Comparison of pKa^{-} values for some amino Schiff bases , derived from 3-acetyl and 4-acetyl pyridines by potentiometric method

Adel Saead Peter Azzouz and Rawaa Dawod Sulayman

Chemistry Dept. , College of Education , Mosul University

(NJC)

(Recevied on 13/2/2012) **(Accepted for publication 23/5/2012)**

Abstract

The study included the preparation of six imine compounds , derived from the mother ketones , namely 3-acetyl and 4-acetyl pyridines by standard method .

The structures of these imines were confirmed by physical methods, namely UV, IR spectra , beside melting points and qualitative diazotization chemical tests.

The main object of the study was the determination of pKa^{-} for conjugate acids of these imines ,by potentiometric titration with standard HCl solution . The last was found simple , precise and accurate . The study showed that pKa^{-} values for any imine , depends on the following factors as :-

1- The chemical structures of imines .

2- The temperature under study .

3- The type of intra or inter molecular hydrogen bonding exist in these

الخلاصة

يشتمل البحث على تحضير ستة مركبات امينية من قواعد شيف المشتقة من الكيتونات الام 3 و 4 – اسيتايل بردبين وبطريقة قياسية .

تم اثبات الهيئات التركيبية للايمينات بالطرق الفيزيائية وذلك باستعمال اطياف UVوIR بجانب درجات الانصهار مع استعمال كاشف الازوتة النوعي . الهدف الرئيسي للدراسة هو تعيين pKa^{-} للاحماض القرينة للايمينات بواسطة التسحيح المجهادي وباستعمال محلول HClالقياسي . لقد وجد ان الطريقة الاخيرة بسيطة , دقيقة و مضبوطة وعالية الدقة . توصلت الدراسة أن قيم pKa^{-} لاي مركب ايميني يعتمد على العوامل التالية :-

1- الهيئات التركيبية للايمينات .
2- درجة الحرارة تحت الدراسة .
3- نوع الاواصر الهيدروجينية الضمنية او البينية الموجودة في الايمينات .

Introduction

Many workers had given a great deal of attention to the chemistry of imines during the last three decades . These were in the direction of UV[1-3] , IR[4-5] , NMR[6] and Mass[6-7] spectra , beside other kinetic[8] , thermodynamic[9-10] , tautomerism[9-11] and dyes[12] studies . Schiff bases had used in different fields as antimicrobial[13] agents , fungicides[14] and biomarkers[15] of oxidative stress in model diabetes mellitus . The present work deals with the determination of pK_a^- values for some imines derived from mother ketones , namely 3-acetyl and 4-acetyl pyridines in 10 % ethanol , by using a simple potentiometric method .

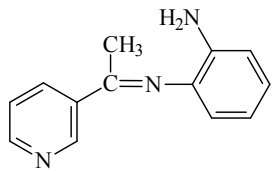
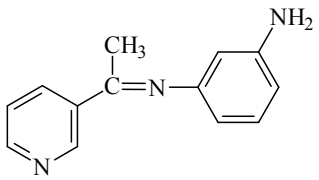
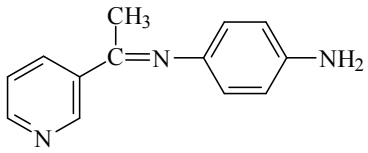
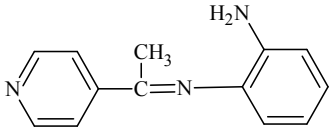
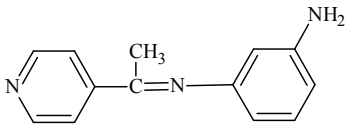
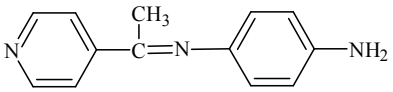
The study illustrated how simple aromatic amino group was converted to a strong nitrilium cation as a strong acid during potentiometric titration of imines under study with HCl titrant . This study might open works to another similar studies in future .

Experimental

All chemicals used in this study were supplied from Fluka, BDH and Molckula companies.

All Schiff bases were prepared by standard method[6], or by the reactions of equimolar amounts from 3-acetyl and 4-acetyl pyridines with o, m, p-amino anilines. Table (1) shows, the number, nomenclature and structures of imines prepared.

Table (1) : Number, nomenclature and structures of imines

Comp. No.	Nomenclature	Structure
1	Methyl-3-pyridyl ketonylidene *o*-amino aniline	
2	Methyl-3-pyridyl ketonylidene *m*-amino aniline	
3	Methyl-3-pyridyl ketonylidene *p*-amino aniline	
4	Methyl-4-pyridyl ketonyliden *o*-amino aniline	
5	Methyl-4-pyridyl ketonyliden *m*-amino aniline	
6	Methyl-4-pyridyl ketonyliden *p*-amino aniline	

Solutions required

0.1M HCl were prepared by usual procedure . 0.01M of benzoic acid as standard for calibration[18] of potentiometric method used for pKa determination of imines under study .

Determination of pKa^- of imines

This required a calibration of pH meter used , by using a buffer solution of pH nine . For determination of pKa^- for any imine under study at any desired temperature , this needs the preparation of the following solutions:-

1. 10^{-2}M of imines .
2. 0.1M HCl .

Pipett 50ml of 10^{-2}M of any imines and placed in a special titration cell containing double layers , for circulating water inside the cell . Water was pumped from any thermostat at any temperature range between (10-50)C° .When the temperature of imine reached an equilibrium temperature , addition of 0.5ml successive quantities of 0.1M HCl was done . The mixture was stirred with magnetic bar placed in side the cell after each addition, followed by measurement of pH after each addition . Titration was continued for about seven times , then followed by calculation of pKa^- from Handerson-Hassellbach equation of the form :-

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

Apparatus

1. Electrothermal melting point apparatus was used for measurement of melting points of imines .
2. FTIR spectrophotometer was used for measurement of IR spectra of solid imines by KBr disc method or in solution after dissolving imines in dry benzene .
3. A computerized double beam Shimadzu 1601 for measurement of UV spectra of imines solutions in solvent ethanol and dry benzene .
4. A memmert thermostat manufactured by Searle company model L200 , for fixation the temperature of imines solution . Water is pumped out from thermostat to cell by using water pump .
5. A digital Philips pH meter model pw 9421 was used for measuring pH of solutions during potentiometric titration .

Results and Discussion

At the beginning of this investigation, it was thought of great importance to confirm[19] the chemical structures of imines by physical method, namely , by using UV-IR spectra beside melting points .

The pKa^- values for conjugate acids (nitrilium ions) for imines 1-6 were determined potentiometric titration with standard hydrochloric acid it was known in literature , that basicity of aromatic amines was increased in order of primary > secondary > tertary . coming back to structures of imines under study , showed that the presence of

both primary amine as NH_2 and tertary amine (C=N-) . Hence it was belived in this study that addition of HCl titrant , would accompany the combination of H^+ with NH_2 , with the $-\overset{+}{N}H_3$ generation of nitrilium cation . The last was regarded as a conjugate acids for imines under study , and their pKa^- were calculated and compared .

Comparison of pKa^- for amino imines derived from 3-acetyl pyridine

This include imines number 1-3 , their pKa^- were shown in Tables 2-4 and concluded the following points : -

1- For any imine stated , the increase in temperature in the range (288 – 328) K was accompanied by the decrease of pKa^- . This was in agreement with other similar studies [16-17] .

2- At any constant temperature between (288 – 328) K , the order of the increasing of acidity was in order of : o-NH_2 > m-NH_2 > p-NH_2 .

The increased of acidity in o-NH_2 substituent or imine numbered 1, as compared with acidites of m-NH_2 and p-NH_2 substituents (imines 2-3) could be interpretted by the occurrence of intramolcular hydrogen bonding in imine 1 . The last resulted to the increase of dissociation of nitrilium ion or lowering its pKa^- as compared with inter molecular hydrogen bondings present in imines 2-3 .

The higher pKa^- values of imines 2-3 could be explained by the two folds reasons as : -

1- The stronger donation property of amino groups in these imines , as confirmed from their sigma meta and para of values -0.16 and -0.68 respectively .

2- The molar extension coefficients ϵ_{max} values of imines 2-3 had a values of 4870 and 3120 in units of liter . $mole^{-1}$. cm^{-1} respectivety . The higher ϵ_{max} value of imine 2 as compared with imine 3 could be explained by greater planarity and the higher possibility dissociation of imine 2 as compared with imine 3 .

These two factors were the main reasons responsible of lowering acidities of imines 2-3 as compared with imine 1 .

Table (2) : pKa values of methyl-3-pyridyl ketonylidene-o-aminoaniline at 10% ethanol at different temperatures

T (K)	ml of (0.1 M) HCl	pH	pKa	$\overline{pKa}$
288	0.2	5.81	6.7633	5.3368
	0.4	5.49	6.0912	
	0.6	5.25	5.6167	
	0.8	5.07	5.2433	
	1.0	4.89	4.8876	
	1.2	4.73	4.5499	
	1.4	4.58	4.2058	
298	0.2	5.65	6.6033	5.1803
	0.4	5.31	5.9107	
	0.6	5.08	5.4463	
	0.8	4.91	5.0827	
	1.0	4.74	4.7367	
	1.2	4.59	4.4085	
	1.4	4.45	4.0738	
308	0.2	5.49	6.4428	5.0087
	0.4	5.14	5.7401	
	0.6	4.91	5.2754	
	0.8	4.73	4.9014	
	1.0	4.57	4.5651	
	1.2	4.43	4.2464	
	1.4	4.27	3.8896	
318	0.2	5.41	6.3623	4.9204
	0.4	5.06	5.6596	
	0.6	4.82	5.1848	
	0.8	4.64	4.8106	
	1.0	4.48	4.4739	
	1.2	4.33	4.1445	
	1.4	4.19	3.8071	
328	0.2	5.36	6.3121	4.8590
	0.4	5.01	5.6094	
	0.6	4.75	5.1142	
	0.8	4.59	4.7669	
	1.0	4.41	4.4029	
	1.2	4.26	4.0729	
	1.4	4.12	3.7346	

Table (3) : pKa values of methyl-3-pyridyl ketonylidene-m-aminoaniline at 10% ethanol at different temperatures

T (K)	ml of (0.1 M) HCl	pH	pKa	$\overline{pKa}$
288	0.2	6.03	6.9838	5.4585
	0.4	5.70	6.3015	
	0.6	5.45	5.8171	
	0.8	5.22	5.3938	
	1.0	5.00	4.9982	
	1.2	4.77	4.5903	
	1.4	4.50	4.1245	
298	0.2	5.92	6.8738	5.3394
	0.4	5.56	6.1612	
	0.6	5.30	5.6669	
	0.8	5.09	5.2635	
	1.0	4.88	4.8776	
	1.2	4.66	4.4793	
	1.4	4.43	4.0534	
308	0.2	5.75	6.6933	5.1956
	0.4	5.40	6.0009	
	0.6	5.16	5.5265	
	0.8	4.95	5.1229	
	1.0	4.73	4.7265	
	1.2	4.54	4.3579	
	1.4	4.32	3.9409	
318	0.2	5.51	6.4628	4.9806
	0.4	5.18	5.7801	
	0.6	4.93	5.2954	
	0.8	5.73	4.9014	
	1.0	4.53	4.5247	
	1.2	4.33	4.1445	
	1.4	4.14	3.7555	
328	0.2	5.37	6.3223	4.8606
	0.4	5.02	5.6196	
	0.6	4.80	5.1646	
	0.8	4.61	4.7803	
	1.0	4.42	4.4131	
	1.2	4.24	4.0524	
	1.4	4.06	3.6721	

Table (4) : pKa values of methyl-3-pyridyl ketonylidene-p-aminoaniline at 10% ethanol at different temperatures

T (K)	ml of (0.1 M) HCl	pH	pKa	$\overline{pKa}$
288	0.2	7.29	8.2442	7.0548
	0.4	7.08	7.6820	
	0.6	6.91	7.2779	
	0.8	6.78	6.9549	
	1.0	6.69	6.6899	
	1.2	6.59	6.4135	
	1.4	6.49	6.1215	
298	0.2	7.07	8.0243	6.8191
	0.4	6.85	7.4520	
	0.6	6.68	7.0479	
	0.8	6.55	6.7249	
	1.0	6.44	6.4399	
	1.2	6.34	6.1634	
	1.4	6.25	5.8815	
308	0.2	7.05	8.0043	6.7063
	0.4	6.80	7.4020	
	0.6	6.60	6.9679	
	0.8	6.44	6.6149	
	1.0	6.31	6.3099	
	1.2	6.16	5.9834	
	1.4	6.03	5.6614	
318	0.2	6.83	7.7842	6.4719
	0.4	6.63	7.2319	
	0.6	6.42	6.7879	
	0.8	6.25	6.4249	
	1.0	6.00	5.9998	
	1.2	5.96	5.7833	
	1.4	5.66	5.2911	
328	0.2	6.69	7.6443	6.2975
	0.4	6.40	7.0019	
	0.6	6.22	6.5878	
	0.8	6.03	6.2048	
	1.0	5.87	5.8698	
	1.2	5.73	5.5532	
	1.4	5.59	5.2210	

Comparison of pKa^- values for amino imines derived from 4-acetyl pyridine .

This included imines numbered 4-6 and their pKa^- values as shown in Tables 5-7 , and summarized the following results :-

1- For any imines as numbered 4-6 , the elevation of temperature in the range stated before , was accompanied by lowering pKa^- value or increasing acidity of imine .

This result was in agreement with this investigation on imines derived from 3-acetyl pyridine and with earlier works[16-17] .

2- At any constant temperature , the acidities of imines 4-6 were in the following arrangements of increasing acidity o-NH_2 > m-NH_2 > p-NH_2 .

The maximum acidity was observed for imine 4 which contained an intramolecular hydrogen bond . Mean while imines 5-6 contained intermolecular hydrogen bond .

Imines 5 and 6 contained an amino groups at meta and para positions respectively . These imines had a molar extension coefficient values of 4870 and 2700 in arbitary units of liter . $mole^{-1}$. cm^{-1} respectively . The increased of the last value for the meta substituent was the reason of increasing acidity of imine 5 as compared with imine 6 .

Table (5) : pKa values of methyl-4-pyridyl ketonylidene-o-aminoaniline at 10% ethanol at different temperatures

T (K)	ml of (0.1 M) HCl	pH	pKa	$\overline{pKa}$
288	0.2	5.75	6.7134	5.3413
	0.4	5.45	6.0511	
	0.6	5.24	5.6068	
	0.8	5.08	5.2534	
	1.0	4.92	4.9178	
	1.2	4.78	4.6003	
	1.4	4.62	4.2463	
298	0.2	5.68	6.6332	5.2280
	0.4	5.35	5.9508	
	0.6	5.13	5.4964	
	0.8	4.95	5.1247	
	1.0	4.78	4.7769	
	1.2	4.65	4.4692	
	1.4	4.52	4.1449	
308	0.2	5.47	6.4226	5.0509
	0.4	5.17	5.7702	
	0.6	4.96	5.3254	
	0.8	4.78	4.9537	
	1.0	4.62	4.6156	
	1.2	4.48	4.2974	
	1.4	4.35	3.9716	
318	0.2	5.34	6.2920	4.9166
	0.4	5.05	5.6496	
	0.6	4.81	5.1747	
	0.8	4.64	4.8125	
	1.0	4.49	4.4841	
	1.2	4.35	4.1649	
	1.4	4.22	3.8381	
328	0.2	5.22	6.1713	4.8179
	0.4	4.90	5.4986	
	0.6	4.71	5.0738	
	0.8	4.56	4.7298	
	1.0	4.41	4.4029	
	1.2	4.26	4.0729	
	1.4	4.16	3.7761	

Table (6) : pKa values of methyl-3-pyridyl ketonylidene-m-aminoaniline at 10% ethanol at different temperatures

T (K)	ml of (0.1 M) HCl	pH	pKa	$\overline{pKa}$
288	0.2	5.92	6.8737	5.3421
	0.4	5.59	6.1913	
	0.6	5.33	5.6969	
	0.8	5.12	5.2935	
	1.0	4.87	4.8675	
	1.2	4.63	4.4490	
	1.4	4.40	4.0227	
298	0.2	5.82	6.7735	5.2361
	0.4	5.44	6.0411	
	0.6	5.23	5.5974	
	0.8	4.99	5.1649	
	1.0	4.77	4.7669	
	1.2	4.54	4.3579	
	1.4	4.33	3.9512	
308	0.2	5.75	6.7034	5.1451
	0.4	5.38	5.9809	
	0.6	5.11	5.4769	
	0.8	4.87	5.0424	
	1.0	4.67	4.6661	
	1.2	4.45	4.2667	
	1.4	4.26	3.8793	
318	0.2	5.47	6.4226	4.9227
	0.4	5.13	5.7300	
	0.6	4.88	5.2452	
	0.8	4.65	4.8208	
	1.0	4.46	4.4537	
	1.2	4.27	4.0832	
	1.4	4.09	3.7034	
328	0.2	5.39	6.3423	4.8735
	0.4	5.09	5.6898	
	0.6	4.83	5.1948	
	0.8	4.60	4.7702	
	1.0	4.41	4.4029	
	1.2	4.22	4.0319	
	1.4	4.07	3.6826	

Table (7) : pKa values of methyl-3-pyridyl ketonylidene-p-aminoaniline at 10% ethanol at different temperatures

T (K)	ml of (0.1 M) HCl	pH	pKa	$\overline{pKa}$
288	0.2	6.74	7.6941	6.3593
	0.4	6.50	7.1021	
	0.6	6.35	6.7185	
	0.8	6.15	6.3255	
	1.0	5.94	5.9397	
	1.2	5.71	5.5332	
	1.4	5.57	5.2025	
298	0.2	6.70	7.6541	6.2664
	0.4	6.44	7.0421	
	0.6	6.23	6.5984	
	0.8	6.06	6.2355	
	1.0	5.86	5.8598	
	1.2	5.65	5.4731	
	1.4	5.37	5.0022	
308	0.2	6.68	7.6342	6.1472
	0.4	6.36	6.9621	
	0.6	6.l2	6.4884	
	0.8	5.91	6.0902	
	1.0	5.67	5.6696	
	1.2	5.40	5.2228	
	1.4	5.33	4.9628	
318	0.2	6.50	7.4542	5.9203
	0.4	6.17	6.7718	
	0.6	5.93	6.2984	
	0.8	5.70	5.8753	
	1.0	5.47	5.4695	
	1.2	5.21	5.0324	
	1.4	4.91	4.5405	
328	0.2	6.33	7.2842	5.7269
	0.4	6.00	6.6018	
	0.6	5.74	6.1082	
	0.8	5.52	5.6952	
	1.0	5.27	5.2691	
	1.2	5.00	4.8216	
	1.4	4.68	4.3085	

Conclusions

1- The chemical structures of imines (1-6) derived from 3-acetyl and 4-acetyl pyridines were confirmed by chemical test , namely diazotization as well as physical method .

2- The last included ,namely , UV , IR spectra and melting points were used for the elucidation of chemical structures .

3- The process of hydrogen bondings in imines (1-6) were investigated by the aid of UV and IR spectra . A dilution method was used to differentiate between inter and intra molecular hydrogen bondings . This showed that imines 1,4 and 2,3,5,6 contain an intra and inter molecular hydrogen bonding respectively .

4- Imines 1 and 4 had maximum acidities among other four imines , due to their occurrence in a forms of chelated structures by the aid of intramolecular hydrogen bondings .

5- The greater planarity or molar extension coefficients of imines 2 and 5 resulted to a higher acidities as compared with imines 4 and 6 .

References

1-A.S.P. Azzouz and A.B.N.AL-Dabagh , ***Nat.J.Chem***. ,2008, **32** ,677.

2-A.A.Saeed , A.W.Sultan , S.A.Selman and N.A.Abood , ***Can.J.Spectrosc*** . , 1983 , **28** , 104 .

3-A.S.P.Azzouz and A.N.Obed Agha , ***Phy. Chem. An Indian J***.2007, **2(3)**, 15 .

4-A.S.P.Azzouz , A.A.Rahman and A.G.Taki , ***J.Edu.Sci.*** , 2003 , **15(2)** ,1 .

5-A.A.Saeed, N.A.Abood , N.A.AL-Mosoudi and G.T.Matti, ***Can.J.Spectrosc.***, 1985 , **30** , 142 .

6- Ed.S.Patai , The Chemistry of Carbon Nitrogen Double Bond , John Wiley , 1979 , New York .

7- A.S.P.Azzouz , ***Spectrosc . Letter*** , 1995 , **28**, 1 .

8- A.S.P.Azzouz and B.O.Kashmola , ***Nat.J.Chem.*** , 2011,**41**,1 .

9- A.S.P.Azzouz , M.A.Hasen and M.Ghanm , ***Nat.J.Chem*** . , 2010, **38** ,361 .

10- A.S.P. Azzouz , ***Nat.J.Chem.*** , 2006 , **22** , 212 .

11-A.S.P.Azzouz, A.A.Rahman and A.G.Taki, ***Nat. J.Chem.***,2005,**20** , 568 .

12- A.S.P.Azzouz , M.M.AL-Niemi , ***Iraqi Nat.J***.,2011,**42**,165 .

13-A.K.Mittal and O.P.Singhal , ***J.Indian Chem. Soc.*** , 1986, **63** ,759 .

14-B.Dash,M.Patra and P.K.Mahapatra, ***J. Indian Chem. Soc.***, 1983 , **60**, 772 .

15- P.Korytar, M.Molnorova, M.Sivonova , F.Zitnanova , O.Ulicna , A.Liptakova , J.Carsky and

Z.Duraskova, ***Gen. Physiol. Biophys***, 2002 , **21** , 337 .

16- A.S.P.Azzouz and M.A.Hussin , ***J.Edue .Sci*** ., 2011 , **24(4)** ,1 .

17- A.S.P.Azzouz and H.J.AL-Mula , AL-Anbar ***J. Pure. Sci***., 2010 , **4(2)** ,59 .

18- A.S.P.Azzouz and H.J.AL-Mula ***Phy. Chem. An Indian J.,*** 2012, **7(1)**, 12.

19. A.S.P.Azzouz and R.D.Sulayman, M.Sc Thesis Mosul University 2009.