Influence of Temperatures and Thermodynamic Parameters on pKa Values for Some Acids and Basic Imines Derived 3-Acetyl and 4-Acetyl Pyridines

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The work is concerned with the influence of temperature on the values of ionization constants for some acids and basic imines in fixed 10 % ethanol in a mixture of ethanol and water. These imines are in a forms of syn or anti oxime and phenolic or amino Schiff bases, containing phenol and amine groups in *ortho*, *meta* and *para* positions on the aromatic rings of primary amine sides. The thermodynamic of ionization for imines confirm that ionization reactions in these imines are accompanied by an increase of parameters $\Delta G°$ and $\Delta H°$. These mean that ionization reactions in these imines are non-spontaneous and endothermic respectively. $\Delta S°$ values of ionization reactions estimated have a negative signs.

Key Words: Thermodynamic parameters, pKa, Imines.

INTRODUCTION

A great numbers of imines whether are aliphatic, aromatic or their mixture are prepared during the last years[1-3]. This is for their wide applications in different fields[4,5]. It had proved in a numerous studies, that temperature had a great influence on many reactions as tautomerism of carbonyl[6], benzoin[7] compounds, pKa of imines[8] and other reactions.

The lack of the influence of temperature on pKa values of some acids and basic imines derived from 3-acetyl pyridine and 4-acetyl pyridine, encourage the researchers to deal with such important topic. The study was conducted at fixed 10 % ethanol solvent and temperature range between (288-328) K. The thermodynamic parameters of ionization namely $\Delta G°$, $\Delta H°$ and $\Delta S°$ were included and discussed[9].

EXPERIMENTAL

All chemicals used throughout this work were of Fluka, BDH and Molckula origin.

All imines in a forms of oximes *syn* and Schiff bases were prepared by mixing equimolar amounts of 3-acetyl pyridine or 4-acetyl pyridine with suitable primary amine as hydroxyl amine, *o*, *m*, *p*-amino phenol and *o*, *m*, *p*-phenylene diamine, according to standard procedure[10,11].

The *syn* aldoximes were converted to their *anti* forms by either catalytic HCl gas method[11] or refluxing *syn* oxime in dry benzene, after addition of dry activated charcoal method[11] (Table-1).

The pKa values for mines were determined[12] by potentiometric method, using sodium hydroxide or HCl titrant using the following equations:

$$pKa = pH + \log \frac{[HA]}{[A^-]} \qquad (1)$$

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

The [HA], [BH$^+$], [A$^-$] and [B] were determined[12] using a proton balance equations.

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. A computerized double beam Shimadzu 1601 for measurement of UV spectra of imines solutions in solvent ethanol and dry benzene; 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; A digital Philips pH meter model pw 9421 was used for measuring pH of solutions during potentiometric titration.

RESULTS AND DISCUSSION

The values of ionization constant pKa for 16 imines under study were determination at five different temperatures in the range (288-328) K. These show that pKa values or ln Ka for any imine were decreased by increasing temperature. This mean that acidity of any imine at any temperature listed in Table-2 was increased by increase of temperature.

TABLE-1
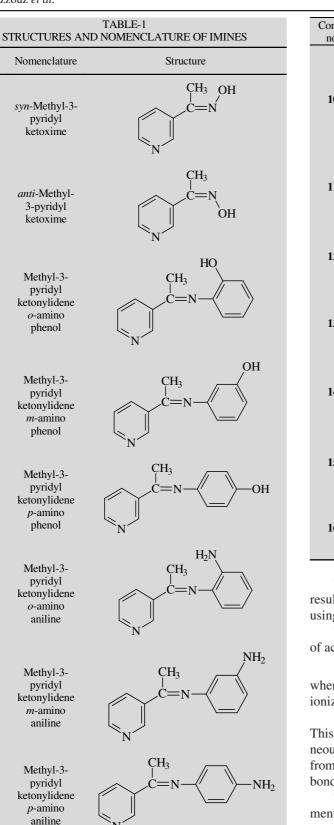STRUCTURES AND NOMENCLATURE OF IMINES

Comp. no.	Nomenclature	Structure
1	*syn*-Methyl-3-pyridyl ketoxime	
2	*anti*-Methyl-3-pyridyl ketoxime	
3	Methyl-3-pyridyl ketonylidene *o*-amino phenol	
4	Methyl-3-pyridyl ketonylidene *m*-amino phenol	
5	Methyl-3-pyridyl ketonylidene *p*-amino phenol	
6	Methyl-3-pyridyl ketonylidene *o*-amino aniline	
7	Methyl-3-pyridyl ketonylidene *m*-amino aniline	
8	Methyl-3-pyridyl ketonylidene *p*-amino aniline	
9	*syn*-Methyl-4-pyridyl ketoxime	

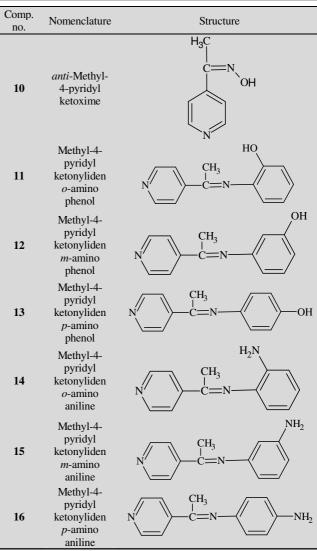| Comp. no.	Nomenclature	Structure
10	*anti*-Methyl-4-pyridyl ketoxime	
11	Methyl-4-pyridyl ketonyliden *o*-amino phenol	
12	Methyl-4-pyridyl ketonyliden *m*-amino phenol	
13	Methyl-4-pyridyl ketonyliden *p*-amino phenol	
14	Methyl-4-pyridyl ketonyliden *o*-amino aniline	
15	Methyl-4-pyridyl ketonyliden *m*-amino aniline	
16	Methyl-4-pyridyl ketonyliden *p*-amino aniline	

This comes in agreement with earlier works[8,13]. These results facilitate the evaluation of thermodynamic parameters using a standard[6,7] equations.

The change in Gibbs free energy ($\Delta G°$) upon ionization of acid was calculated from an equation of the form:

$$\Delta G° = - RT \ln K_a \qquad (1)$$

where R = 8.314 J mol⁻¹ deg⁻¹, T = absolute temperature, K_a = ionization constant of acid.

All values of $\Delta G°$ listed in Table-2 had a positive signs. This means that ionization process of imines is non-spontaneous. The last can be accepted[8], because ionization of ions from oxime, phenol or conjugate acid of imines have a covalent bonding properties or are difficult to ionize solutions.

The change of enthalpy ($\Delta H°$) upon ionization of acids mentioned were calculated from the integrated Van't Hoff equation of the form:

$$\ln K_a = \text{constant} - \Delta H°/RT \qquad (2)$$

$\Delta H°$ = change in enthalpy upon ionization, R = 8.314 J mol⁻¹ deg⁻¹, T = Absolute temperature.

From equation (2) using Microsoft excel program, the plot of ln K *versus* T⁻¹, showed a straight lines for all acids with negative slopes. Their correlation coefficients had a range values between 0.874-0.9954.

TABLE-2
THERMODYNAMIC PARAMETERS FOR IMINES UNDER STUDY IN 10% ETHANOL

Comp. no.	Temp. (K)	ln Ka	$\Delta H°$ (J mol^{-1})	$\Delta G°$ (J mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	$\overline{\Delta H°}$ (J mol^{-1})	$\overline{\Delta G°}$ (J mol^{-1})	$\overline{\Delta S°}$ (J mol^{-1} K^{-1})
1	288	-21.842	24038.90	52299.18	-98.13			
	298	-21.781	24722.45	53963.99	-98.13			
	308	-21.781	24975.88	55198.71	-98.13	24483.90	54706.71	-98.13
	318	-21.781	24800.65	56004.72	-98.13			
	328	-20.560	23881.63	56066.96	-98.13			
2	288	-25.293	41675.81	60562.37	-65.58			
	298	-24.951	42275.55	61817.89	-65.58			
	308	-24.546	42657.11	62855.24	-65.58	42048.44	62240.56	-65.58
	318	-23.689	41776.29	62630.21	-65.58			
	328	-23.689	41857.42	63367.11	-65.58			
3	288	-21.684	21147.62	51920.86	-06.85			
	298	-21.404	21188.19	53029.95	-06.85			
	308	-21.312	21663.62	54573.89	-06.85	21298.37	54208.64	-106.85
	318	-21.047	21666.37	55645.15	-06.85			
	328	-20.489	20826.04	55873.34	-06.85			
4	288	-22.908	18506.56	54851.65	-26.19			
	298	-22.771	18809.73	56416.79	-26.19			
	308	-22.685	19220.70	58089.75	-26.19	18773.24	57642.29	-126.19
	318	-22.369	19009.29	59140.33	-26.19			
	328	-21.897	18319.93	59712.94	-26.19			
5	288	-23.394	39120.23	56015.34	-58.66			
	298	-23.063	39658.49	57140.24	-58.66			
	308	-22.507	39565.56	57633.94	-58.66	39382.04	57450.42	-58.66
	318	-21.932	39329.94	57984.96	-58.66			
	328	-21.444	39235.96	58477.62	-58.66			
6	288	-12.288	22196.38	29422.78	-25.09			
	298	-11.928	22075.17	29552.48	-25.09			
	308	-11.533	21804.46	29532.69	-25.09	22065.72	29793.95	-25.09
	318	-11.329	21973.05	29952.19	-25.09			
	328	-11.188	22279.52	30509.59	-25.09			
7	288	-12.569	27899.92	30095.62	-7.62			
	298	-12.294	28187.34	30459.27	-7.62			
	308	-11.963	28285.62	30633.79	-7.62	28057.60	30405.77	-7.62
	318	-11.468	27895.28	30319.69	-7.62			
	328	-11.192	28019.84	30520.49	-7.62			
8	288	-16.244	33581.91	38895.15	-18.45			
	298	-15.702	33405.10	38902.84	-18.45			
	308	-15.442	33860.29	39542.51	-18.45	33574.49	39256.71	-18.45
	318	-14.902	33532.04	39398.95	-18.45			
	328	-14.501	33492.92	39544.11	-18.45			
9	288	-24.687	38701.20	59111.34	-70.87			
	298	-24.100	38590.66	59709.49	-70.87			
	308	-23.678	38805.03	60632.54	-70.87	38693.15	60520.66	-70.87
	318	-23.202	38806.46	61342.65	-70.87			
	328	-22.665	38562.39	61807.27	-70.87			
10	288	-24.006	37958.93	57480.73	-67.78			
	298	-23.675	38456.87	58656.52	-67.78			
	308	-23.182	38484.94	59362.43	-67.78	38223.32	59102.44	-67.78
	318	-22.595	38182.51	59737.84	-67.78			
	328	-22.103	38041.34	60274.70	-67.78			
11	288	-21.929	22885.98	52507.49	-102.85			
	298	-21.312	22151.97	52802.01	-102.85			
	308	-21.296	22854.35	54532.92	-102.85	22665.25	54344.27	-102.85
	318	-21.074	23009.44	55716.54	-102.85			
	328	-20.595	22426.78	56162.40	-102.85			
12	288	-23.953	44043.18	57353.83	-46.22			
	298	-23.401	44204.84	57977.66	-46.22			
	308	-23.013	44694.67	58929.67	-46.22	44265.25	58500.24	-46.22
	318	-22.463	44691.67	59388.85	-46.22			
	328	-21.581	43691.87	58851.21	-46.22			

Comp. no.	Temp. (K)	ln Ka	ΔH° (J mol^{-1})	ΔG° (J mol^{-1})	ΔS° (J mol^{-1} K^{-1})	$\overline{\Delta H}^\circ$ (J mol^{-1})	$\overline{\Delta G}^\circ$ (J mol^{-1})	$\overline{\Delta S}^\circ$ (J mol^{-1} K^{-1})
13	288	-23.206	38619.79	55565.19	-58.84			
	298	-22.859	39101.04	56634.82	-58.84			
	308	-22.558	39642.38	57764.54	-58.84	39026.19	57148.36	-58.84
	318	-22.008	39475.35	58185.89	-58.84			
	328	-21.119	38292.42	57591.34	-58.84			
14	288	-12.299	24502.22	29449.12	-17.18			
	298	-12.038	24706.35	29825.01	-17.18			
	308	-11.630	24490.65	29781.08	-17.18	24399.22	29847.90	-17.18
	318	-11.321	24468.85	29931.05	-17.18			
	328	-11.094	24619.28	30253.25	-17.18			
15	288	-12.301	22514.84	29453.91	-24.09			
	298	-12.057	22692.08	29872.09	-24.09			
	308	-11.847	22915.81	30336.76	-24.09	22774.48	30046.62	-24.09
	318	-11.335	22306.18	29968.06	-24.09			
	328	-11.222	22699.48	30602.30	-24.09			
16	288	-14.643	22514.84	35061.67	-22.33			
	298	-14.429	22692.08	35748.89	-22.33			
	308	-14.154	22915.81	36244.32	-22.33	28933.27	35811.34	-22.33
	318	-13.632	22306.18	36040.99	-22.33			
	328	-13.187	22699.48	35960.84	-22.33			

The change of entropy ΔS° accompanied ionization of acids were also calculated from Gibbs equation of the form:

$$\overline{\Delta G}^\circ = \overline{\Delta H}^\circ - T \overline{\Delta S}^\circ$$

$$\Delta S^\circ = S_2^\circ - S_1^\circ$$

where S_2° = entropy for products, S_1° = entropy for reactions.

Actually the change of entropy ΔS° for any ionization reaction mean the change of system from order into random. This must accompany by an increase of entropy for the product S_2° relative to the entropy of reaction S_1° *i.e.* $S_2^\circ > S_1^\circ$. $\Delta S^\circ = S_2^\circ - S_1^\circ$ must be positive value.

It was shown in Table-2 that all ΔS° value had a negative signs. This was in contrary to our expectation. This can be interpreted by main two reasons:

(1) The interaction of solvent with products of ionization reaction. This was accompanied by an increase of order of ions products. In this case, a possible interaction can happen between anion of acids A$^-$ with polar 10 % ethanolic solvent which contains 90 % water. The last resulted to a decrease of random of ion system product and finally resulted to a negative values of $\overline{\Delta S}^\circ$ thermodynamic parameter.

(2) The existence of intermolecular hydrogen bonding in oximes numbered 2, 4, 7, 9, 10, 15 as confirmed in this study from measurements of IR spectra resulted to a negative values of $\overline{\Delta S}^\circ$.

Finally all thermodynamic study were in full agreement with other earlier similar studies[8,12,13] in the same field.

Conclusion

The thermodynamic parameters for ionization reactions of acids in this study, were calculated at 10 % ethanol solvent from standard equations. These give a positive signs of $\overline{\Delta G}^\circ$ and $\overline{\Delta H}^\circ$ thermodynamic parameters. These mean that ionization process in acids were non spontaneous and endothermic respectively. A suitable interpretation for non spontaneous process was given due to the covalent bonding property of the weak ionized oxime and phenol groups. The negative sign of ΔS° thermodynamic parameter was due to two folds reasons as: (1) The interactions between 10 % ethanol solvent with anions of acids. (2) The presence of intermolecular hydrogen in most acids.

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