evaluated has a positive sign. This agrees with experimental findings. Also ΔS are calculated for the tautomerism process in Schiff bases at five different temperatures. These ΔS values for any Schiff base are very close to each other. This means the non dependence of ΔS at a narrow temperature range between (298-328)k. Actually $\Delta S = S_2 - S_1$, where S_2 and S_1 are entropies of keto and enol forms respectively. Mostly as founded here S_1 Should have greater value than S_2. Therefore it is not astonishing to obtain a negative signs ΔS values for the tautomerism reactions founded here in the first five Schiff bases as in Tabels (2-3). This can happen by either the greater hydrogen bonding or the greater solute – solvent interactions of keto tautomers as compared with enols.

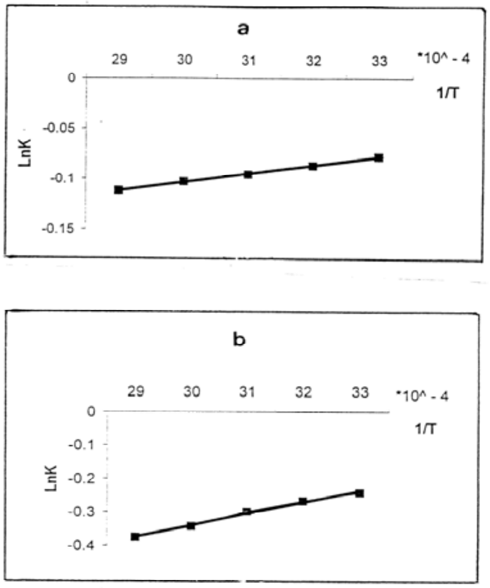


Fig.1 The relationship between lnK versus 1/T for disalicylidene o-aminoaniline in solvents : a- 1,2-DCE b- Ethanol

Table (2) Thermodynamic parameters and equilibrium constants of tautomerism reactions in Schiff bases in 1,2-DCE

No.	Temp.(C°)	lnK	ΔG J.mole^{-1}	ΔS J.mole^{-1} K^{-1}	$\overline{\Delta H}$ J.mole^{-1}	$\overline{\Delta G}$ J.mole^{-1}	$\overline{\Delta S}$ J.mole^{-1} K^{-1}
1	25	0.2350	-582.2	-409.6	-122649.5	-5.7	-385.7
	35	0.0149	-38.2	-398.1			
	45	0.0300	-79.3	-385.4			
	55	-0.070	190.9	-374.5			
	65	-0.171	480.5	-364.3			
2	25	-0.575	1424.6	-10.6	-1729.3	1637.8	-10.6
	35	-0.600	1536.4	-10.6			
	45	-0.618	1633.9	-10.6			
	55	-0.638	1739.8	-10.6			
	65	-0.660	1854.6	-10.6			
3	25	-1.304	3230.7	-21.9	-3300.7	3658.8	-21.9
	35	-1.340	3431.3	-21.9			
	45	-1.378	3643.2	-21.8			
	55	-1.425	3885.9	-21.9			
	65	-1.460	4102.9	-21.9			
4	25	-0.078	193.3	-3.0	-698.0	253.1	-3.0
	35	-0.087	222.8	-3.0			
	45	-0.096	253.8	-3.0			
	55	-0.103	280.9	-3.0			
	65	-0.112	314.7	-3.0			
5	25	-0.138	341.9	-14.8	-4060.0	622.6	-14.7
	35	-0.176	450.7	-14.6			
	45	-0.235	621.3	-14.7			
	55	-0.285	777.2	-14.7			
	65	-0.328	921.7	-14.7			
6	25	-0.050	123.87	-356.9	106228.0	-88.7	-334.3
	35	-0.014	35.8	-345.0			
	45	0.040	-105.8	-333.7			
	55	0.030	-81.8	-323.6			
	65	0.148	-415.9	-313.1			

Table (3) Thermodynamic parameters and equilibrium constants of tautomerism reactions in Schiff bases in ethanol

No.	Temp.(C$^{\circ}$)	lnK	ΔG J.mole^{-1}	ΔS J.mole^{-1} K^{-1}	$\overline{\Delta H}$ J.mole^{-1}	$\overline{\Delta G}$ J.mole^{-1}	$\overline{\Delta S}$ J.mole^{-1} K^{-1}
1	25	-0.730	1808.6	-13.5	-2219.8	2067.6	-13.5
	35	-0.750	1920.5	-13.4			
	45	-0.780	2062.2	-13.5			
	55	-0.807	2200.6	-13.5			
	65	-0.835	2346.4	-13.5			
2	25	-0.020	1424.6	-26.4	-6446.5	1632.5	-25.4
	35	-0.085	1536.4	-25.9			
	45	-0.180	1633.9	-25.4			
	55	-0.240	1713.2	-24.9			
	65	-0.330	1854.6	-24.6			
3	25	-0.440	1090.1	-35.5	-9500.0	1795.1	-35.5
	35	-0.560	1433.9	-35.5			
	45	-0.670	1771.3	-35.4			
	55	-0.795	2167.9	-35.6			
	65	-0.894	2512.2	-35.5			
4	25	-0.243	602.1	-11.5	-2818.4	814.1	-11.4
	35	-0.268	686.3	-11.4			
	45	-0.300	793.2	-11.4			
	55	-0.343	935.4	-11.4			
	65	-0.375	1053.8	-11.5			
5	25	0.400	-991.0	-13.2	-4921.9	-737.3	-13.2
	35	0.350	-896.3	-13.1			
	45	0.278	-735.0	-13.2			
	55	0.212	-578.2	-13.2			
	65	0.173	-486.2	-13.1			
6	25	-0.820	2031.6	-12.7	1745.9	2048.1	-11.9
	35	-0.810	2074.2	-12.4			
	45	-0.750	1982.9	-11.7			
	55	-0.760	2072.5	-11.6			
	65	-0.740	2079.5	-11.3			

Conclusions

1. The occurrence of Schiff bases (1-6) as mono and bi folds intramolecular hydrogen bondings , which gives an additional stability to the molecules.
2. The stability of the molecules stated above facilitate the study of influence of pH in a range between 4-7 on tautomerism process in Schiff bases by aid of UV spectra.
3. A nitrilium ion is observed with some Schiff bases at a pH range 4-7 with enol and keto tautomers. Other Schiff bases show the enol tautomer at moderate acidic pH as well the keto tautomer and the phenoxide ion at higher basic pH.
4. Generally the keto tautomers in Schiff bases absorb UV at longer wavelengths when compared to the same enol tautomers. The wavelengths of keto and enol tautomers are very sensitive to the pH of the medium.
5. A direct relationships are observed between lnk versus T^{-1} for Schiff bases (1-5)with exclusion of Schiff bases (6) and in 1,2-DCE and ethanol solvents.
6. The thermodynamic parameters namely the $\overline{\Delta G}$, $\overline{\Delta H}$ and $\overline{\Delta S}$ calculated confirm that the tautomerism reactions in Schiff bases are exothermic $\overline{\Delta H}$ =- mainly nonspontaneous ($\Delta G^{=}$+) and are accompanied by an increase of order of keto tautomers ($\overline{\Delta S}$ =-) as compared with enol.

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