Thermodynamic Study on Tautomerism of Salicylidene – 3, 4 – dimethyl aniline Via Coupling with Diazotized Sulfanilic Acid Salt.

Ebtehag . Z . Sulyman
Department of Chemistry, College of Education for Girls, University of Mosul, Mosul, Iraq

(NJC)

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Abstract

A new spectrophotometric method has been developed for the determination of trace amounts of Salicylidene – 3, 4 – dimethyl aniline (I) via coupling with sulfanilic acid sodium salt at pH =7.2 . The method is simple, precise and selective for the determination of enol contents of in a range 1.65 to 3.47 ppm.

The study is extended to study a tautomerism reaction of type enol ⇆ keto in molecule (I), beside the thermodynamic study of such reaction in solution state. The results show the enol content in molecule (I), is predominant as evident from the positive value of average ΔG function of value 1.552kJ. mol^{-1}. Moreover, other calculated ΔH and ΔS parametrs have an avarage negative values of about – 9.016 kJ. mol^{-1} and –33.765 J. mol^{-1}. K^{-1} respectively, these support the tautomerism reaction.

الخلاصة

تم في هذا البحث تحضير المركب Salicylidene – 3, 4 – dimethyl aniline (1) وتم التوصل الى تطوير طريقة لتقدير كميات ضئيلة من المركب (1) المتضمنة ازدواج المركب مع ملح حامض السلفانيليك المؤززوت في دالة حامضية متعادلة PH=7.2 .كما توصلت نتائج البحث الى دراسة ظاهرة التوتمرية في المركب (1) من خلال التفاعل keto ⇆ enol وفي الحالة السائلة .اكدت نتائج البحث بان النسبة الانيولية في المركب (1) هي السائدة والمدعمة بقيمة (+ΔG)والبالغة قيمته ا .1.552 kJ كذلك حسبت قيمة (+ΔH) والبالغة قيمتها 9.016 kJ. mol^{-1} – وقيمة (-ΔS)البالغة 33.765− J. mol^{-1}. K^{-1}.، كما ان تفاعل تكوين صبغة الآزو يقوم على أساس ميكانيكية المانح – المستقبل keto ⇆ enol .

Introduction

During the last few years, a considerable attention has been brought to the spectroscopical studies of imines by IR[1-2], UV[3], NMR[4-5] and mass spectra[6-8] , Theoretical studies[9-12] beside other kinetic[13], thermodynamic[14]and association[15]– properties. This is because of their wide application in various fields[13,15,16].

The extent of enol ⇆ keto tautomreism study, in phenol[16] or phenolic Schiff bases[17] have received a great deal of attention by many workers. NMR[18] and UV[19] spectroscopical method had mainly been used for the evaluation of tautomerism equilibrium constants in these phenolic compounds. Various factors were experimentally[3,19] observed in affecting the extent of tautomerism reaction in Schiff bases as, temperature, type of the solvent and pH of the medium.

A little tautomerism study is observed for phenols in the gas state if compared with solution state, due to the experimental difficulties[20,21]. This encouraged Azouzz [22] to use the integrated ion current curve by mass spectrotrmetry to study the tautomerism reaction in some carbonyl and phenol compounds. This study shows that all enolization reaction of Salicylidene– 3, 4 –dimethyl aniline are nonspontaneous as evident from positive value of ΔG function. The negative signs of ΔH and ΔS thermodynamic parameters support the enolization reaction stated before.

The study deals with the development of a new spectrophotometric method for determination of enol in a Schiff base under neutral condition. The thermodynamics of ketonization reaction in such molecule are evaluated. Finally a study of the extent of ketonization reaction in(I)is given and discussed.

Experimetals

Materials and Method

All chemicals used through this work are of Fluka origin. Pure Salicylidene was obtained by distillation of commercial sample under reduced pressure. Its boiling point is 197°C at 20 mm Hg[23].

The following chemicals are used without further purification as o-amino phenol, sodium nitrite, sulfanilic sodium salt and sodium bicarbonate.

Salicylidene – 3, 4 – dimethyl aniline is prepared by the standard method [24-25] as follows:

In a 100 ml round bottom flask, attached to a reflux condenser, 2.42 gm of the solid 3, 4 dimethyl aniline was placed and dissolved with sufficient methanol. 2.5 ml of in Salicylidene was mixed in the reaction vessel and the final mixture was refluxed for about one hour, cooled filtered and the precipitate washed with about 10ml of methanol. The product has a faint yellow color, m. p. = 77-79°C. The IR spectrum of the product shows the following peaks, 3390cm^{-1}, 1660-1645 $cm^{-1}$and 1615 cm^{-1} They are assigned to the phenolic group, the azomethine group and the aromatic structure, respectively.

Stock reagents

$5x10^{-3}$M of diazotized sulfanilic acid is prepared by literature[26] procedure, cooled at 5°C diluted to $2x10^{-3}$M.

$2x10^{-3}$M Salicylidene–3, 4– dimethyl aniline or phenol are prepared by dissolving 0.0418 g and 0.0188 g of these materials respectively per 100ml ethanolic solution.

0.1M $NaHCO_3$ was prepared by dissolving 0.84 g of $NaHCO_3$ per 100ml of water.

Determination of enol in Salicylidene–3, 4–dimethyl aniline or phenol alone

1-Solution state

To a series of 50ml volumetric flasks, transfer an aliquot of 0.1ml of stock ethanolic dissolving 0.0418g and 0.0188 g of these materials respectively per 100ml ethanolic solution.

or phenol.

Add the required ml'**s** of sulfanilic acid and the stock solution of $NaHCO_3$ till pH=7.2, and dilute to the mark with distilled water. Mix the solution and allow the reaction to stand for the required time. Measure the absorbances against the reagent blank solution using 1cm cells. A summary of optimization conditions is shown in Table 1.

Determination of enols in a mixture of Salicylidene–3, 4–dimethyl aniline and phenol

A similar procedure is used to that stated before, by using 0.1ml each of dissolving 0.0418 g and 0.0188 g of these materials respectively per 100ml ethanolic solution.

and phenol. The measurements of the absobances are made against the reagent blank at optimum conditions is shown in Table 1.

Instruments

Absorbance and spectral measurements are performed on a Pye-Unicam SP 3000 UV double beam digital spectrophotometer using 1cm optical silica matched cells.

The IR spectrum of the solid Salicylidene–3, 4–dimethyl aniline is measured by KBr disc using Pye-Unicam SP 1100 spectrophotometer.

Results and Discussion

The free energy[27] of ketonization of phenol had been estimated to be 18.6 Kcal. mol^{-1}, corresponding to K_t =[enol] / [keto] = 10^{14} at 25°C, making it impossible to determine the equilibrium concentration of keto of phenol by direct methods. This indicates that phenol exists nearly in a 100% enol form[27-28] and can be used as internal standard in the determin-

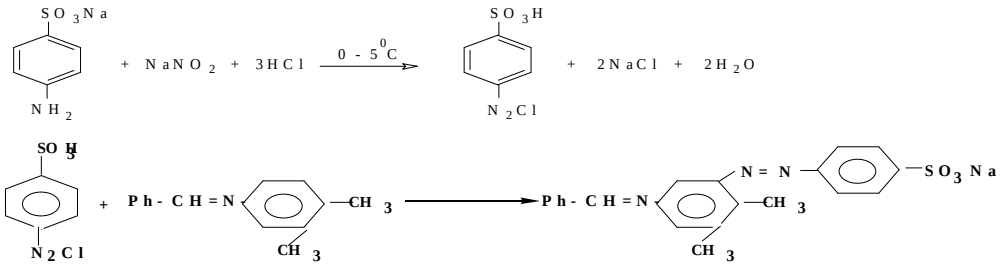
ation of enol ⇆ keto forms of dissolving 0.0418 g and 0.0188 g of these materials respectively per 100ml ethanolic solution.

, using a standard addition method[25].

The extent of enol ⇆ keto form equilibrium forms in phenolic compounds is a pH dependent[29-30]. In a recent study[31] and in our laboratory, it is proved that the most stable favorable form of phenol is enol, under acidic condition. This agrees with the greater stability of aromatic structure of phenol. On the contrary to that, the keto form of phenol is predominant under basic conditions.

One of the problems facing chemists for a longtime, is the ease of tautomerization reaction of phenols or phenolic compounds under the action of acid-base catalysts[20]. To avoid the acid base catalyzed tautomerism of phenol, it is of great importance to study the tautomerism reaction in Salicylidene–3, 4–dimethyl aniline at neutral condition i.e pH = 7.2 The benefit of such study is to study the real tautmerism reaction taking place in Salicylidene–3,4–dimethyl aniline under ordinary conditions. In other words, the catalysed tautomerism reaction is completely omitted.

The most sensitive and generally applicable method[32] for trace quantities of phenol is the coupling with diazotized aromatic amine yield a colored azo dye. So the reaction of Salicylidene–3,4–dimethyl aniline with diazotized sulfanilic acid passes through the following steps.



A similar reaction is occurred with diazotized sulfanilic acid and phenol alone. Obviously the optimization conditions for the determination of enol content in Salicylidene–3, 4–dimethyl aniline are of great importance. The result obtained from such a study is shown in Table 1.

Table 1 shows that the diazotized method for the determination of enols content in the mixture of Salicylidene–3, 4–dimethyl aniline and phenol is selective[30]. This is due to the difference in optimal wavelengths of azo complexes formed by the reaction of Schiff base and phenol with sulfanilic acid, with a $\Delta\lambda_{max}$ value as: $\Delta\lambda$ = 482 nm – 411=72 nm. Moreover, the method is found to be simple, satisfactory and comparable[28, 32].

The thermodynamics of tautomerism in Salicylidene–3, 4–dimethyl aniline are studied by measuring the tautomerism equilibrium constant at a range of the temperatures between (288–338)K. The result obtained is tabulated in Table 2.

It is clear from Table 2 that all equilibrium constant values of ketonization reaction are less than unity, and inversely proportional to absolute temperatures. In other words, the extent of keto form in the Schiff base is less than its enol form. This is highly accepted, since enol form has a greater stability by its resonance aromatic structure over its keto form. Another confirmation of the smaller predominant structure of keto is obtained from the positive value of ΔG thermodynamic function. The Gibbs free energy ΔG is calculated from equation (1) of the form :-

$\Delta G = - RT \ln K$……(1)

This indicates that ketonization process in the Schiff base is non-spontaneous. The heat of ketonization reaction in Salicylidene–3,4 –dimethyl aniline is evaluated by using Vant Hoff equation of the form as in the equation (2):-

$\ln K$ = constant $- \Delta H/RT$ ……..(2)

the inverse of absolute temperature using statgraph programme as shown in Fig. 1. The plot shows the straight line of slope equal 873.3899, intercept value equal -4.0613, correlation coefficient 0.984877 and standard error 0.00988721. The calculated heat of ketonization ΔH values, listed in Table 2 has negative signs with a range of values near to –8.9 – – 9.0 kJ. mol^{-1}. This means that ketonization process is exothermic. In addition to that, the ΔH values are comparable with literature[20]. The entropy from the standard equation (3) of a form:-

$\Delta G = \Delta H - \Delta S$ ……(3)

The entropy of ketonization is listed in Table 2 has a value of about 33.7 J. $mol^{-1}.K^{-1}$. In otherwords, ketonization is directed toward less random process. This can happen either with higher salvation[3] of keto form or with molecular association of keto form by dipole– dipole[33] .

Conclusions

The possibility of enol enol ⇆ keto keto tautomerism reaction in

Salicylidene–3, 4–dimethyl aniline is achieved by the development of a new spectrophotometric method for the determination of enol content using a diazotized sulfanilic acid sodium salt. The advantage of the diazotized coupling method is twofold as follows:
1-It is simple, precise and selective.
2-It permits the evaluation of real equilibrium constant exerted in Salicylidene–3, 4–dimethyl aniline at neutral condition, the side catalysed[20, 29-30] acid-base tautamerism reaction is completely omitted.

The tautomerism reaction of Salicylidene–3,4–dimethyl aniline in solution state is confirmed from the evaluation of ΔH and ΔS thermodynamic functions[20], which have average values of –8.9 – – 9.0 kJ. mol^{-}and 33.7 J. mol^{-1}. K^{-1} respectively. In addition to that, the tautomerism process is nonspontaneous as evident from the positive signs of ΔG thermodynamic parameter which has a value of 1.552 kJ. mol^{-1}. This is highly accepted, because a greater stability is expected for the enol form by its greater resonance aromatic structures. Hence, conversion of enol tautomer to keto form is regarded to be unfavorable process. This will reduce the possibility of occurrence of tautomerism reaction stated above.

Table 1: Optimization condition for quantitative determination of enol in Salicylidene–3, 4–dimethyl aniline at (I), phenol (II) and their mixture (III).

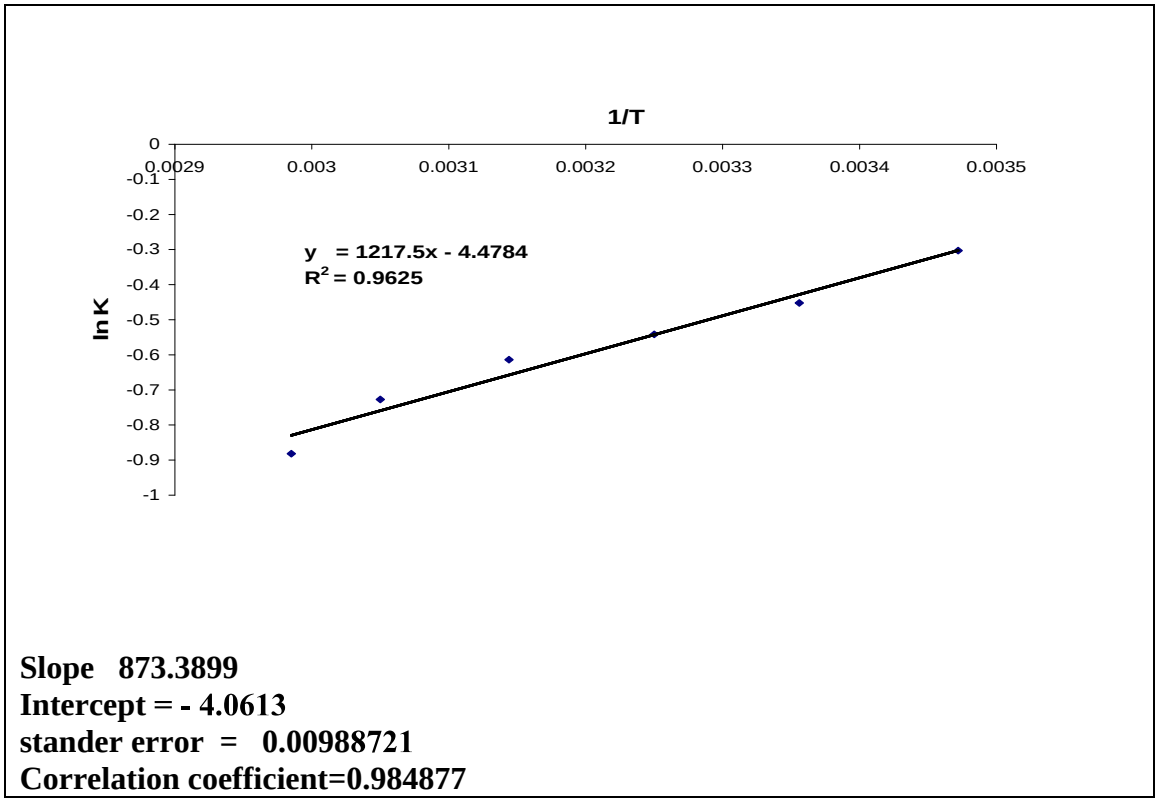
Parameter [a]	Optimum condition
(I)	
1-Volume of stock Schiff base	0.1ml
2-Volume of excess sulfanilic acid	1.5ml
3-Volume of $NaHCO_3$	2.0ml
4-development time	35 min.
5-Stability period	20 min.
6-Wavelength of colored complex	482 nm
(II)	
1-Volume of stock phenol	0.1ml
2-Volume of excess sulfanilic acid	1.7ml
3-Volume of $NaHCO_3$	2.0ml
4-development time	25 min.
5-Stability period	25 min.
6-Wavelength of colored complex	411 nm
(III)	
1-Volume of stock of each Schiff base and phenol mixture	0.1ml
2-Volume of excess reagent	3.8ml
3-Volume of $NaHCO_3$	4.0ml
4-development time	43 min.
5-Stability period	43min.
6-Wavelength of colored Schiff base complex	482 nm
7-Wavelength of colored phenol[b] complex	411 nm
8-Working range of Schiff base	1.65 to 3.47 ppm
9-Molar absorptivities of Schiff base and phenol respectively	20000 and 18970 in arbitrary unit

a means per 50ml total volume

Table (2) Thermodynamic of enol–keto tautomerism of Salicylidene–3, 4–dimethyl aniline at pH=7.2

T(K)	Tautomerism constant (K)	LnK	ΔG J. mole^{-1}	ΔH J. mole^{-1}	ΔS J. mole^{-1}. K^{-1}
288	0.8077	–0.3031	725.752	– 8998.75	– 33.765
298	0.6363	– 0.4519	1119.614	– 8942.54	–33.765
308	0.5817	– 0.5417	1387.137	– 9012.68	–33.765
318	0.5413	– 0.6136	1622.267	– 9115.20	–33.765
328	0.4833	– 0.7270	1982.523	– 9092.60	–33.765
338	0.4141	–0.8816	2477.412	– 8935.37	–33.765

ΔG = 1552.450 J. mole^{-1}.
ΔH = – 9016.19 J. mole^{-1}.
ΔS = – -33.765J. mole^{-1}. K^{-1}.



Slope 873.3899
Intercept = - 4.0613
stander error = 0.00988721
Correlation coefficient=0.984877

Fig(1): Plot of lnK versus the inverse of absolute Temperature of to a tautomerism reaction of Salicylidene–3, 4– dimethyl aniline

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