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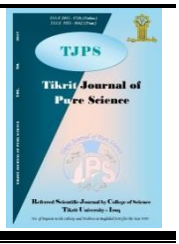

Determination of Stability for imines derived from carbonyl compounds by conductivity measurements

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Abstract

The project explained for the first time, how conductivity method was used in the determination of stability of some imines derived from mother compounds 2-acetyl pyridine, 3 or 4 –hydroxy benzaldehyde, and others.

The method as found, simple precise and fast for the determination of stability of imines in 10% ethanol aqueous medium, as measured by evaluation of their conductance. Different conductance values for 10^{-2} M imine solutions in the range (5.53-180) μmho were collected experimentally as interpreted and discussed.

Introduction

As know in literature [1] , faster reactions in general could expressed by thermodynamic and kinetic methods. In the former method, heat of formation for the reaction, especially of negative sign could used as a measure for a fast reaction. Meanwhile, in the last kinetic method by using half life could used in the investigation of fast or slow reactions. This latter method had been used by Azzouz[2] etal in the determination of stability of benzaldoximes and its substitutents .This kinetic stability of aromatic aldoximes were calculated by half life method for the first order Beckmann rearrangement reactions in the presence of perchloric acid as a catalyst. Then after, this study was extended to include 2-pyridine aldoxime[3] and others hetro cyclic aldoximes[4] .

The lack of conductivity method for the determination of stability of some imines derived from aromatic carbonyl compounds, namely 2-acetyl pyridine, 3 or 4 –hydroxyl benzaldoximes and others, increased our curiosity to deal with such important topic.

Experimental

All chemicals used throughout the work, were supplied from Fluka or BDH origin.

All imines in the forms of syn oxime or Schiff base were prepared by reactions of their appropriate aldehyde or ketone with primary amine using 1:1 mole ratio method as a standard method[5]. All anti oximes were prepared by thermal[6] catalysis reaction i.e refluxing syn oxime in dry benzene after addition of activated charcoal. Table(1) shows compound number, nomenclature and structures of imines.

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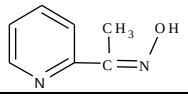
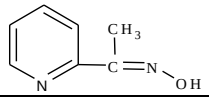
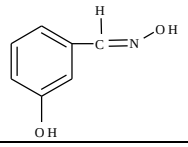
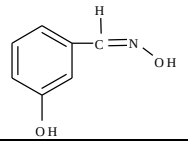
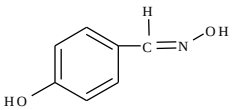
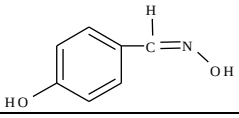
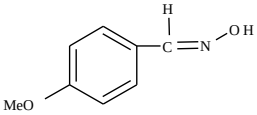
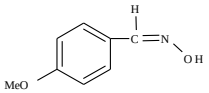
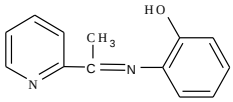
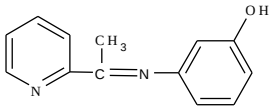
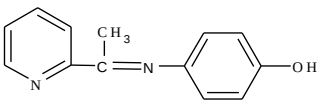
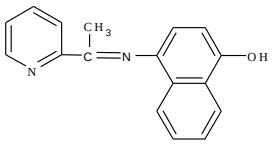
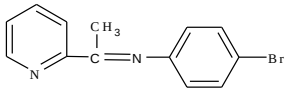
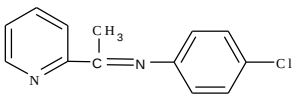
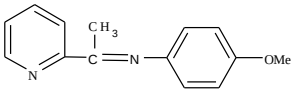
Table (1) : Compound number, nomenclature and structures of imines

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	
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	

Instrumentation

1. All conductance of imines were measured by using:-
(Wissenschaftlich- Technisches Werkstatten) , model (D8120-Weilheim).
2. A water thermostat model L200 manufactured by Searle company was
used for fixation of temperature during conductance measurements.

Results and discussion

At the beginning of this investigation, it was thought of great importance to confirm the chemical structures of imines under study, by the available physical means, namely, IR-UV spectra and melting points or boiling points[7]. Some chemical tests were applied to the imines as ferric chloride and others specified reagents for ether and halogen linkages .

Table (2) : Conductance (µmho) of 10^{-2}M imines solutions at 10% ethanol

Comp.No. / T(min)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
0	6.6	5.35	180	15.05	125	16.5	90.5	7.1	15.5	10.5	27.1	8.9	10.5	9.4	20.5
5	6.6	5.35	180	15.05	125	16.5	90.5	7.1	15.5	10.7	27.1	8.9	10.5	9.4	20.5
10	6.6	5.35	180	15.05	125	16.5	90.5	7.11	15.5	10.7	27.1	8.9	10.5	9.4	20.9
15	6.6	5.38	180	15.05	125	16.5	90.5	7.15	15.5	11	27.1	8.9	10.5	9.4	21.1
20	6.6	5.39	180	15.05	125	16.5	90.9	7.19	15.5	11	27.1	8.9	10.5	9.4	21.9
25	6.6	5.4	180	15.05	125	16.5	91.7	7.20	15.5	11	27.1	8.9	10.55	9.5	21.9
30	6.6	5.4	180	15.05	125	16.5	92.09	7.25	15.5	11.1	27.1	8.9	10.55	9.5	22.0
35	6.6	5.45	180	15.05	125	16.5	92.2	7.25	15.5	11.1	27.1	8.9	10.57	9.5	22.1
40	6.6	5.48	181	15.05	125	16.5	92.9	7.29	15.5	11.1	27.1	8.9	10.59	9.5	22.2
45	6.6	5.49	181	15.05	125	16.5	92.9	7.3	15.5	11.3	27.1	9.0	10.6	9.5	22.5
50	6.6	5.5	181	15.05	125	16.5	93.1	7.35	15.5	11.5	27.1	9.0	10.6	9.5	22.5
55	6.6	5.5	181	15.05	128	16.5	93.1	7.39	15.9	11.5	27.2	9.1	10.61	9.5	22.9
60	6.6	5.55	181	15.05	128	16.5	93.5	7.41	15.9	11.5	27.5	9.1	10.61	9.5	22.9
65	6.6	5.55	185	15.05	129	16.5	93.5	7.41	15.9	11.5	27.5	9.1	10.61	9.5	22.98
70	6.65	5.55	185	15.05	129	16.5	93.9	7.41	15.9	11.5	27.5	9.1	10.61	9.6	23
75	6.69	5.55	185	15.05	129	16.5	93.9	7.45	15.9	11.5	27.7	9.1	10.61	9.6	23
80	6.70	5.6	185	15.05	129	16.5	93.9	7.5	15.9	11.5	27.8	9.1	10.61	9.6	23
85	6.7	5.6	185	15.05	129	16.5	93.9	7.5	15.9	11.5	27.9	9.1	10.61	9.6	23
90	6.7	5.6	185	15.05	129	16.5	93.9	7.5	15.9	11.5	27.9	9.1	10.61	9.6	23

It was stated in literature[8], that was some Schiff base under go a side reactions as hydrolysis or solvolysis up dissolution in ethanol –water medium. Most chemistry of imines as pKa measurement[9] and other [10] was in urgent need for the medium stated, especially from solubility point of view.
This encourage the workers in this investigation to deal with stability of imines by using conductivity measurements. The last technique was chosen on the basis of change in the number or concentration of ions oximes and Schiff bases, when any type of side reaction mentioned were happen .
The conductance of any electrolytic solution depend on concentration or number of ions , type of solvent or medium, the ambient temperature and the degree of ionization of any imine. Experimentally, the concentration of any imine under study was fixed of a value 10^{-2}M , the solvent used was 10% ethanol, the temperature was 20°c. This means that the first three parameters were fixed in this study. The degree of ionization of any imine has also a constant value and varied from imine to imine depending on their structures and other factors as types of hydrogen bonding and syn or anti isomer in imines.
Table(2) shows the following different orders of conductance arrangements for imines as :-
(180, 125, 90.5, 27.1, 20.5, 16.5, 15.5, 15.05 , 10.7, 9.4, 8.9, 7.1, 6.6, 5.35).

These conductance values for imines as in Table (2) were related to the stability on negative ions of imine were worthy to be discussed .
Table (2) summarized the following points :-
1-The conductance values of imines were varied in a range (185-5.35) µmho. Maximum conductance was given for imine numbered (13). This was due to the higher degree of ionization among other imines as in Table (2). A reverse for such result was given to imine number (2) .
2- A stable conductance were given for imines solution numbered (4, 6, 14) for the whole period of 90 minutes .
3- A conductance for imines number (1-3, 5, 7-13) for a period of about 20 minutes. Then after a slight changes in conductances were happen. This might due to the high sensitivity of conductance instrument or to the fluctuation voltage during measurements which cause an instrumental errors.
It was concluded from conductance of imines as in Table(2), that a stable imine solution up to 20 minutes in 10% ethanol aqueous medium as observed experimentally. In other words these imines solutions can be subjected to a numerous physical studies safely .
This encourage the workers to explain the variation of conductance values for imines under study, as follows :-

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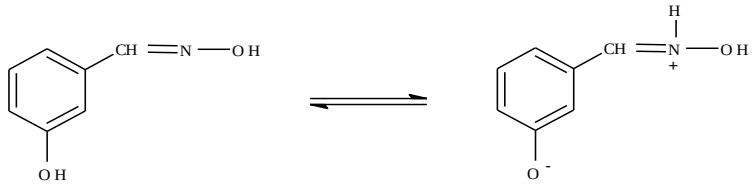
1- Imine (3) was a 3- hydroxyl benzaldoxime which had a maximum conductance value among others imines as in Table (2). The reason for that was the following :-

i- It had 3- phenolic group in its structure which acted as electron withdrawing group of sigma value $\sigma_{=+}$0.121 from Hammett equation. Hence such group mentioned may increase the acidity of oxime group in the molecule, hence a greater possibility of ionization for imine (3) was observed. The last was attributed to a number of ions or maximum conductance values for its solution.

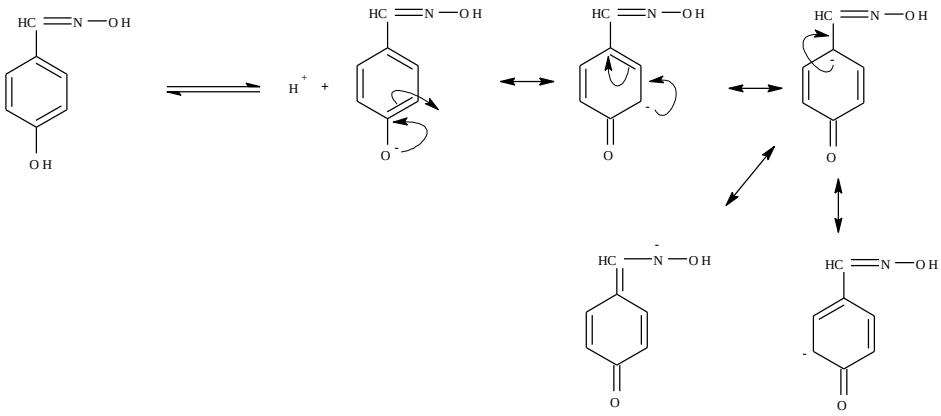
ii- 3-Hydroxy benzaldoxime solution had proved its existence in zwitter ion formation[9] as in the following reaction :-



This might responsible on increasing the number of ions or its maximum conductance in solution.

It was believed in this study that these two folds reason i and ii paragraphs might contribute to a different degrees in increasing conductances of imine (3) to a maximum value .

2- Imine (5) is 4-Hydroxy benzaldoxime had a little lower conductances value of 125 μmho. The reason for that due to its similar existence in zwitter ion formation[9], beside the formation of five resonance structures as in scheme (1)



Scheme (1) : Resonance numbers in 4-hydroxy benzaldoxime

This imine had a similar structure to Schiff base number (11) i.e. methyl 2-pyridyl ketonylidene -4-hydroxy aniline, which contain p-phenolic group of conductances value 27.1 μmho. A great differences were obserived in conductances value between imines (5) and (11) . This could be explained by the non real existence of Schiff base (11) in zwitter ion formation.

3-On comparison of conductances of syn 4- Hydroxy benzaldoxime with its anti isomers i.e imines numbered (5) and (6) respectively. These showed a value of 125 and 16.5 units μmho. The higher conductance of imine (5) could be explained by their resonance structures as in Scheme (2). The lower conductances value of imine (6), explained by the idea that the geometry of anti isomer might led to a decrease in the formation of ions or a decrease in the possibility of ionization process.

4-Generally speaking a higher conductances values were observed for the syn diacidic imine contained oxime and phenol groups in imines numbered (3) and (5) as compared with its syn mono acidic oxime group only as number (7). Others syn or anti monoxime as numbered (1) and (2) behave similarly.

5-Others phenolic , halogenated and methoxy Schiff bases numbered (9-15) had relatively lower conductivities of a range value (8.9-27.5) μmho. These were due to their lower tendencies for ionization in 10% ethanol medium .

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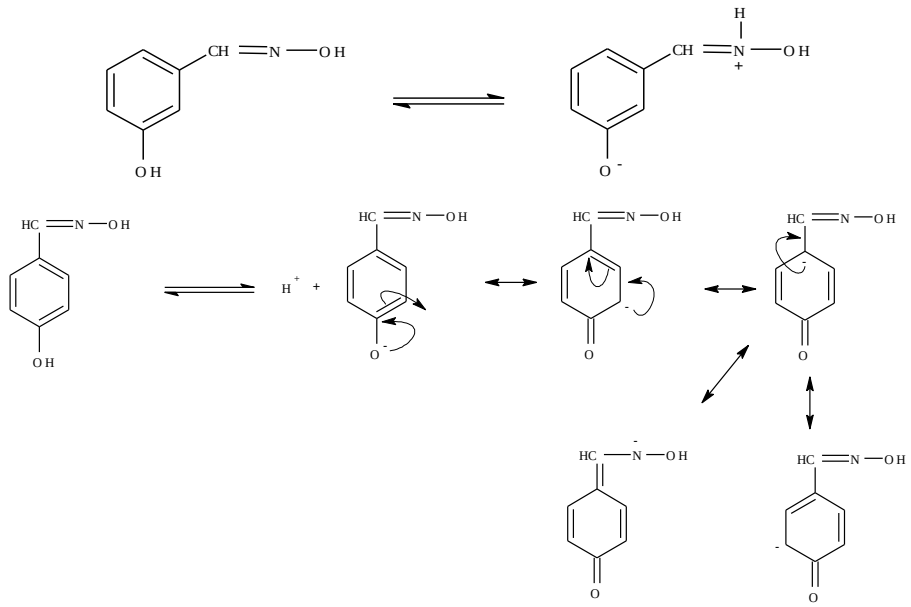

Scheme (2) : Resonance numbers in 3-hydroxy benzaldoxime

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تعيين استقرارية الايمينات المشتقة من المركبات الكاربونيلية من قياسات المواصلة الكهربائية

عادل سعيد عزوز ، دنيا بطرس ال بكزو

قسم الكيمياء ، كلية التربية ، جامعة الموصل ، الموصل ، العراق

الملخص

يتضمن البحث وللمرة الاولى، كيفية استخدام المواصلة الكهربائية في تعيين استقرارية الايمينات المشتقة من المركبات الام 2–استايل بردين و 3 او 4 هايدروكسي بنزالدهايد و مركبات اخرى.

الطريقة المستعملة في البحث وجد انها بسيطة، دقيقة وسريعة في تعيين استقرارية الايمينات في وسط 10% ايثانول في الماء. تم الحصول على اختلاف قيم التوصيل الكهربائي عملياً لمحاليل الايمينات وفي المدى (5,53-180) مايكرو موه و التي فسرت ونوقشت.