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A new developed potentiometric method for the determination of pKa values for syn and anti isomer pair in 3 and 4- hydroxybenzaldoximes

A.S.P.Azzouz*, D.P.Al-Bakzo
Chemistry Department, College of Education, Mosul University, Mosul, (IRAQ)
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ABSTRACT

Four syn and anti isomers derived from 4-hydroxybenzaldoxime and 3-hydroxybenzaldoxime were prepared by standard method. Their structures were confirmed by using physical methods, namely UV-IR spectra and melting points. The main object of the study is the determination of pKa values for four isometric oximes by potentiometric method. This method was developed for the first time in studying pKa values for diacidic syn and anti isometric oximes derived from 3 or 4-hydroxybenzaldohyde, or for acidic compounds containing simultaneous oxime and phenol groups. This gives a new development for potentiometric method over other methods used for pKa determination. Generally the pK_1 of phenol and pK_2 of oxime groups were found to depend on the type of syn and anti isomer, the temperature and other factors.

KEYWORDS

pKa;
Developed potentiometry;
Phenolic oximes;
Syn and anti isomers;
Thermodynamics.

INTRODUCTION

The methods available for the determination of ionization constants had been reviewed by Albert[1] and Serjeant. By far, the most convenient method for the determination of ionization constant was potentiometric titration method.

Potentiometric method had applied successfully for the determination of pKa for amide[2], aryl azo pyrimidine[3], imines[4], acidic diimine derived from benzil[5] and dibenzamide[6]. In these studies, they found that acidities of all compounds mentioned were depend on their structures, the temperature and the type of solvent used. In one of these studies, the workers[5] had noticed a variation of pKa for syn and anti isomers derived from α or β-benzil monoxime, and was theoretically acceptable. R. Aydin[7] et al were used potentiometric and spectroscopic methods for the determination of acid dissociation constants of some phenols and salicylic acids. In addition, the first and second dissociation constants of salicylic acid derivatives were determined by potentiometry.

The coupled photometric-potentiometric method were applied[8] for the investigation of pKa for 50 water insoluble compounds in an equivalent volumes of methanol, dioxane and acetonitril solvent mixture.

The lack of simple fast and developed potentiometric method for the determination of pKa of bi acidic compounds from 3 or 4-hydroxybenzaldoxime, arises our curiosity to increase experimentation in this field.

These compounds mentioned, having phenolic and oxime groups in their structures. The influence of syn and anti isomers on pKa were included and discussed.

EXPERIMENTAL

3-hydroxyl benzaldehyde, 4-hydroxybenzaldehyde, hydroxylamine. HCl, sodium hydroxide and acid HCl were 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 following equation:

$$pKa = pH + \log \frac{[acid]}{[salt]}$$

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

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

At the beginning of this investigation, it was thought of great importance to confirm the structures of imines under study by physical method[11,12], namely IR,UV spectra and melting points as in TABLE 1. The UV spectra of imines in ethanol and benzene show a bands with E_{max} values greater than 1000 in units liter. $mole^{-1}$ cm^{-1}. They were assigned[1,12] for $\pi \rightarrow \pi^*$ transitions or hydrogen bonding bands in imines under study. From these absorptions were possible to evaluate the change in wave numbers ΔV for characteristic absorptions of imines in ethanol and benzene solvents from an equation of the form.

$$\Delta V = \Delta V_{ethanol} - \Delta V_{benzene}$$

ΔV values collected in TABLE 1 had a negative signs. These mean that imines or oximes under study had a non specified hydrogen bondings.

The FR spectra of solids oximes were measured by KBr disk method. These showed the following stretching absorptions:

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1 The imines linkage C=N have a medium to sharp absorptions in the range 1611.51cm^{-1} to 1656.25cm^{-1}.
2 The phenolic or oximeic groups showed a different intensities in the range 3105.31 cm^{-1} to 3306.45 cm^{-1}.
3 The keto tautomers in oximes numbered (1-4) showed a different intensities for carbonyl stretching vibrations. These were assigned to tautomerism of phenol to carbonyl system.
4 All oximes under study showed tautomerism of oxime to nitroso group N=O, with a strong medium intensity band in a range of values 1509.94 cm^{-1} to 1539.69 cm^{-1}. These tautomerism studies were in agreement with literature[13,14].

In order to check the type of hydrogen bondings in oximes, the dilution[12] method was applied. This showed that all oximes had intermolecular hydrogen bondings.

As known, the melting point of any sample is related to the chemical structure and the process of association[11]. Comparing the melting points of oximes as in TABLE 1 shows that the melting point of syn isomers were greater than their anti analogues.

TABLE 1 : Melting points, UV and IR spectra of syn and anti oximes

No.	Name	UV spectra λ_{nm} (E_{max})			IR cm^{-1}				Melting points (^oC)
		Ethanol	Benzene	ΔV cm^{-1}	V_{OH}	$V_{C=N}$	$V_{C=O}$	$V_{N=O}$	
1.	Syn 4-hydroxybenzaldoxime	298.8 (95700)	246.8 (21720)	-50	3105.31 \(vb)	1636.66 (m)	1792.45 (vw)	1539.65 (s)	88
2.	Anti 4- hydroxybenzaldoxime	248.6 (99600)	239.6 (19920)	-1500	3288.57 (b)	1611.51 (s)	1734.9 (s)	1509.94 (s)	62
3.	Syn 3- hydroxybenzaldoxime	299.6 (6310)	278.2 (12220)	-2500	3226.29 (vb)	1656.25 (m)	1687.5 (w)	1538.87 (m)	112
4.	Anti 3- hydroxybenzaldoxime	294.8 (10680)	289.2 (5710)	-700	3306.45 (b)	1613.45 (m)	1735.88 (w)	1532.1 (m)	82

This was due to the greater extent of polymerization of syn isomer by the aid of intermolecular hydrogen bondings.

The UV, IR spectra of oximes beside the melting points to confirm the chemical structures of oximes. This encourage the workers to proceed for pKa measurements.

The conductance of 10^{-3} M oxime solutions in 10% ethanol as in TABLE 2, showed that the conductance of syn was greater than it anti analogue. This was arised from the greater extent of ionization of syn isomer as compared with its anti isomer. Also TABLE 2 shows that a stability of oxime solutions by the measurements of conductance during about 90 minutes. This means a stable oxime solutions during the time mentioned. Hence oxime solutions can be subjected to potentiometric titrations with NaOH safely.

In our previous study, the Iriving Rossoti potentiometric method had been used in studying pKa of benzaldoxime[15] and its substituents. The study showed the benzaldoxime had pKa value equal 11.5 at 298 K. Then after, the method was applied for the determination of pKa values for oximes and Schiff bases derived from benzil[16].

TABLE 2 : Conductance (μmho) of 10^{-3} oximes solution in 10% ethanol aqueous medium versus time (minutes)

Oxime number	1	2	3	4
Minutes				
0	125	16.5	180	15.1
5	125	16.5	180	15.1
10	125	16.5	180	15.1
15	125	16.5	180	15.1
20	125	16.5	180	15.1
25	125	16.5	180	15.1
30	125	16.5	180	15.1
35	125	16.5	180	15.1
40	125	16.5	181	15.1
45	125	16.5	181	15.1
50	128	16.5	181	15.1
60	129	16.5	181	15.1
70	129	16.5	185	15.1
80	129	16.5	185	15.1
90	129	16.5	185	15.1

Actually, the stated method was accurate and precise, but required a difficult procedure, graphing and calculations with longer time to calculate pKa of unknown.

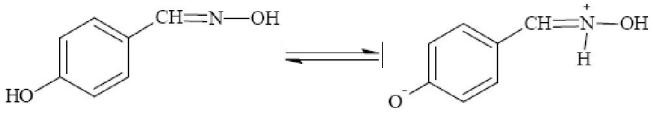
Phenol has pKa equal 9.9 at 298 K. On compari-

son the acidities of benzaldoxime with phenol, showed that relative acidity Kr of these systems has a value of:

$$K_r = \frac{K_a \text{phenol}}{K_a \text{benzaldoxime}} = \frac{1.25\text{x}10^{-10}}{3.16\text{x}10^{-12}} = 39.6$$

This mean that phenol had about 40 times greater acidity than oxime group in benzaldoxime. This difference of acidity stated, encourage the workers to applied the simple potentiometric method for the determination of pKa values of phenol and oxime groups present in 3 or 4-hydroxybenzaldoxime with their syn or anti oximes isomers. As shown in the experimental section, showed that till one millimeter of sodium hydroxide titrant, neutralization was started with the greater acidity of phenol in acids mentioned as a first step, then after in the second step the neutralization of oxime begin, after addition of titrant with 1.4milliliter.

TABLE 3 shows pK_1 values for syn4-hydroxybenzaldoxime at a range of temperature (298-333) k. The pK_1 values estimated had a range of values between (5.677-6.398). These values were faraway from the normal phenol value stated above. These values were referred to the zwitter ion formation as shown in the following reversible reaction:



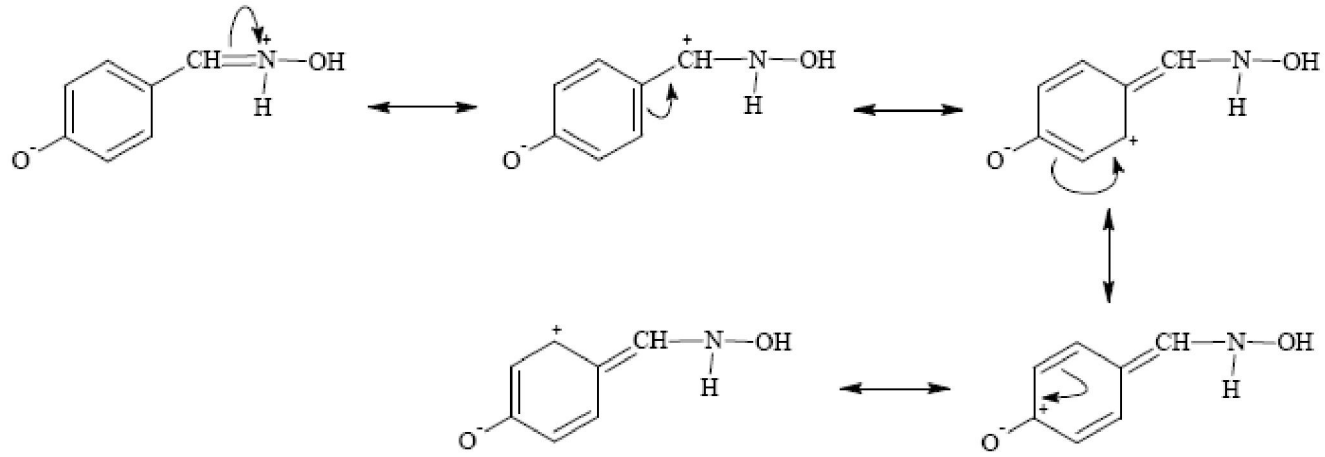
This reaction was confirmed by measuring the U.V. spectrum of 4- hydroxybenzaldoxime in ethanol. It gave a main absorption band at 249.8nm with E_{max} molar extinction coefficient value of 95700 in unit of Liter.mole^{-1}.cm^{-1}. Then after, upon addition of the dilute NaOH to the previous solution, resulted to the appearance of a new band at 246.8nm with E_{max} value 21700 in the same arbitary unit. This blue shift observed in the U.V. spectrum confirm[1] the zwitter ion stated.

The pK_2 values for syn 4-hydroxybenzaldoxime were supposed to refer to the oxime group. Actually

TABLE 3 : pKa for syn 4-hydroxy benzaldoxime in 10% ethanol at different temperatures

$T_{(K)}$	ml of (0.1M) NaOH	pKa	$\overline{pKa}$
293	0.8	6.065	6.398*
	1	6.730	
	1.2	7.234	
	1.4	8.048	7.659**
303	0.8	5.595	6.073*
	1	6.550	
	1.2	6.964	
	1.4	7.513	7.239**
313	0.8	5.705	6.068*
	1	6.400	
	1.2	6.884	
	1.4	7.493	7.189**
323	0.8	5.223	5.732*
	1	6.230	
	1.2	6.714	
	1.4	7.353	7.034**
333	0.8	5.214	5.677*
	1	6.140	
	1.2	6.613	
	1.4	7.253	6.933**

*** For pK_1; * * For pK_2**



Scheme 1

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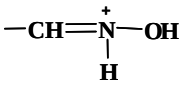
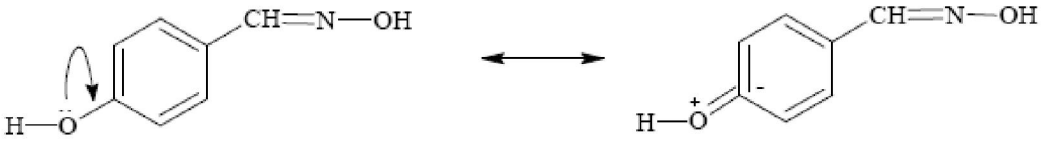
the formation of nitrilium ion  during zwitter ion formation as a good electrophile, influence on the normal pK_2 value of oxime group, in a direction of lowering pK_2 value or increasing acidity of such group. The pK_2 values estimated had a range of values between 8.99-9.47 at a range of temperatures stated before.

The resonance happened in nitrilium ion stabilized such ion with the formation of five resonance structures or hybrids as in scheme 1.

These five resonance structures might increase the acidity of oxime group pK_2. Also TABLE 4 showed pK_1 and pK_2 values for anti 4- hydroxybenzaldoxime. On comparison of these values with other syn isomer stated above, showed that the previous values had lower acidities on compared with its syn isomer, but influenced and faraway from the normal values of phenol and oxime group stated above pK_1 values could be interpreted by an increase in planarity[10] of the anti isomer as compared with its syn isomer, with their molar extension coefficients values of 99600 and 95700 in units Liter.mole^{-1}.cm^{-1} respectively. The increase in planarity of anti isomer was the reason of the increase in acidity of phenol group. pK_2 values for the anti 4-hydroxybenzaldoxime had a range of values (9.47-8.99) at temperatures range (298-333) k respectively. These increased in acidities values of oxime group and can be interpreted by two main reasons as:

1 The increased in planarity of anti isomer.
2 The possible formation of phenoxonium ion by resonance of phenol as in scheme 2.



Scheme 2

TABLE 4 : pKa for anti 4-hydroxy benzaldoxime in 10% ethanol at different temperatures

T(K)	ml of (0.1M) NaOH	pKa	$\overline{pKa}$
293	0.8	8.636	*8.895
	1	9.153	
	1.2	9.431	
	1.4	9.509	**9.470
303	0.8	8.356	*8.869
	1	8.982	
	1.2	9.249	
	1.4	9.334	**9.292
313	0.8	8.646	*8.854
	1	9.062	
	1.2	9.168	
	1.4	9.181	**9.175
323	0.8	8.799	*8.810
	1	8.821	
	1.2	8.986	
	1.4	9.029	**9.008
333	0.8	8.586	*8.769
	1	8.952	
	1.2	8.910	
	1.4	9.069	**8.990

*** For pK_1; * * For pK_2**

TABLE 5 : pKa for syn 3-hydroxy benzaldoxime in 10% ethanol at different temperatures

$T_{(K)}$	ml of (0.1M)NaOH	pKa	$\overline{pKa}$
293	0.8	6.83	6.94*
	1	7.05	
	1.2	10.098	
	1.4	10.099	10.099**
303	0.8	6.286	6.633*
	1	6.980	
	1.2	10.078	
	1.4	10.076	10.076**
313	0.8	6.336	6.568*
	1	6.800	
	1.2	9.77	
	1.4	9.730	9.750**
323	0.8	5.755	6.133*
	1	6.510	
	1.2	8.880	
	1.4	8.878	8.878**
333	0.8	5.860	5.944*
	1	6.028	
	1.2	8.80	
	1.4	8.780	8.780**

*** For pK_1; * * For pK_2**

Similar results were obtained for pK_1 for phenol group in syn 3- hydroxybenzaldoxime with syn 4-hydroxybenzaldoxime i.e on the basis of zwitter ion formation as in TABLE 5. The pK_2 values estimated for anti 3- hydroxybenzaldoxime had a range of values (10.099-8.870) at temperature range stated earlier. These values represent the normal acidities of oxime group which were influenced by both zwitter ion formation in the molecule and the change temperatures during pKa determination.

Finally, pK_1 and pK_2 values for anti 3-hydroxybenzaldoxime as in TABLE 6 were represent the normal values of phenol and oxime group in the molecule. Their values were influenced by the variation of temperatures and in a direction of increasing acidity by elevation of temperature.

TABLE 6 : pKa for anti 3-hydroxy benzaldoxime in 10% ethanol at different temperatures

$T_{(K)}$	ml of (0.1M)NaOH	pKa	$\overline{pKa}$
293	0.8	9.178	9.578*
	1	9.977	
	1.2	10.282	
	1.4	10.439	10.361**
303	0.8	9.147	9.505*
	1	9.863	
	1.2	10.107	
	1.4	10.213	10.160**
313	0.8	9.167	9.469*
	1	9.770	
	1.2	9.948	
	1.4	10.032	9.990**
323	0.8	9.107	9.408*
	1	9.709	
	1.2	9.853	
	1.4	9.857	9.855**
333	0.8	9.200	9.350*
	1	9.500	
	1.2	9.780	
	1.4	9.782	9.781**

*** For pK_1; * * For pK_2**

CONCLUSIONS

1 The chemical structures of oximes numbered (1-4) had be confirmed by physical methods, namely by UV-IR spectra and melting points.

2 For the first time, the simple potentiometric method was developed here, for the simultaneous determination of pK_1 for phenol and pK_2 of oxime groups in oximes mentioned.

3 The existence of syn isomers in 4-hydroxybenzaldoxime and 3-hydroxybenzaldoxime in zwitter ions formations, resulted to lower pK_1 and pK_2 values in these molecules.

4 The acidity of oximes group pK_2 in syn and anti isomers of 4-hydroxybenzaldoxime were increased by the formation of nitrilium ion and planarity[10] of the molecule respectively.

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