Comparison of $\overline{pKa}$ values for phenolic and naphtholice Schiff bases derived from 2-acetyl pyridine (Part II)*

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Abstract

The study includes the preparation of four phenolic Schiff bases derived from the 2-acetyl pyridine as a mother compound with primary amines o , m , p-amino phenols and 4-amino naphthol . The structures of these phenolic and naphtholic Schiff bases were confirmed by physical method , namely UV visible and IR spectroscopy and melting points.

The main aims of the study was the determination of $\overline{pKa}$ values for these hydroxy Schiff bases by potentrometric titration method. This method as found simple , precise and accurate . $\overline{pKa}$ estimated , depend on the following factors :-

1. The chemical structure of imine .
2. The ambient temperature .
3. The influence of phenolic group , whether its donating or withdrawing behavior .
4. The resonance numbers of phenoxide ion in Schiff base .

* See part I in reference (16) .

Keywords : comparison $\overline{pKa}$, phenolic-naptholic Schiff bases , potentiometry Resonance numbers

الخلاصة

تشمل الدراسة تحضير 4 قواعد شيف الفينولية المشتقة من 2- اسيتايل بريدين كمركب ام مع الامينات الاولية اورثو ، ميتا وبارا فينول و 4 امينو نفثول . الهيئات التركيبية لقواعد شيف الفينولية والنفثولية قد تم اثباتها بالطريقة الفيزيائية وذلك بأستعمال اطياف الاشعة فوق البنفسجية – المرئية وتحت الحمراء مع درجات الانصهار .

الهدف الرئيسي للدراسة هو تعيين قيم $\overline{pKa}$ لقواعد شيف الحاوية على مجاميع هايدروكسيلية بطريقة التسحيح المجهادي . هذه الطريقة وجد انها بسيطة ، مضبوطة ودقيقة . ان قيم $\overline{pKa}$ المحسوبة وجد انها تعتمد على العوامل التالية :-

1. الهيئة التركيبية لقاعدة شيف .
2. درجة الحرارة اثناء القياس .
3. تأثير المجموعة الفينولية اذا كان دافعاً او ساحباً للالكترونات .
4. اعداد الرزونانس لايون الفينوكسيد في قاعدة شيف .

Introduction

The chemistry of imines had faced a great importance and attention[1-4] during the last four decades . Recently an extensive efforts had been done by many workers to synthesis Schiff bases by using various techniques as grinding[5] , free solvent[6] , green alternative appoach[7] and without solvent under microwave irradiation[8] .

A tremendous efforts had been done in our laboratory on phenolic Schiff bases or phenolic oximes in a directions of synthesis[9-10] , temperatures[11-12] and their influence on pKa of ionization , percentage of ethanol solvent[13] on pKa of imines and comparison[14] of pKa by the variation of structures.

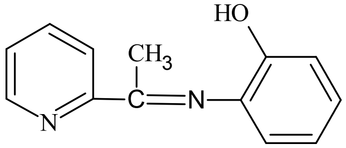
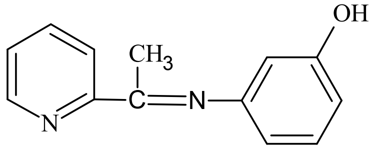
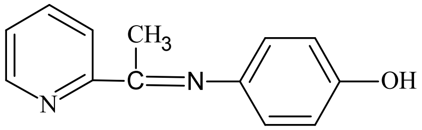
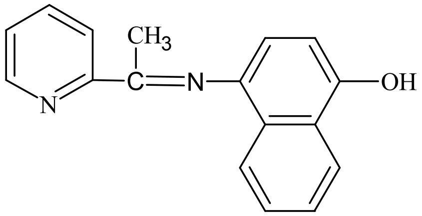
This investigation is an extension of previous studies[8-13] , it deals with the determination of $\overline{\text{pKa}}$ for phenolic and naphtholic Schiff bases derived from 2-acetyl pyridine at temperature range (293-333)K . A comparison of $\overline{\text{pKa}}$ for these positional phenolic Schiff base isomer that contain phenol groups on ortho , meta and para positions was also considered.

Experimental

All chemical used in this study was supplied from Fluka, BDH and Molckula companies.

All Schiff bases were prepared by standard method[1,15] , or by the reactions of equimolar amounts from 3-acetyl and 4-acetyl pyridines with o, m, p-amino phenols and p-amino naphthol . Table (1) shows, the number, nomenclature and structures of imines prepared.

Table (1) : The number, nomenclature and structures of imines .

Comp. No.	Nomenclature	Structure
1	Methyl-2-pyridyl ketonylidene-0-hydroxyaniline	
2	Methyl-2-pyridyl ketonylidene-m-hydroxyaniline	
3	Methyl-2-pyridyl ketonylidene-p-hydroxyaniline	
4	Methyl-2-pyridyl ketonylidene-4-amino naphthol	

The $\overline{pKa}$ for these phenolic Schiff bases were determined by potentiometic titration with 0.1M NaOH , at different temperatures range (239-333)K , using the following equation :-

$$pKa = pH + \log\frac{[HA]}{[A^{-}]}$$

Results and discussion

Table (1) shows , compound No. , nomenclature and structure of imines under investigation . The structures of these imines were confirmed[16] recently by physical and chemical methods. The former method includes UV-IR spectra , melting point or boiling point. The latter method include specific reagents for oxime , phenol and ether groups in imines. This encourage the same workers deal with the influence of temperature in the range (239-333)K on thermodynamic[17] parameters namely ΔG° , ΔH° and ΔS° on ionization reactions of these imines .

Comparison of $\overline{pKa}$ for phenolic Schiff bases derived from 2-acetyl-pyridine

This manuscript includes a comparison of $\overline{pKa}$ for phenolic Schiff bases contain phenol groups on ortho , meta and para positions on primary amine side of the Schiff bases ,These imines have different structures and regarded as positional[7] isomer .

Phenol group has two reverse effects , the first one as electron withdrawing group , called inductive effect , the second effect as electron donating group called mesomeric or

resonance effect. The net effects for these inductive and resonance effects can be understand by the corresponding Hammet[18] constant (σ) at meta and para positions.

Experimentally was proved that imines numbered 1-2 3-4 contained intra and inter molecular hydrogen bonding respectively.

Comparison of $\overline{pKa}$ for phenolic Schiff bases

Tables(2-4) show $\overline{pKa}$ for phenolic Schiff bases (2-4) at temperature range (293-333)K . These show the following results.

1. A depression of $\overline{pKa}$ values or the increase of acidity of phenolic Schiff bases by an elevation of temperatures. These acidities order for Schiff bases were in the following arrangement O-OH > m-OH > p-OH .

The increase of acidity of O-OH phenolic Schiff bases as compared with m-OH was due to the three folds reasons :-

a) The occurrence of intra molecular hydrogen bonding with five membered ring of type N ······ H-O in imine 1. This last bonding resulted to an increase of acidity of ortho OH phenolic Schiff base . This comes with agreement of greater acidity[19] of salicylic acid which contains intramolecular hydrogen bond as compared with benzoic acid having intermolecular hydrogen bond .

b) The presence of steric effect in imine 1 which contains an ortho phenolic group. Such physical factor may responsible on increasing acidity or dimishing $\overline{pKa}$ value for such phenolic Schiff base.The resonance numbers for phenolic Schiff bases 1-2 or for their phenoxide ions generated by ionization processes were shown in Schemes 1-2.

Table (2) : Experimental $\overline{pKa}$ for methyl–2- pyridyl ketonylidne o-hydroxy aniline at 10% ethanol at different temperatures.

$T_{(K)}$	ml of (0.1M) NaOH	pKa	$\overline{pKa}$
293	0.8	11.646	11.798
	1	11.760	
	1.2	11.904	
	1.4	11.883	
303	0.8	11.711	11.702
	1	11.700	
	1.2	11.714	
	1.4	11.683	
313	0.8	10.936	11.618
	1	11.688	
	1.2	11.943	
	1.4	11.906	
323	0.8	10.646	11.366
	1	11.399	
	1.2	11.595	
	1.4	11.824	
333	0.8	10.997	11.238
	1	11.289	
	1.2	11.302	
	1.4	11.362	

Table (3) : Experimental $\overline{\mathrm{pKa}}$ for methyl–2- pyridyl ketonylidne m-hydroxy aniline at 10% ethanol at different temperatures.

$T_{(K)}$	ml of (0.1M) NaOH	pKa	$\overline{\mathrm{pKa}}$
293	0.6	12.355	12.585
	0.8	12.297	
	1.0	12.559	
	1.2	12.758	
	1.4	12.955	
303	0.6	11.531	11.967
	0.8	11.985	
	1.0	12.067	
	1.2	12.082	
	1.4	12.171	
313	0.6	11.131	11.803
	0.8	11.922	
	1.0	11.937	
	1.2	11.961	
	1.4	12.064	
323	0.6	10.892	11.669
	0.8	11.602	
	1.0	11.793	
	1.2	11.971	
	1.4	12.089	
333	0.6	10.985	11.383
	0.8	11.317	
	1.0	11.536	
	1.2	11.535	
	1.4	11.542	

Table (4) : Experimental $\overline{\mathrm{pKa}}$ for methyl–2- pyridyl ketonylidne p-hydroxy aniline at 10% ethanol at different temperatures.

$T_{(K)}$	ml of (0.1M) NaOH	pKa	$\overline{\mathrm{pKa}}$
293	0.8 1 1.2 1.4	11.629 12.731 12.849 12.823	12.758
303	0.8 1 1.2 1.4	12.062 12.056 12.030 12.039	12.047
313	0.8 1 1.2 1.4	11.931 11.915 11.895 11.868	11.902
323	0.4 0.6 0.8 1.0 1.2	11.843 11.828 11.692 11.610 11.535	11.702
333	0.2 0.4 0.6 0.8 1.0	11.563 11.574 11.351 11.437 11.335	11.452

Scheme (1-2) show eight and four resonance numbers for imines (1-2) respectively , having a greater influence on the stabilities of their phenoxide ions mentioned.

The increase in resonance numbers for imine 1 , means an increase of stability of o-OH phenoxide ion. This means spreading of negative ion on large area in space , resulted by increasing of stability for o-OH phenolic Schiff bases . Finally , it was concluded that the three fold reasons a , b and c mentioned might contribute totally to a different degrees in increasing acidity of Schiff base 1.

c) On comparison of acidity of o-OH phenolic Schiff base with m-OH Schiff base at all temperatures , showed that the acidity of latter was lowered . This can be interpreted by the lower resonance numbers of phenoxide ion for m-OH as compared to o-OH Schiff base . The increase of resonance numbers of OH phenolic Schiff base may responsible in increasing[20] its acidity.

2- On comparison of acidites of m-OH and p-OH Schiff bases i.e. Schiff bases (2-3) , showed acidity of former was greater than latter. This was due to the two folds reasons as :

a. The influence of positions of phenolic groups in meta and para in imines 1-2 on their acidites . This led to the consideration of Hammet sigma constants having values +0.121 and -0.37 for meta and para phenolic groups respectively . The positive charge of σ_m OH means such group is an electron withdrawing behavior , resulted in increasing acidity of meta phenolic Schiff base . Conversely the negative charge acidity of σ_p OH resulted to an inverse behavior i.e. diminishing acidity of p-OH Schiff base .

b. The presence of intramolecular hydrogen bond in imine (2)

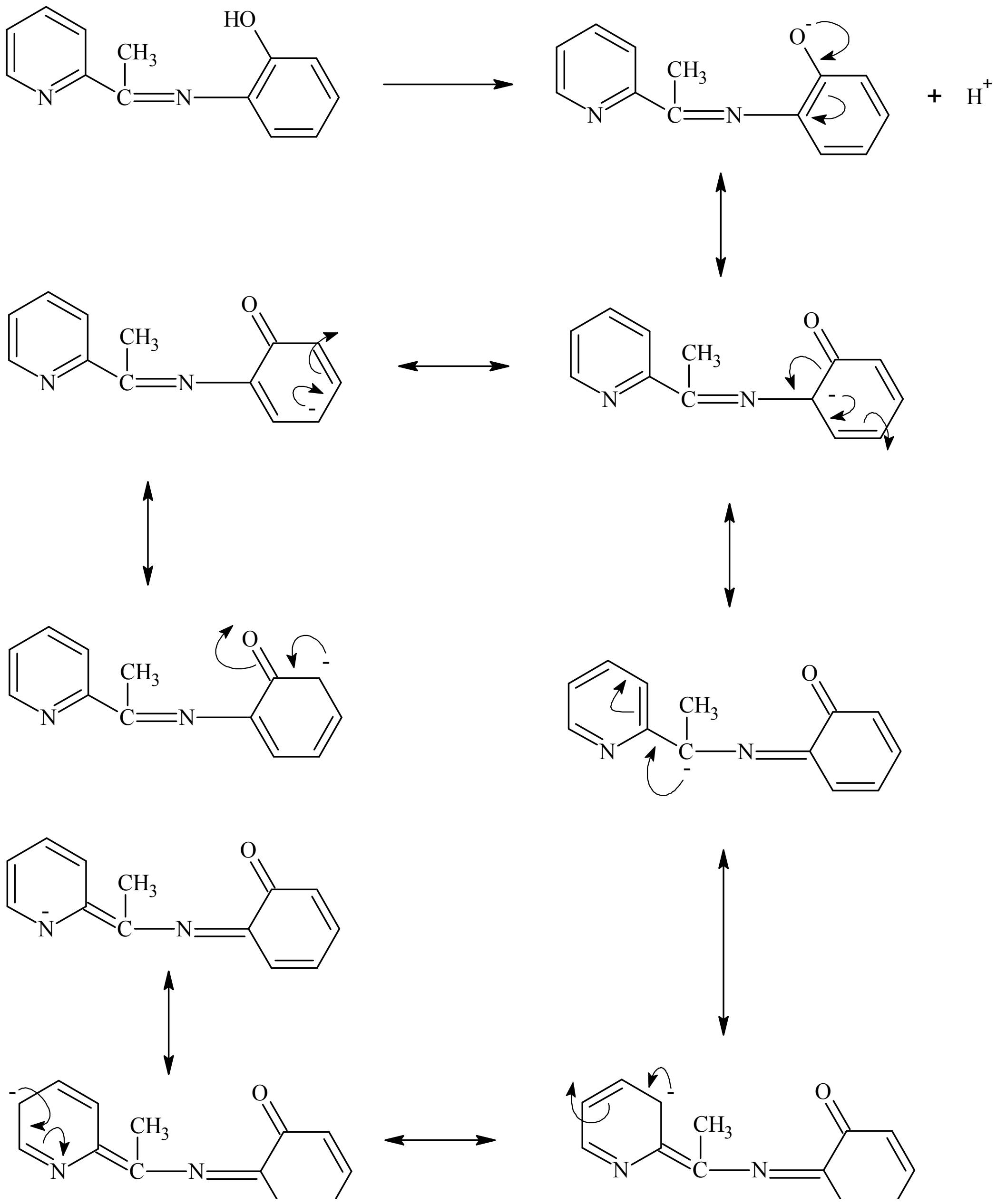
Hence , it was concluded finally , that both a and b paragraphs might responsible on increasing acidity of meta phenolic Schiff base as compared with para phenolic Schiff bases .

2. Comparison of $\overline{pKa}$ for naphtholic and phenolic Schiff bases.

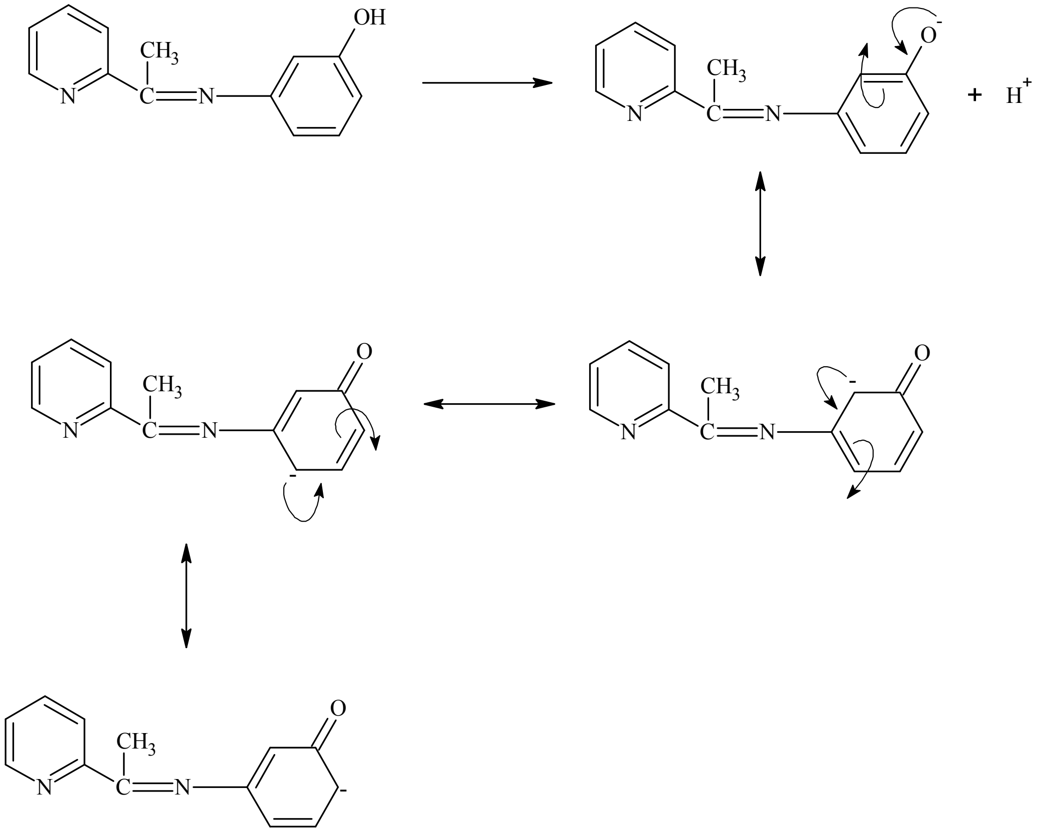
Table (5) shows the $\overline{pKa}$ values were decreased by increasing temperature i.e. increasing acidity by elevation of temperatures.

On comparison of structures for Schiff bases 3 and 4 , showed the only difference between them was by the composition of primary amine sides . These having one and two aromatic rings respectively . It was cleared from Tables (4-5) that acidity of naphtholic Schiff bases was lower than acidity phenolic Schiff base at all temperatures . Actually these naphtholic and phenolic Schiff bases contain phenol groups , in addition of their occurance in intermolecular hydrogen bonding . In order to interpret this difference in acidites , this led to the consideration of resonance numbers of phenoxide ions in molecules , 4 and 5 as shown in schemes 3-4 . These showed a values 8 and 10 for Schiff bases numbered 3 and 4 respectively.

The greater numbers of resonance for in phenolic ion Schiff base (4) was theoretically led to the expectation of higher acidity as compared with Schiff base (3) . The reverse of this result can be accepted by considering large donation effect of naphthol ring in Schiff base (5) as compared with phenol ring in Schiff base (4) . Hence the two aromatic rings in naphthol donate electrons to a greater extent as compared with phenol ring , resulting in diminishing acidity of Schiff base (5) .



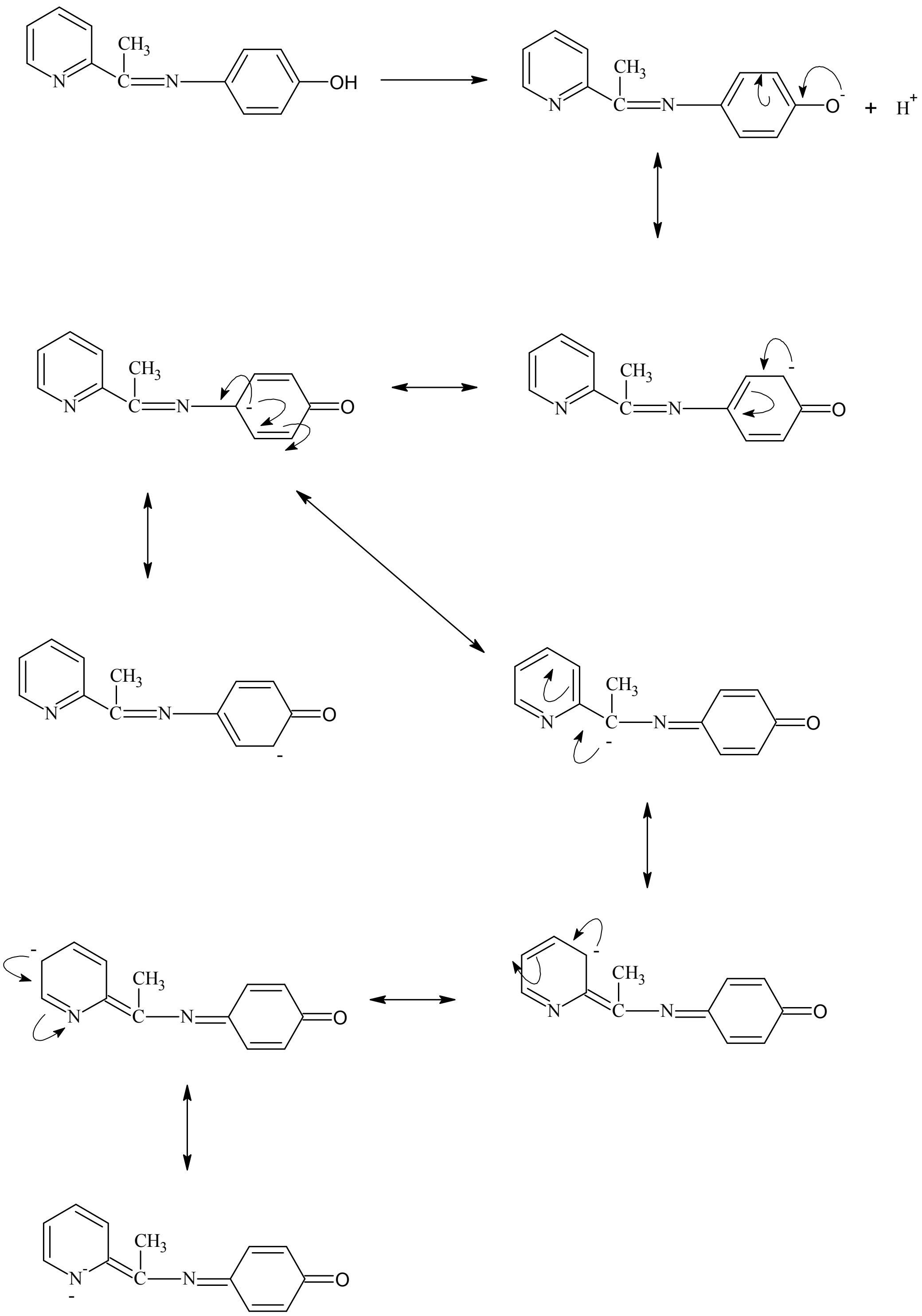
Scheme (1) : Resonance numbers of phenoxide ion in imine 1.



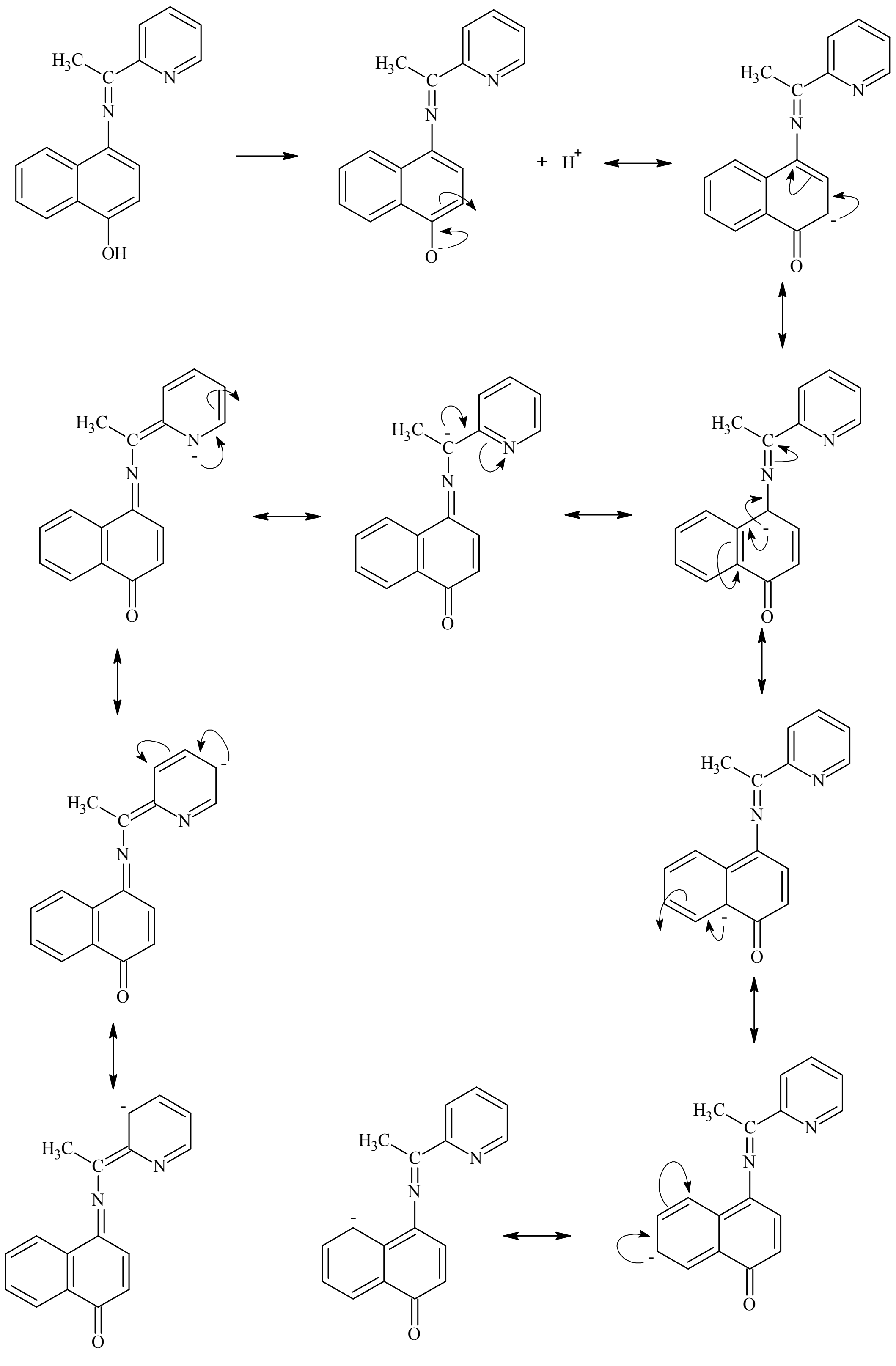
Scheme (2) : Resonance numbers of phenoxide ion in imine 2.

Table (5) : Experimental $\overline{\mathrm{pKa}}$ for methyl–2- pyridyl ketonylidne para amino naphthol at 10% ethanol at different temperatures.

$T_{(K)}$	ml of (0.1M) HCl	pKa	$\overline{\mathrm{pKa}}$`
293	0.2	5.188	4.109
	0.4	4.468	
	0.6	3.972	
	0.8	3.639	
	1.0	3.280	
303	0.2	4.952	3.887
	0.4	4.226	
	0.6	3.803	
	0.8	3.407	
	1.0	3.046	
313	0.2	4.773	3.671
	0.4	4.019	
	0.6	3.579	
	0.8	3.156	
	1.0	2.829	
323	0.2	4.565	3.406
	0.4	3.762	
	0.6	3.296	
	0.8	3.891	
	1.0	2.517	
333	0.2	4.404	3.057
	0.4	3.437	
	0.6	2.914	
	0.8	2.491	
	1.0	2.041	



Scheme (3) : Resonance numbers of phenoxide ion in Schiff base 3.



Scheme (4) : Resonance numbers of phenoxide ion in Schiff base 4.

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