Influence of Temperatures and Thermodynamic Parameters on pK_a 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 ΔG° and ΔH° . These mean that ionization reactions in these imines are non-spontaneous and endothermic respectively. ΔS° values of ionization reactions estimated have a negative signs.

Key Words: Thermodynamic parameters, pK_a , Imines.

INTRODUCTION

A great numbers of imines whether are aliphatic, aromatic or their mixture are prepared during the last years¹⁻³. 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 carbonyl⁶, benzoin⁷ compounds, pK_a of imines⁸ and other reactions.

The lack of the influence of temperature on pK_a 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 ΔG° , ΔH° and ΔS° were included and discussed⁹.

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* aldioximes were converted to their *anti* forms by either catalytic HCl gas method¹¹ or refluxing *syn* oxime in dry benzene, after addition of dry activated charcoal method¹¹ (Table-1).

The pK_a values for mines were determined¹² by potentiometric method, using sodium hydroxide or HCl titrant using the following equations:

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

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

The $[HA]$, $[BH^+]$, $[A^-]$ and $[B]$ were determined¹² 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 pK_a for 16 imines under study were determination at five different temperatures in the range (288-328) K. These show that pK_a values or $\ln K_a$ 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	<i>syn</i> -Methyl-3-pyridyl ketoxime	
2	<i>anti</i> -Methyl-3-pyridyl ketoxime	
3	Methyl-3-pyridyl ketonylidene <i>o</i> -amino phenol	
4	Methyl-3-pyridyl ketonylidene <i>m</i> -amino phenol	
5	Methyl-3-pyridyl ketonylidene <i>p</i> -amino phenol	
6	Methyl-3-pyridyl ketonylidene <i>o</i> -amino aniline	
7	Methyl-3-pyridyl ketonylidene <i>m</i> -amino aniline	
8	Methyl-3-pyridyl ketonylidene <i>p</i> -amino aniline	
9	<i>syn</i> -Methyl-4-pyridyl ketoxime	

Comp. no.	Nomenclature	Structure
10	<i>anti</i> -Methyl-4-pyridyl ketoxime	
11	Methyl-4-pyridyl ketonylidene <i>o</i> -amino phenol	
12	Methyl-4-pyridyl ketonylidene <i>m</i> -amino phenol	
13	Methyl-4-pyridyl ketonylidene <i>p</i> -amino phenol	
14	Methyl-4-pyridyl ketonylidene <i>o</i> -amino aniline	
15	Methyl-4-pyridyl ketonylidene <i>m</i> -amino aniline	
16	Methyl-4-pyridyl ketonylidene <i>p</i> -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 (ΔG°) upon ionization of acid was calculated from an equation of the form:

$$\Delta G^\circ = -RT \ln K_a \quad (1)$$

where $R = 8.314 \text{ J mol}^{-1} \text{ deg}^{-1}$, T = absolute temperature, K_a = ionization constant of acid.

All values of ΔG° listed in Table-2 had a positive signs. This means that ionization process of imines is non-spontaneous. The last can be accepted⁸, 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 (ΔH°) upon ionization of acids mentioned were calculated from the integrated Van't Hoff equation of the form:

$$\ln K_a = \text{constant} - \Delta H^\circ/RT \quad (2)$$

ΔH° = change in enthalpy upon ionization, $R = 8.314 \text{ J mol}^{-1} \text{ deg}^{-1}$, 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	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)
1	288	-21.842	24038.90	52299.18	-98.13	24483.90	54706.71	-98.13
	298	-21.781	24722.45	53963.99	-98.13			
	308	-21.781	24975.88	55198.71	-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	42048.44	62240.56	-65.58
	298	-24.951	42275.55	61817.89	-65.58			
	308	-24.546	42657.11	62855.24	-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	21298.37	54208.64	-106.85
	298	-21.404	21188.19	53029.95	-06.85			
	308	-21.312	21663.62	54573.89	-06.85			
	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	18773.24	57642.29	-126.19
	298	-22.771	18809.73	56416.79	-26.19			
	308	-22.685	19220.70	58089.75	-26.19			
	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	39382.04	57450.42	-58.66
	298	-23.063	39658.49	57140.24	-58.66			
	308	-22.507	39565.56	57633.94	-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	22065.72	29793.95	-25.09
	298	-11.928	22075.17	29552.48	-25.09			
	308	-11.533	21804.46	29532.69	-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	28057.60	30405.77	-7.62
	298	-12.294	28187.34	30459.27	-7.62			
	308	-11.963	28285.62	30633.79	-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	33574.49	39256.71	-18.45
	298	-15.702	33405.10	38902.84	-18.45			
	308	-15.442	33860.29	39542.51	-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	38693.15	60520.66	-70.87
	298	-24.100	38590.66	59709.49	-70.87			
	308	-23.678	38805.03	60632.54	-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	38223.32	59102.44	-67.78
	298	-23.675	38456.87	58656.52	-67.78			
	308	-23.182	38484.94	59362.43	-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	22665.25	54344.27	-102.85
	298	-21.312	22151.97	52802.01	-102.85			
	308	-21.296	22854.35	54532.92	-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	44265.25	58500.24	-46.22
	298	-23.401	44204.84	57977.66	-46.22			
	308	-23.013	44694.67	58929.67	-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	39026.19	57148.36	-58.84
	298	-22.859	39101.04	56634.82	-58.84			
	308	-22.558	39642.38	57764.54	-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	24399.22	29847.90	-17.18
	298	-12.038	24706.35	29825.01	-17.18			
	308	-11.630	24490.65	29781.08	-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	22774.48	30046.62	-24.09
	298	-12.057	22692.08	29872.09	-24.09			
	308	-11.847	22915.81	30336.76	-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	28933.27	35811.34	-22.33
	298	-14.429	22692.08	35748.89	-22.33			
	308	-14.154	22915.81	36244.32	-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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