Kinetic and thermodynamic study on tautomerism of dyes formed by reactions of aromatic imines with diazotized sulphanilic acid

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Received: 24ᵗʰ November, 2010 ; Accepted: 4ᵗʰ December, 2010

ABSTRACT

The diazotization coupling reactions were carried out by reactions of salicylidene aniline (SA) and salicylidene-4-aminoaniline (S-P-AA) with diazotized sulphanilic acid at optimal conditions. At pH 9, a reverse calibration curves from theortical and practical point of view for these imines were observed at 30 and 15 minutes respectively from the beginning of reactions. These were due to the side reactions or tautomerism of dye under basic medium. The tautomerism reaction order was found to be of pseudo first order with respect to imines, the last were supported by thermodynamic method, which showed that the tautomerism reactions were spontaneous ($\Delta G° = -$) or nonspontaneous ($\Delta G° = +$), endothermic ($\Delta H° = +$) and were accompanied by an increase of entropy ($\Delta S° = +$). The average recoveries for the determination of trace amounts were 99.3% and 100.38% for S-P-AA and SA respectively and precision (RSD) was less than 6.3%. The kinetic method was found simple and fast during determination of imines under study.   © 2011 Trade Science Inc. - INDIA

INTRODUCTION

During the last years, a considerable importance had been paid to the spectroscopical studies of imines by UV[1,2], IR[3,4] and mass[5] spectra, beside other kinetic[6] and thermodynamic[7] studies.

Azzouz[8-11] et al. had given a special attention to the thermodynamic of tautomerism of deoxy benzoin[8] with some related compounds, phenolic Schiff base[9] and some aromatic mono and bi Schiff bases[10]. In these studies the enthalpies and entropies changes (ΔH and ΔS) had a negative signs. Converesly, in imines[11] derived from 2-hydroxyl-1-napthylaldehyde ΔH values were possessed a positive sign, whereas ΔS signs re-

main as stated before. The signs of ΔG parameter were varied from positive or negative values depending on the value of equilibrium constant for tautomerism reaction.

During the last few years ago, some workers had applied the kinetic method for the quantitative determination of aromatic amines[12,13], free vanadium[14] (IV) and (V), Hg – phenylacetate[15], copper(II)[16] and 2-methyl-1,4-napthoquinone[17]. Most of these determinations as found to be applied to micro gram or nano gram amounts of substance, sensitive and rapid.

In the last years, some workers had used the diazotization reaction for quantitative determinations of 4-amino antipyrine[18], aniline[19] and 1-napthylamine[20]. When this reaction was applied to imines such as

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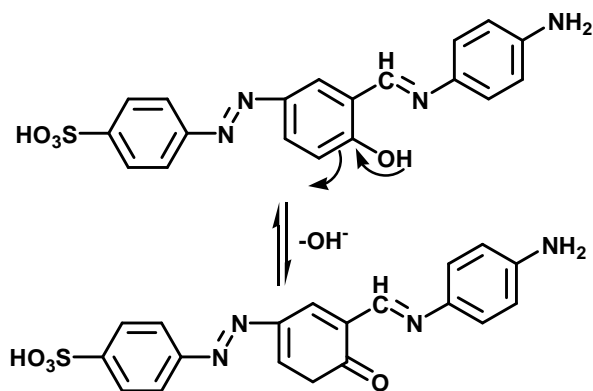
Scheme 1 : Mechanism for enol – keto tautomerism of dye S-P-AA

salicylidene-p-amino aniline (S-P-AA) and salicylidene aniline (SA), the results collected were unencouraging. This arise our curiosity to increase experimentation in the direction of kinetic.

The study explained the main reason for the failure determination of imines under study by the usual spectrophotometric method.

Finally a confirmation of the kinetic study was performed by thermo dynamic study. All thermodynamic parameters collected $\Delta G°$, $\Delta H°$ and $\Delta S°$ for enol $\leftrightarrows$ keto tautomerism of dyes were discussed.

EXPERIMENTAL

Reagents and chemicals

All chemical were supplied form Fluka or BDH companies. They were used as supplied.

S-P-AA and SA imines were synthesised by standard method[21] They had a melting points of 217-220°C and 50-52°C respectively.

The 15×10^{-3} diazotized sulphanilic acid (DSA) was prepared by standard method[22]. This was accomplished by mixing 0.25959 of sulphanilic acid, 50ml of distilled water. Add 2ml of 11.8M hydrochloric acid. The mixture was cooled in a range 0-5°C, followed by addition of 0.1035g $NaNO_2$. Mixing and dilution of the mixture to 100 ml. DSA should be stored in a dark bottle and can be used after 1 hour from preparation. A minium 7 stability days were reported[23] for DSA.

A 4.0×10^{-3}M S-P-AA and SA solutions were prepared by dissolving 0.01g of imines in 5-10 ml of absolute ethanol. The mixture was diluted to 100 ml by the same alcohol.

TABLE 1 : Optimal conditions for dyes formation

No.	S-P-AA dye	λnm enol	λnm keto	Temp. °C
1	3 ml. 1M NaOH + 3 ml. 0.015M DSA + 1 ml. 0.0004M S-P-AA	398	530	40

	SA dye	λnm enol	λnm enol	Temp. °C
2	1 ml. 0.0005M SA + 4 ml. 0.01M DSA + 1.5 ml.1M NaOH	382.5	528	40

TABLE 2 : % Recovery and (RSD) for imines dyes

Imines	Amount added (ml)/(μg)	Amount found (ml)/(μg)	Recovery* (%)	Average recovery (%)	RSD* (%)
S-p-A-A	1.6	1.56	97.50		5.00
	3.2	3.28	102.50	99.33	0.13
	5	4.90	98.00		6.25
SA	2.4	2.29	95.42		0.35
	3.2	3.37	105.31	100.38	1.20
	4.8	4.82	100.41		1.73

*Average of four determinations

Kinetic study

The dyes formation at optimal conditions was accomplished according to the following procedure per 25 ml as in TABLE 1.

The kinetic of decay dyes were followed by measuring absorbances of enol at time indicated later.

The temperature controlled during kinetic was achieved by immersing the silica cells in a small beaker containing water taken from thermostat at 40°C. The beaker assembly was hold with clamp and wholly immersed in water bath, near the spectrophotometer. Absorptions for enol form of dyes were collected at wavelength cited above, during a periode of about 2 hours.

Thermodynamic study

The temperature controlled during this study was accomplished by using a similar procedure stated in kinetic study. Absorbances of keto and enol forms of anydye were collected at wavelengths cited above. Equilibrium constants K for tautomerised dyes were collected at temperature range of 313-328° K.

Instrumentation

All absorption measurements were made on a computerized double beam Schimadzu UV 1650 pc. A

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TABLE 3 : Sigma constants for NH$_2$ and OH groups

Functional groups	Sigma at para position σ_p	Sigma at meta Position σ_m
NH$_2$-	0.66-	0.16-
OH-	0.37-	0.121+

matched silica cells of dimensions $1\times1\times3$ cm^3 were used.

The temperature was controlled during this study, by using a water bath BS-1 Lab.

Electrothermal melting point apparatus was used in measurement of melting points of Schiff bases.

RESULTS AND DISCUSSION

The UV absorption spectra of dyes formation were shown in figure 1. Following the absorbances with time for the dye formed from imines S-P-AA, showed the appearance of two bands at wavelengths 398nm and 530nm. The absorbance of the first band was increased up to 30minuts, then started to decay thereafter. The absorbances of the second band increased with increasing time tell equilibrium was attained as in figure 1. Similarly, SA dye showed two bands at 382.5nm and 528nm with similar result as above, or in a direction of increasing absorbance with the first band up to 15 minutes, then a decay was happened suddenly, while a simultaneous increased of absorbances of the second band as in figure 1.

Actually the decay of absorbance seen above or the side reactions occurred during dye formation of S-P-AA and SA were started at times more than 30 minutes and 15 minutes respectively. Upon measuring the pH of the media of dyes formations at optimal conditions showed values of 12.1 and 10.2 minutes for imines S-P-AA and SA respectively. At such strong basic media, the following side reactions were expected:-

The zwitter ion formation

As known zwitter formation[24] was happened to o, m and p-amino phenols. Typical example was the zwitter ion happened in p – aminophenol as in the reversible reaction 1.

This reaction had a similar structure to S-P-AA or a near closed structure to SA. The expected zwitter ion formation in SA resulted to the formation of phenoxide-nitrilium[25] ion.

The zwitter ion formation in imines S-P-AA and
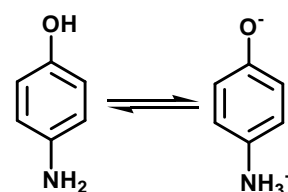
Reaction 1 : Zwitter ion formation

SA were examined by measuring and comparing the UV absorption spectra of imines stated, before and after addition of successive amounts of NaOH as shown in figure 2.

The last spectra showed the appearance of bands at longer and shorter wavelengths as compared with original spectrum. The longer wavelength absorption for imine S-P-AA dye after addition of a base was in contradiction to zwitter ion formation, but the shorter wavelength agreed[24]. Also the workers here did not expect the formation of zwitter ions in dyes S-P-AA and SA, due to the similarity in their structures. Therefore, the idea of zwitter ion in dyes stated above was no longer to be considered.

Enol - keto tautomerism

More than tautomers can be expected for the dyes. The dyes mentioned before contain a phenolic group. As known in literature[26] by 1,3 shift rule the conversion of phenolic group to its more stably keto form under basic condition. This was in our expection, or the enol forms of dyes were converted to their keto forms according to the following equation.

This was in full agreement with tautomerism[27] reactions happened in o- hydroxybenzlidene aniline and o- hydroxynapthylidene aniline. The keto tautomers in dyes were highly confirmed in this study by their longer wavelenghth absorptions[11,28] as compared with enol as in figure 1 and with keto tautomers of o-hydroxy-1-napthylaldehyde[11] and hydroxy benzylidene 2-amino propane[28].

Hence it could be concluded that formation of keto tautomers in dyes S-P-AA and SA, represent, the main side reactions occurred at basic medium.This resulted in obtaining a reverse calibration curve during quatitative study of S-P-AA and SA.

Kinetic study

This study was started by comparing the molar concentrations of dye reactants at optimal condition

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TABLE 4 : Thermodynamic of tautomerism for (a) S-P-AA and (b) SA dyes

(a)

T (K)	T/1 (K)$^{-1}$	Abs. $\lambda_{398.}$	Abs. λ_{530}	K	Ln K	$\Delta G°$ J.mol.$^{-1}$	$\Delta H°$ J.mol^{-1}.	$\Delta S°$ J.mol^{-1}.deg.$^{-1}$
313	0.00319	0.453	0.800	1.81	0.59	-1535.3	123374.2	399.1
318	0.00314	0.406	0.814	6.36	1.85	-4891.1	128676.3	420.0
323	0.00309	0.360	0.827	7.31	1.99	-5344.0	131075.4	422.4
328	0.00304	0.149	0.895	19.08	2.95	-8044.6	135722.4	438.2

(b)

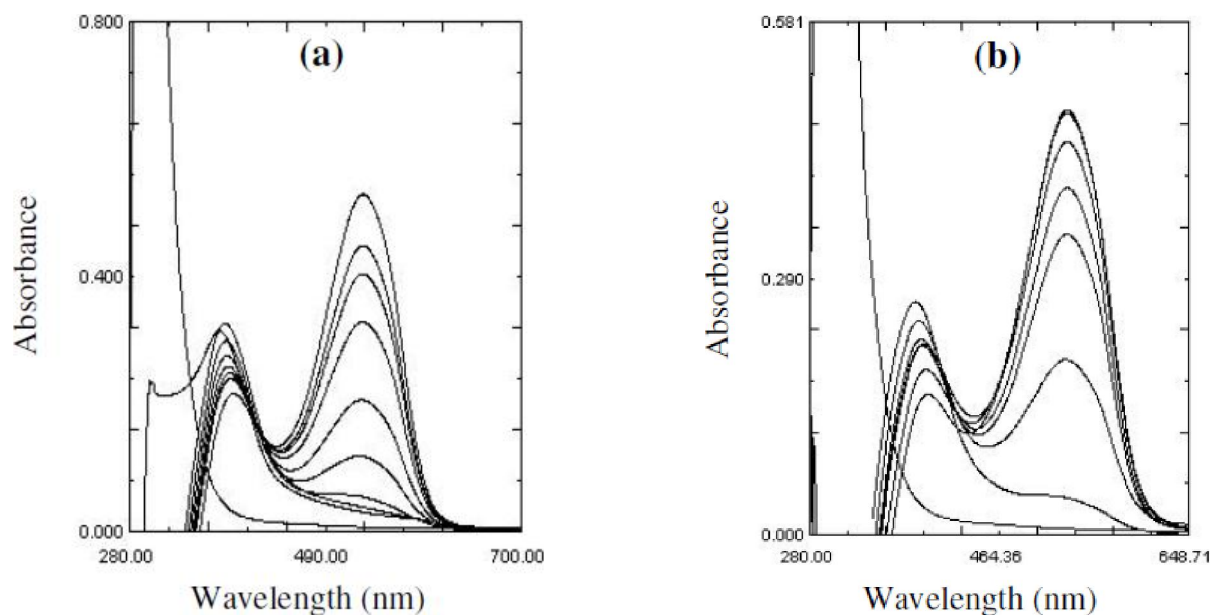| T (K)	T/1 (K)$^{-1}$	Abs. λ_{398}	Abs. λ_{530}	K	Ln K	$\Delta G°$ J.mol.$^{-1}$	$\Delta H°$ J.mol^{-1}.	$\Delta S°$ J.mol^{-1}.deg.$^{-1}$
313	0.00319	0.291	0.198	0.53	-0.63	1639.4	98652.5	309.9
318	0.00314	0.204	0.221	0.84	-0.17	449.5	99012.5	309.9
323	0.00309	0.153	0.345	1.76	0.56	-1503.8	98608.6	309.9
328	0.00304	0	0.346	∞	∞	-	-	-

Figure 1 : The UV absorptions of dyes at different times for: (a) S-P-AA, (b) SA
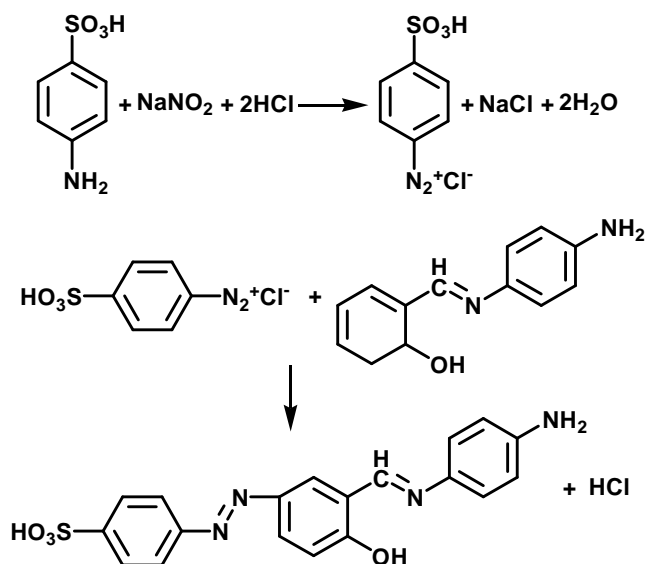
during quantitative determination seen above. This included the following final concentrations:

0.000016M, 0.0018M and 0.08M were concentrations of S-P-AA, DSA and NaOH respectively. Upon division of all last numbers by the lowest concentration of S-P-AA, hence the relative concentrations terms had values of 1:113 and 5000 in order of S-P-AA, DSA and NaOH respectively. These relative numbers confirm the presence of excess concentrations of DSA and NaOH during quantitative study at optimal conditions. Therefore, as a theoretical expectation, the kinetic of tautomerism reactions stated before could have any numbers as a pseudo first order with respect to S-P-AA. Similarly, the dye formed from reaction of SA with DSA and NaOH at optimal conditions had relative concentrations values of 1:80:3000 in order of SA, DSA and NaOH respectively. This also might show a similar order as before.

Order of tautomerism of dyes reaction

In order to evaluate the order of dye reaction with respect to S-P-AA, experimentally, three concentrations of S-P-AA were chosen at optimal conditions of dye formation. A kinetic spectrophotometric method was used in this respect, due to direct relationship between absorbance and concentration, according to Beer – Lambert low.

Figure 2 : Absorption spectra of S-P-AA before (a) and after (b) addition of alkali

The dye reaction included firstly a formation of dyes up to 30 and 15 minutes in imines S-P-AA and SA respectively. A secondly decay reaction was occurred over the times stated.

Kinetic for the decay of enol dyes

This study was started when enol forms of dyes S-P-AA and SA, began to decay at times stated before. This resulted to a gradual conversion of enol form of dye to its keto form at basic medium as in figure 1.

Experimentally, the absorbances of dyes were followed with time stated above at wavelengths 398nm and 382.5nm with respect to imines S-P-AA and SA respectively. A pseudo first order kinetic equation was applied to the decay data of the form:

$$\ln\frac{A_o}{A} = k_1 t \qquad (1)$$

A_o = maximum absorbances of dyes at times 30 and 15 minutes of imines. S-P-AA and SA respectively. A = Absorbance of dye over 30 and 15 minutes in imines S-P-AA and SA. k = Rate constant for the decay dye. t = Time in minutes.

Figure 3 and 4 showed the kinetic plot of tautomerism reactions of dyes S-P-AA and SA at 40°C and for three and two concentrations of imines. Figure 3 showed three straight lines of R^2 range values 0.959-0.9726 of concentrations 7.5×10^{-6}M, 8.86×10^{-6}M and 28.3×10^{-6}M of imines S-P-AA with equal slopes of a value 0.003min^{-1}, which represent the rate constant for the decay of dye. These plots mean that the decay data agreed well with first order reaction and did not de-
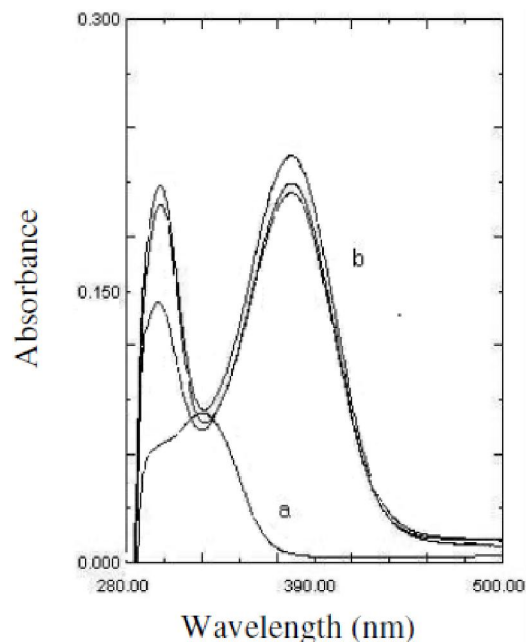
pend of concentrations of S-P-AA. This was an individual case for pseudo first order kinetic.

Also figure 4 showed two lines of R^2 range value (0.927-0.981) for kinetic plot for concentrations 7.5×10^{-6}M and 22.64×10^{-4}M for SA dye with equal slopes or with a rate constant value of 0.003min^{-1}. These observations added other support that rate constants of decay for S-P-AA and SA dyes were equal.

Application of kinetic

The decay kinetic had been applied successfully for the determination of S-P-AA and SA. Accordingly three concentrations of S-P-AA and SA were chosen, the result as indicated in TABLE 2 are accurate, recovery % 99.3% for S-P-AA and 100.38% for SA and RSD values less than 6.3% for S-P-AA and less than 1.8% for SA. Upon using a pseudo first order in the determination of S-P-AA and SA, the rate constant was substituted by 0.003min^{-1} for S-P-AA and SA, t was given after 30 minutes of S-P-AA and after 15 minutes for SA. The remaining absorbance (a-x) from equation (1) was calculated experimentally for each imine. Finally, the initial absorbance (a) was calculated for each imine from equation (1) and their initial concentration were found from calibration curve prepared in this study.

The structure of dyes

Diazotization coupling reaction was happened
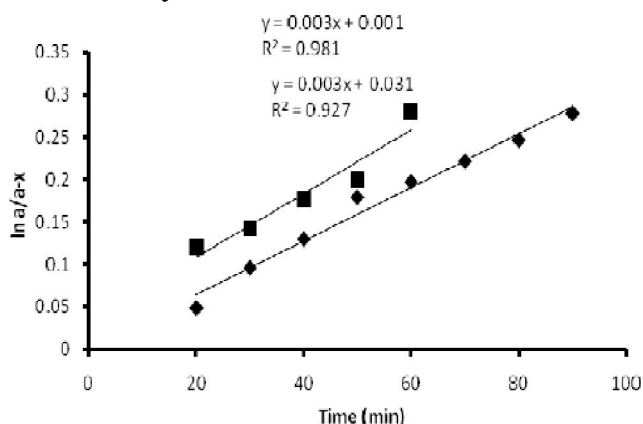
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Figure 3 : First order kinetic plot for tautomerism reaction of dye S-P-AA at 40°C
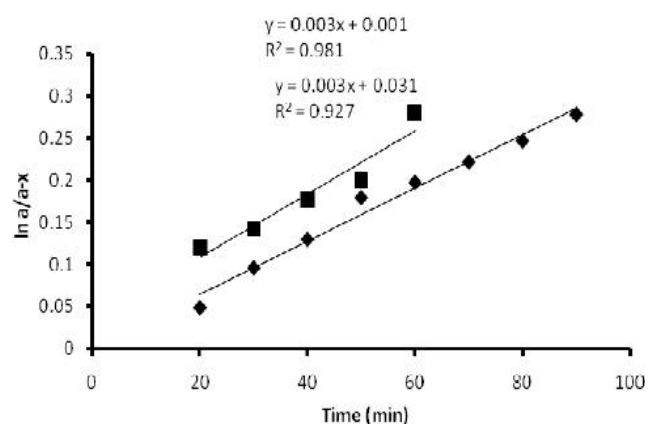

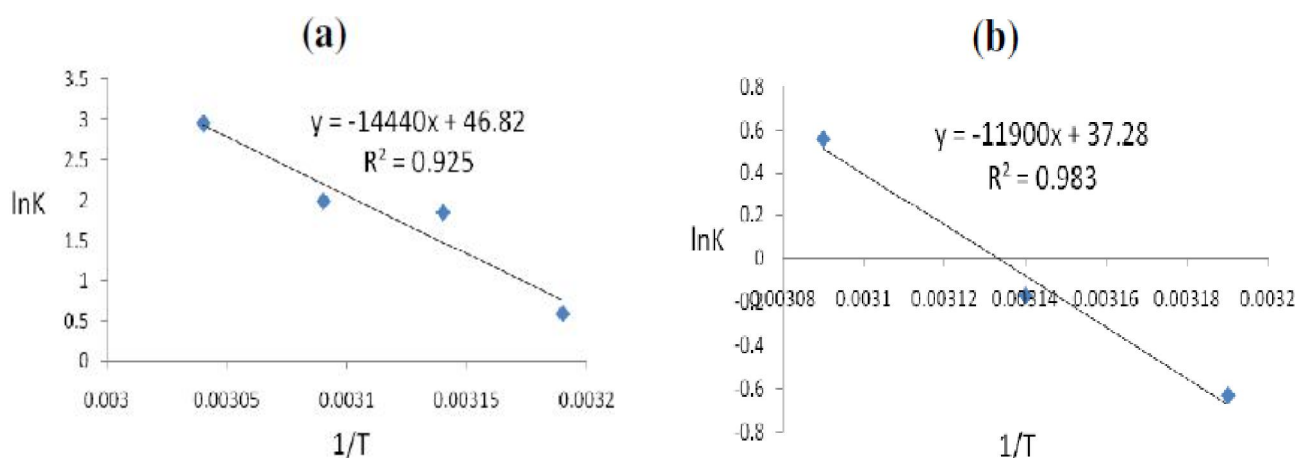**Figure 4 : First order kinetic plot for tautomerism reaction of dye SA at 40°C**

Figure 5 : vant Hoff plots for tautomerism of dyes from (a) S-P-AA and (b) SA

through the following steps:

1) Conversion of sulphanilic acid to diazo sulphanilic acid
2) Coupling the diazotized sulphanilic acid with imines S-P-AA and SA
3) The dye reaction was happened through donor–acceptor mechanism[29]. In other words S-P-AA and SA were donors while the diazo sulphanilic acid regarded as acceptor as in literature[22], the worker had noticed that azo group entered the donor molecule at ortho or para positions with respect NH_2 or OH groups
4) Examination of structure S-P-AA, showed the presence of both and OH and NH_2 groups, in order to confirm the proper position of entering the azo group in S-P-AA, this led to introduce the sigma constants taken from Hammett equation(30) as in TABLE 3

   The negative signs of sigma constants σp for NH_2, OH and σm for NH_2 mean that these groups were elec-

tron donor. Their presence increased the electron density on aromatic ring. Conversely, the positive sign of σm for OH means that such group was an electron acceptor. This would increase the positive signs on aromatic ring of imine. Therefore, unstable dye was expected to form by electro static ruplusion between the positive azo group PhN_2 and the position of entering at S-P-AA and SA. Upon comparison of σp for OH and NH_2, the ones which posses the more negative sign were favored in entering the azo group. Therefore, σp for NH_2 was favored one as in TABLE 3. The σp position with respect to NH_2 group in S-P-AA was busy by chemical bonding. Hence σp for OH was the final most proper position of entering the azo group is S-P-AA as shown in the following equation.

SA contains one phenolic group, so there was a favored position of entering the azo group at para position with respect to such group. The last was experimentally proved by observing the same rate constant

value of 0.003 min⁻¹ for kinetic decay of S-P-AA and SA as shown previously in this work.

Thermodynamic of tautomerism of dyes

The calculated thermodynamic parameters for conversion of dyes mentioned from enol form to keto form had been performed by measurements of equilibrium constant for the reversed reaction seen in figure 1. As stated previously, the enol form of dye formed from S-P-AA after 30 minutes began to decay or converted to keto form of dye. Similarly, the enol form of dye formed from SA was converted to its keto tautomer after 15 minutes. These keto forms of dyes were confirmed by their longer wavelengths of absorption[10,11,31] when compared to their enol forms.

The equilibrium constants for tautomerism reactions of dyes were evaluated by Hartman[32] and from absorbance ratios of keto dye and enol dye with absorption coefficients of enol α_1 and keto α_2 using equation (2):

$$K = \frac{A_{keto}\ \alpha_1}{A_{eno}\ \alpha_2} \qquad (2)$$

Plot of A_{enol} versus A_{keto} showed a straight lines of α_1/α_2 values of 3.18 with $R^2 = 0.999$ and 0.78 of $R^2 = 0.800$ for dyes S-P-AA and SA respectively.

Heats of tautomerism reaction of dyes were evaluated from the integrated vant Hoff equation (3) of the form:-

Plot of lnK versus the inverse of absolute temperature showed straight lines of negative slopes with R^2 range values 0.925-0.982 as in figure 5. Free energy changes $\Delta G°$ for tautomerism were calculated from Gibbs free energy and from equation (4) of the form :

The changes of entropy for tautomerism were estimated from equation (5).

The thermodynamic data collected for tautomerism of dyes were seen in TABLE 4. Values of $\Delta G°$ were depending on the equilibrium constant. Their signs were varied from either positive value at equilibrium constant value less than unity to negative values at equilibrium constant values more than unity. These positive or negative $\Delta G°$ signs were explained by non-spontaneous to spontaneous reaction respectively. The heats of reactions $\Delta H°$ for dyes had positive values. These mean that tautomerism of dyes were occurred in endothermic processed.

$\Delta S°$ values for tautomerism of dyes had a positive signs. These mean that tautomerism reactions were directed toward a more entropy and agreed with other study[11] and literature[26].

CONCLUSIONS

1 The beginning of diazotization coupling reactions between S-P-AA or SA with diazotized sulphanilic acceptor led to the formation of enol tautomer of dyes.

2 After 30 and 15 minutes from a diazotizations reaction in S-P-AA and SA respectively, a spontaneous conversion of enol form of dye to its keto form as called side reaction at basic medium.

3 The enol $\leftrightarrows$ keto tautomerism of dyes resulted to the failure quantitative determination of imines S-P-AA and SA by the usual spectrophotometric method.

4 Keto tautomerism of dyes in S-P-AA and SA, absorb[11,31] light at longer wavelength when compared compared with enol tautomer.

5 The kinetics for tautomerism of dyes at optimal condition was found to be of pseudo first order with respect to imines.

6 Rate constants of tautomerism of S-P-AA and SA had equal values of 0.003 min⁻¹. In other word, the aldehyde part of imines was effective in tautomerism reaction.

7 A successful kinetic method was observed during quantitative determination of S-P-AA and SA imines.The method as found simple and fast.

8 Thermodynamic parameters estimated, namely, $\Delta G°$, $\Delta H°$ and $\Delta S°$ supported the tautomerism of dyes. The process of tautomerism for S-P-AA dye was spontaneous ($\Delta G° = -$) at all temperatures studied. A similar result was obtained for SA dye at 323K and converted to non spontaneous at a range of temperature between 313-318° K. Tautomerism reactions of S-P-AA and SA dyes were accompanied by an increase of entropy.

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