Thermodynamic study on pKa values of some imines and their acids conjugate derived from different aromatic carbonyl compounds

Adel Saead Pitriz Azzouz Dunia Pitriz Bakzo

Chemistry Department College of Education, Mosul University

(NJC)

(Received on 23/6/2013) (Accepted for publication 27/2/2014)

Abstract

The project was concerned with synthesis of mono acidic or diacidic Schiff bases having oxime or phenol groups or a combination of them respectively . Other syn and anti oximes were derived from 2-acetyl pyridine , and others included and synthesized by a standard methods .

Potentiometric titration was found previously , an accurate , simple and fast method for determination of pKa for acids or pKa for acid conjugates of Schiff bases using NaOH and HCl titrant respectively . This method was applied successfully in this investigation for the determination of ionization constants of imines in a range of temperature (293-313)K . This encourage the workers in this study to deal with thermodynamic parameters such as ΔG° , ΔH° and ΔS° for the ionization reactions of imines at 10% ethanol solvent as interpreted and discussed .

Keywords : pKa , Aromatic imines , Schiff bases , syn or anti oximes , Thermodynamic parameters.

خلاصة

يتضمن البحث تخليق قواعد شيف الحامضية او القاعدية و الحاوية على مجاميع اوكزيمية او فينولية او مجموع كليهما. كما يحوي البحث على اوكزيمات سين و انتي المشتقة من 2–اسيتايل بردين و مركبات اخرى و بطرق قياسية. لقد وجد ان التسحيح المجهادي هي طريقة دقيقة , سريعة و بسيطة في تقدير pKa للأحماض او pKà للاحماض القرينة و عند استعمال مادتي NaOH و HCl كمواد مسححة على الترتيب . الطريقة المذكورة طبقت بنجاح في تعين ثوابت التأين للايمينات في مدى من درجات الحرارة المطلقة و المحصورة بين 233–333. ذلك شجع الباحث بالدراسة الثرمو ديناميكية و لتفاعلات تأين الأيمينات في مذيب 10% ايثانول مع مناقشة و تفسير هذه المتغيرات.

مفتاح الكلمات : ثرموديناميك : ثابت التوازن : الايمينات : الاحماض القرينه وتفاعل التاين

Introduction

The chemistry of imines in forms of oximes and Schiff bases had met a great deal attentions during the last three decades . This was for their multiple applications in many fields as chemistry[1] , biology[2,3] , medicine[4,5], industry[6] and others[6,7] .

One of the most important factors that affecting chemical reaction is the temperature This factor was studied extensively by many workers dealing with kinetics and thermodynamic studies[8]. The concept of temperature affects on chemical reactions as associations between phenol and benzil mono benzylidene[9] aniline and of substituted benzoic acids[10] , in addition to tautomerisum reactions of phenolic Schiff base[11] or some benzoin[12] compounds and macro bi imines[13] derived from benzoin and acetyl acetone and pKa studies on acids derived aromatic and aliphatic carbonyl compounds[14] and imines [15] synthesized from N- formyl pi pyridine .

This investigation is an extension for the last work , it deals with thermodynamic study for fifteen imines in forms of Schiff bases and oximes in syn or anti isomeric forms . Thermodynamic parameters accompanied ionization reactions in these imines and their acid conjugates , such as ΔG° , ΔH°, ΔS° were calculated and discussed .

Experimental

Pure 3-hydroxyl benzaldehyde, 4-hydroxybenzaldehyde, other aldehydes, hydroxylamine. HCl, sodium hydroxide and acid HCl were purchased from of Fluka or BDH origin.

Syn aldoximes were prepared by standard method[9,10]. Syn 3-hydroxybenzaldoxime or 4-hydroxybenzaldoxime were prepared by mixing equivalent[10] amounts of their aldehydes with hydroxylamine HCl. The collected oximes were purified by recrystallization from 50% ethanol-water by volume. Their anti isomers were prepared by charcoal method[10] in benzene solvent.

pKa determination

The pKa of any syn or anti aldoxime under study was determined by manufacturing glass cylindrical cell of maximum capacity about 30 ml. The cell contains two walls for insertion of pumped water from thermostat to maintain a fixed temperature during pKa determination. The whole cell assembly was completely insulated from the surrounding by thick insulation material.

20 ml of 0.01 M solution of any oxime in 10% ethanol, was placed in the cell. After equilibrium temperature was attained a successive 0.2 ml of 0.1 N NaOH was added, till 1.4ml of base was added, followed by measuring the final equilibrium pH of solution. The pK_1 for phenolic group in any oxime was estimated at a range of volumes of (0.8-1.0) ml of base, hence the average pK_1 was calculated. Similarly, the pK_2 for oxime group was calculated at range of volumes of (1.2-1.4) ml of base.

The pK_1 or pK_2 was calculated by using a standard method[1], using the equations (1-2):

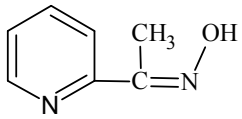
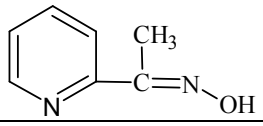
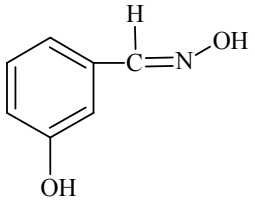
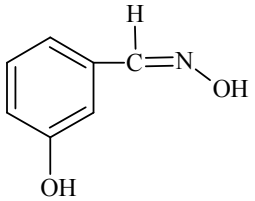
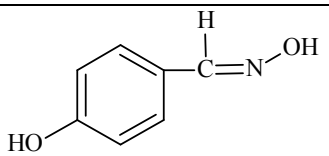
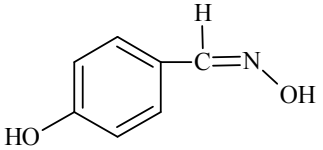
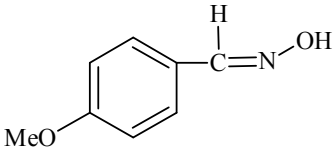
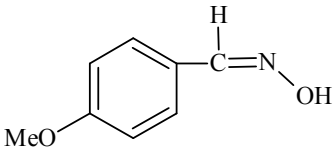
$$pKa = pH + \log \frac{[acid]}{[salt]} \quad \ldots(1)$$

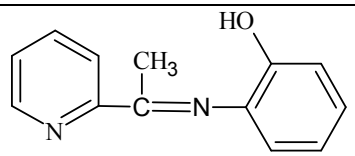
Both pK_1, and pK_2 for phenolic and oxime groups for any oxime isomer were calculated at a temperature range (293-333) K.

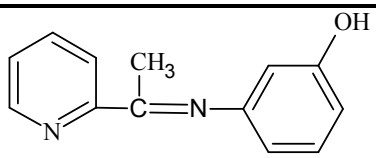
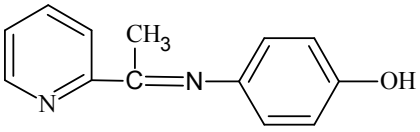
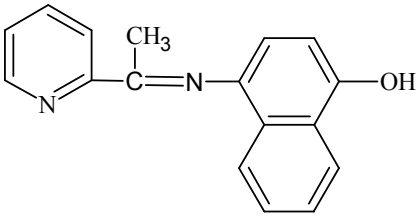
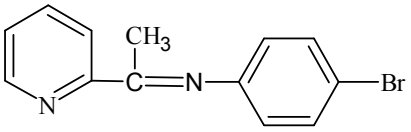
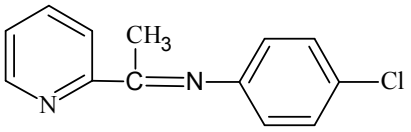
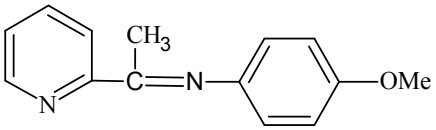
The $\overline{pKa}$ for acids conjugates were determined by titrations of imines with 0.1M HCl using the following equation :-

$$pKa = pH + \log \frac{[BH^+]}{[B]} \quad \ldots(2)$$

Table (1): Shows the imines prepared in this investigation

Comp. No.	Nomenclature	Structure
1	Syn-methyl-2-pyridyl ketoxime	
2	Anti-methyl-2-pyridyl ketoxime	
3	Syn-3-hydroxy benzaldoxime	
4	Anti-3-hydroxy benzaldoxime	
5	Syn-4-hydroxy benzaldoxime	
6	Anti-4-hydroxy benzaldoxime	
7	Syn-4-methoxy benzaldoxime	
8	Anti-4-methoxy benzaldoxime	

9	Methyl-2-pyridyl ketonylidene-0-hydroxyaniline	

Comp. No.	Nomenclature	Structure
10	Methyl-2-pyridyl ketonylidene-m-hydroxyaniline	
11	Methyl-2-pyridyl ketonylidene-p- hydroxyaniline	
12	Methyl-2-pyridyl ketonylidene-4-amino naphthol	
13	Methyl-2-pyridyl ketonylidene-p-bromo aniline	
14	Methyl-2-pyridyl ketonylidene-p-chloro aniline	
15	Methyl-2-pyridyl ketonylidene-p-methoxy aniline	

Instrumentations

1. The U.V. spectra of syn and anti aldoximes were measured by double beam computerized U.V. 1601 Shimadzu spectrophotometer, using matched quartz cells of dimensions 1x1x3 cm^3.
2. The IR spectra of solids and liquid aldoximes had measured by using a computerized FTIR Brucker Tensor 27 spectrophotometer.
3. Memmert Searl L200 water thermostat.
4. The melting points of solids syn and anti oximes was measured by using Electrothermal melting point apparatus.
5. The pH of any solution during potentiometric titration, was measured by WTW Weilheium German company model 82362.

6. The conductivity of syn and anti isomer of aldoximes under study, was measured by Weilheium company model D8120.
7. In order to fix the temperature of aldoximes solution during pKa determination, a pumped water apparatus was bought from local market.
8. All graphs needed for thermodynamic study was performed by using Excel computer programme.

Results and Discussion

In our earlier publications[15] , it was observed that pKa values of an imines derived from N-formyl pi pyidine , show an depression by an increase in temperature . This interesting result encouraged the workers in this investigation to deal with thermodynamic parameters evaluation on imines under study . The last includes the evaluation of ΔG° , ΔH° and ΔS° thermodynamic parameters for the ionization reactions of imines and for their conjugate acids forms .

These thermodynamic parameters such as ΔG° , ΔH° and ΔS° were calculated from standard equations shown in our previous publications[9,10] using equations (3-5) of the forms :-

$$\Delta G^{\circ} = -RT \ln Ka \quad \ldots\ldots\ldots(3)$$

Ka = Ionization constant of imine
R = 8.314 $J.mole^{-1}.deg.^{-1}$
T = Absolute temperature

Table (2) : Thermodynamical parameters for imines at different temperatures in 10% ethanol

Com. No.	Temp. k	Ln k	ΔH^{o} $J.mole^{-1}$	ΔG^{o} $J.mole^{-1}$	ΔS^{o} $J.mole^{-1}.k^{-1}$	$\overline{\Delta H^{\circ}}$ $J.mole^{-1}$	$\overline{\Delta G^{\circ}}$ $J.mole^{-1}$	$\overline{\Delta S^{\circ}}$ $J.mole^{-1}.k^{-1}$
1	293	-29.16	36471.8	71043.2	-117.99	37060.1	73991.2	-117.99
	303	-29.11	37590.6	73332.2	-117.96			
	313	-28.59	37452.4	74386.2	-117.99			
	323	-27.93	36903.1	75009.7	-117.98			
	333	-27.52	36882.8	76184.6	-118.02			
2	293	-29.39	38488.8	71599.1	-113.00	38312.2	73674.8	-112.98
	303	-28.58	37761.9	71993.4	-112.98			
	313	-28.55	38930.1	74305.3	-113.02			
	323	-27.63	37703.3	74188.6	-112.96			
	333	-27.56	38676.8	76287.8	-112.95			
3#	293	-15.98	47453.3	38927.2	+29.099	47620.2	38513.9	+29.1
	303	-15.27	47284.3	38474.9	+29.080			
	313	-15.12	48454.5	39355.3	+29.070			
	323	-14.12	47317.1	37919.8	+29.094			
	333	-13.69	47591.6	37892.1	+29.130			
3##	293	-23.25	72013.1	56646.3	+52.450	73300.2	56876.4	52.5
	303	-23.20	74344.9	58446.2	+52.470			
	313	-22.45	74846.8	58421.8	+52.480			
	323	-20.44	71840.4	54896.3	+52.460			
	333	-20.22	73455.5	55971.2	+52.510			
#4	293	-22.05	10550.3	53721.2	-147.34			

	303	-22.89	10499.8	55134.1	-147.31			
	313	-21.80	10612.1	56735.0	-147.35	10556.0	56673.7	-147.3
	323	-21.66	10575.2	58173.6	-147.36			
	333	-21.53	10542.7	59604.8	-147.33			
	293	-23.86	28218.6	58113.1	-102.03			
	303	-23.39	27997.7	58933.5	-102.09			
##4	313	-23.00	27906.9	59859.8	-102.08			
	323	-22.69	27965.9	60937.5	-102.07	28144.1	60039.3	-102.1
	333	-22.52	28631.2	62352.4	-102.10			
	293	-14.73	34250.2	35884.2	-5.58			
	303	-13.98	33529.8	35223.8	-5.59			
5#	313	-13.97	34610.4	36356.3	-5.58			
	323	-13.20	33642.9	35443.3	-5.57	34072.7	35819.5	-5.6
	333	13.07	34330.2	36190.0	-5.59			
	293	-17.64	32462.3	42960.1	-35.83			
	303	-16.67	31126.5	41987.2	-35.84			
5##	313	-16.55	31841.5	43073.3	-35.88			
	323	-16.20	31905.5	43491.0	-35.87	31915.7	43141.7	-35.9
	333	-15.96	32242.67	44196.8	-35.89			
	293	-20.48	5841.5	49890.2	-150.3			
	303	-20.42	5889.8	51445.0	-150.4			
#6	313	-20.39	6006.1	53053.0	-150.3			
	323	-20.29	5929.4	54475.9	-150.3	5900.6	52953.0	-150.3
	333	-20.19	5836.1	55901.1	-150.4			
	293	-21.81	24131.0	53118.2	-98.93			
	303	-21.39	23896.6	53895.7	-99.01			
##6	313	-21.13	24008.7	54973.4	-98.93			
	323	-20.74	23728.4	55697.1	-98.97	24022.8	54998.2	-98.96
	333	-20.70	24349.5	57306.7	-98.97			
	293	-27.44	19527.0	66852.1	-161.52			
	303	-27.25	19714.8	68634.9	-161.45			
7	313	-26.98	19662.8	70149.0	-161.46			
	323	-26.65	19404.9	71557.5	-161.46	19613.2	70152.5	-161.47
	333	-26.56	19756.5	73519.2	-161.44			
	293	-26.91	24028.7	65556.4	-141.73			
	303	-26.67	24244.2	67187.6	-141.73			
8	313	-26.10	23561.1	67925.0	-141.74			
	323	-25.98	23991.6	69779.8	-141.76	24017.9	68380.9	-141.74
	333	-25.81	24263.7	71455.7	-141.72			
	293	-27.17	27546.3	66177.0	-131.85			
	303	-26.94	27907.1	67877.3	-131.92			
9	313	-26.75	28333.7	69616.3	-131.89			
	323	-26.17	27681.3	70280.7	-131.88	27840.8	69117.7	-131.88
	333	-25.88	27735.5	71637.4	-131.84			
	293	-28.98	52510.5	70589.4	-61.70			
	303	-27.56	50725.4	69416.2	-61.69			
10	313	-27.18	51410.7	70723.3	-61.70			
	323	-26.87	52220.7	72156.7	-61.72	51775.5	71090.1	-61.71
	333	-26.21	52010.2	72564.9	61.73			

	293	-29.38	65772.1	71560.9	-19.76			
	303	-27.74	63885.4	69877.9	-19.78			
11	313	-27.41	65135.1	71427.9	-20.11			
	323	-26.63	65121.5	71505.0	-19.76	65072.6	71283.2	-19.84
	333	-26.02	65448.8	72044.1	-19.81			
	293	-29.46	63565.0	71757.2	-27.96			
	303	-28.46	63467.3	71958.9	-28.02			
12	313	-27.98	64052.6	72820.5	-28.01			
	323	-26.96	63359.9	72407.8	-28.01	63659.8	72425.0	-28.00
	333	-26.43	63854.1	73180.7	-28.01			
	293	-11.99	49178.0	29199.9	68.18			
	303	-11.46	49521.3	28868.1	68.16			
9*	313	-10.90	49698.4	28373.2	68.13			
	323	-10.23	49487.0	27465.5	68.18	49448.5	28115.3	68.16
	333	-9.63	49357.9	26669.8	68.13			
	293	-11.01	41529.0	26812.6	50.23			
	303	-10.63	41989.1	26790.4	50.16			
10*	313	-10.04	41839.5	26122.6	50.21			
	323	-9.60	41994.6	25781.1	50.20	41802.7	26090.8	50.20
	333	-9.01	41661.3	24947.3	50.19			
	293	-14.51	50478.8	35344.1	51.65			
	303	-13.83	50488.6	34847.3	51.62			
11*	313	-13.32	50827.8	34663.6	51.64			
	323	-12.68	50733.0	34045.9	51.66	50612.0	34446.0	51.65
	333	-12.04	50531.8	33329.0	51.66			
	293	-9.46	49090.3	23050.0	88.87			
	303	-8.95	49481.0	22545.5	88.90			
12*	313	-8.45	49812.9	21997.7	88.87			
	323	-7.84	49766.2	21061.9	88.87	49448.5	21629.1	88.88
	333	-7.04	49092.1	19490.5	88.89			
	293	-6.88	39780.0	16771.2	78.53			
	303	-6.24	39525.3	15722.4	78.56			
13*	313	-5.25	38253.5	13651.5	78.60			
	323	-5.18	39287.7	13923.2	78.53	39392.6	14797.4	78.56
	333	-5.04	40116.5	13954.6	78.56			
	293	-8.55	53558.0	20834.5	111.68			
	303	-7.62	53043.1	19189.3	111.73			
14*	313	-7.42	54273.2	19299.0	111.74			
	323	-6.40	53268.0	17192.6	111.69	53557.2	18591.0`	111.71
	333	-5.94	53643.7	16439.5	111.72			
	293	-12.65	53826.0	30816.4	78.53			
	303	-12.18	54479.0	30675.6	78.56			
15*	313	-11.42	54299.2	29708.2	78.57			
	323	-10.72	54154.2	28694.9	78.51	54185.6	29601.5	78.54
	333	-10.12	54169.7	28012.4	78.55			

* : ايونات النتريليوم

: $\ln K_1$

: $\ln K_2$

Tables (2) shows that ΔG° values for all imines have a positive signs with a range of values (14797.4-73991.2) $J.mole^{-1}$. These positive signs mentioned mean that ionization processes in these imines occurred in non spontaneous processes . These results were expected due to the fact that imines under consideration having a covalent bondings . Hence they are ionized with difficulty as compared with ionic bondings . The heat or enthalpy of ionization reactions ΔH° was calculated from the integrated Vant Hoff equation (4) of the from :-

$$\ln Ka = \text{constant} - \frac{\Delta H^{\circ}}{RT} \ldots\ldots\ldots(4)$$

ΔH°= Enthalpy of Ionization reaction

From equation (4) , the plots of lnKa versus the inverse of absolute temperature (T^{-1}) for imines showed a straight lines using Microsoft Excel programme of correlation coefficient range values (0.8672-0.9985) , as shown in typical examples in Fig (1-4) .

Figs (1-2) Showed $\ln K_1$ and $\ln K_2$ for phenol and oxime groups respectively .

Table (2) showed that all ΔH° values at a range of temperature(293-333) K had a positive signs of a range values (5900.6-73300.2) J. $mole^{-1}$. These values indicated that ionization reactions in imines were endothermic . These results are in full agreement with theoretical expectation of breaking covalent bond in imines or ionization of imines under study after absorption of heat energy .

The change in the entropy ΔS° for ionization reactions of imines were calculated from Gibbs equation (3) of the from :

$$\overline{\Delta G^{\circ}} = \overline{\Delta H^{\circ}} - T\,\overline{\Delta S^{\circ}} \ldots\ldots(5)$$

$$\overline{\Delta S^{\circ}} = S_2 - S_1$$

S_2= Entropy of ionization products

S_1= Entropy of reactants

Theoretically $\overline{\Delta S^{\circ}}$ values for ionization reactions in imines under study have a positive values . This was for an increase in random of the system by ionization reactions . This result is in a full agreement with ΔS° values as in Table (2) for imines numbered (2-3,9-10) . The other rest of imines numbered (1-2,4-12) have a negative signs for ΔS° parameters . These were happen by considering the two folds reasons :-

1- By the strong interactions of the solvent (ethanol or water) molecules with the positive or negative ions produced by ionization of imines .

2- By the occurrence of inter molecular hydrogen bonding in imines as observed experimentally by dilution method in IR spectra in imines numbered (1-2,8-3,11-12) . Hence it was concluded that reasons (1-2) , each of them , contribute to different degrees in altering ΔS° sign from positive to negative values in imines outlined in Table (2)

Finally , these thermodynamic study was in full agreement with other similar studies[14,15,19,20] .

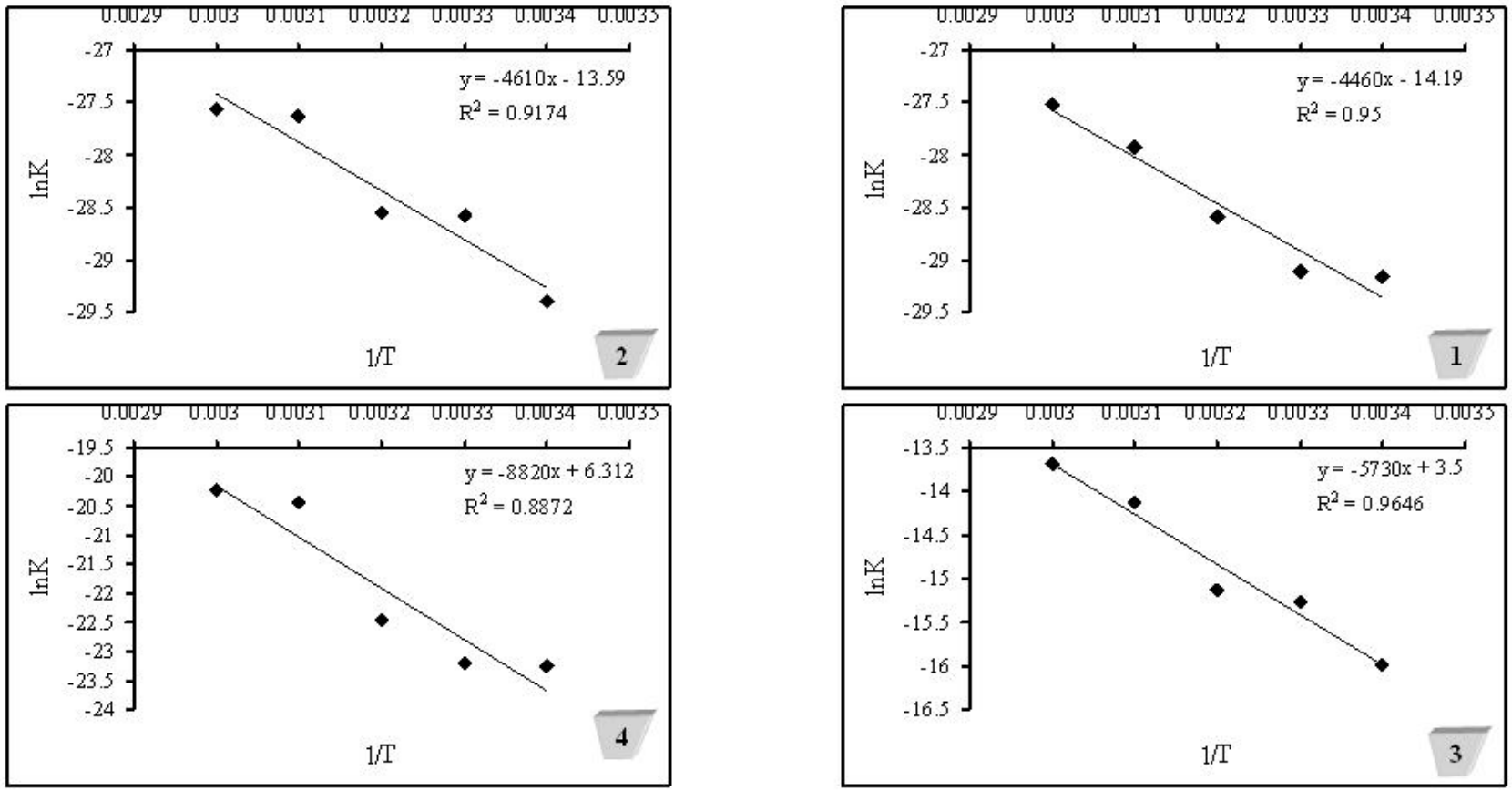


Fig (1) : Relationship between lnKa versus T^{-1} for geometrical isomer in :-

1- syn methyl 2-pyridyl ketoxime
2- anti methyl 2-pyridyl ketoxime
3- syn 3 hydroxy benzaldoxime (lnK_1)
4- syn 3 hydroxy benzaldoxime (lnK_2)

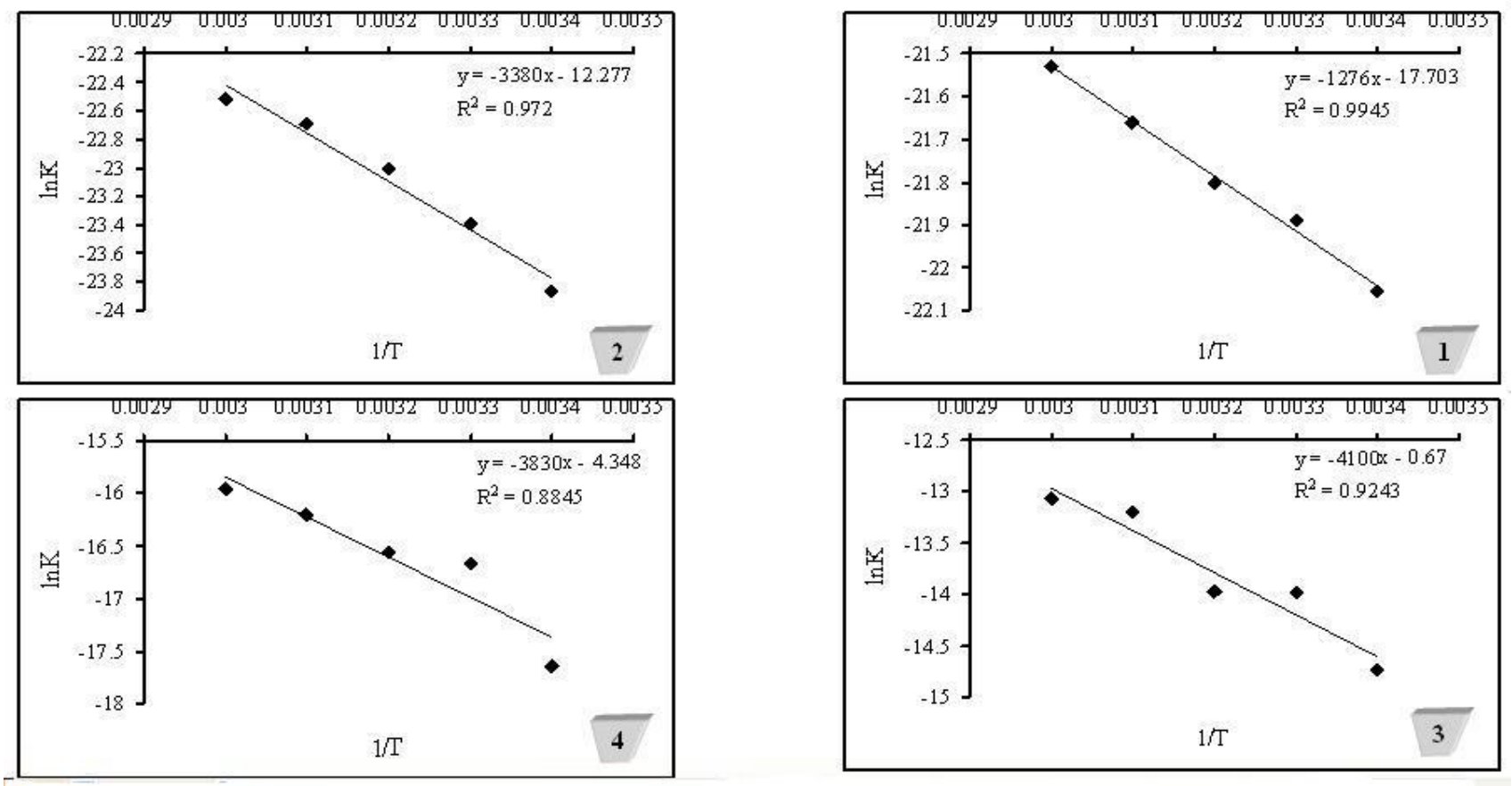
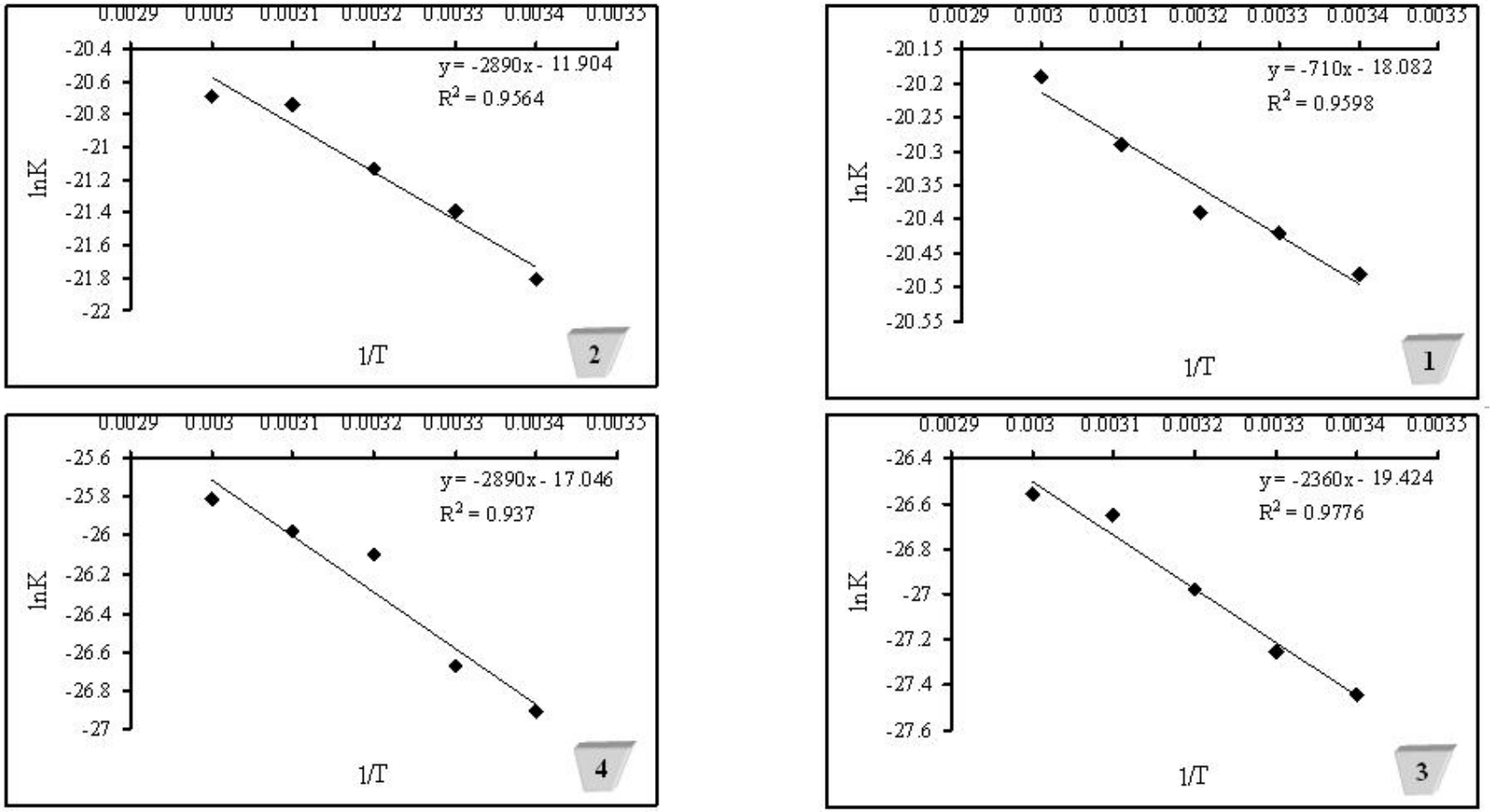


Fig (2) : Relationship between lnKa versus T^{-1} for geometrical isomer in :-

1- **Anti 3-hydroxy benzaldoxime (lnK_1)**
2- **Anti 3-hydroxy benzaldoxime (lnK_2)**
3- **syn 4 hydroxy benzaldoxime (lnK_1)**
4- **syn 4 hydroxy benzaldoxime (lnK_2)**



Fig(3) : Relationship between lnKa versus T^{-1} for geometrical isomer in :-

1- Anti 4-hydroxy benzaldoxime (lnK_1)
2- Anti 4-hydroxy benzaldoxime (lnK_2)
3- syn 4 methoxy benzaldoxime
4- syn 4 methoxy benzaldoxime

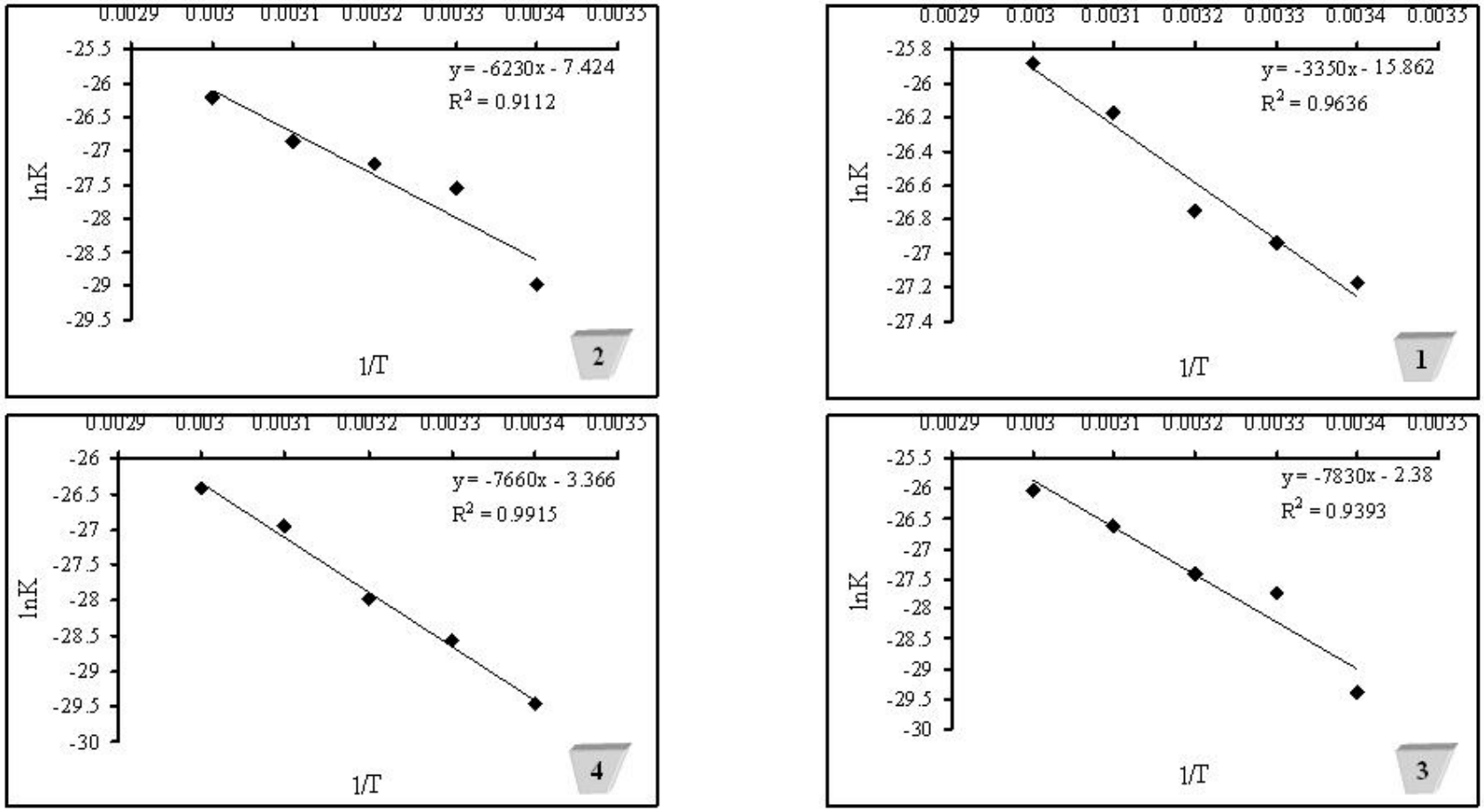


Fig (4) : Relationship between lnKa versus T^{-1} for phenolic Schiff bases in :-

1- Methyl 2-pyridyl ketonylidene o-hydroxy aniline
2- Methyl 2-pyridyl ketonylidene m-hydroxy aniline
3- Methyl 2-pyridyl ketonylidene p-hydroxy aniline
4- Methyl 2-pyridyl ketonylidene p-amino napthol

Conclusions

1- Fifteen imines in a forms of Schiff bases and syn and anti oximes were prepared by standard methods using aromatic aldehydes and ketones.

2- The pK_a for these imines and their acids conjugate were estimated by accurate and simple potentiometric method in 10% ethanol solvent at temperature range between (293-333)K.

3- The thermodynamic parameters calculated for ionization reactions proved that these reactions were occurred in non spontaneous and endothermic process. Also ionization reactions were accompanied by an increase or decrease in entropy as discussed properly in a scientific way and supported by suitable references [14-15,19-20].

References

1-S.Aureus , E.Coli , C.Styphi , A. Rhizopussp and A.Niger , 2010, Organic Chemistry International , Article ID 648589 , 7 pages.

2-J.Salimon ,N.Salish , E.Yousif , A.Hameed and H.Ibraheem, Australin ***J. Basic and Applied Sciences*** , 2010 , **4(7)** 2016.

3-S.Rao and A.S.Mitlra ***,J. Indian chem. Soc***., 1978 , **55**,420.

4-A.K.Mittal and O.P.Singhal, ***J.Indian chem..Soc***. ,1986 , **63**,739.

5-S.J.Yan and W.H.Burton, P.L.Chlen and C.C.Cheng, ***J.Hetrocyclic chem.*** , 1978 , **15** , 297.

6- T.Papenfushs, Ger. Offen .***Chem. Abst***. , 1976, **84** , 6481.

7-M.N.Ibrahim and S.A.Sharif, E ***Journal of Chemistry*** , 2007, **4(4)** , 531.

8-A.R.Butler , Problems in Physical Organic Chemistry , 1972 , John Wiley , London.

9-A.S.P.Azzouz, Z. ***Phys.Chem***., 2002 , **216** ,1053

10- A.S.P.Azzouz ,M.M.H.AL- Niemi, Z. ***Phys.Chem*** .,2005, **219**, 1591.

11- A.S.P.Azzouz, Nat. ***J.Chem.***, 2006 , **22** , 214.

12- A.S.P.Azzouz, M.A.Hussin and M.G.AL-Dabbagh, Nat. ***J.Chem***., 2010, **38** ,361.

13-A.S.P.Azzouz, S.A.Ahmed and R.H.AL-Hyali, Nat. ***J.Chem***., 2010, **39** , 499.

14- A.S.P.Azzouz, M.A.Hussin, ***J.Edu.Sci.***, 2011 , **24(4)**,1.

15-A.S.P.Azzouz andH.J.S.AL-Moula,,AL-Anbar ***J.Pure Sci.***, 2010, **4(2)**, 59.

16- A.F.Vogel, Textbook of Practical Organic Chemistry ,1978, 4th ed., Logman, London, 847.

17-J.R.Majer and A.S.P.Azzouz, ***J.Chem. Soc*** . Farad. Trans. 1, 1983, **79**, 675.

18-A.S.P.Azzouz and D.P.AL-Bakzo, ***Phy. Chem An Indian J.***,2012 ,**7(1)**,2.

19- A.S.P.Azzouz and N.A.AL-Azzawi, ***J.Edu.Sci***.,2002, **1(14)** ,20.

20- A.S.P.Azzouz and R.D. Sulayman , ***Asian J.Chem***.,2013,**25(10),**5303