Kinetic Study of Beckmann rearrangement of Anti Benzaldoximes in Perchloric acid

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Abstract

The paper deals with kinetic data of Beckmann rearrangement of substituted anti benzaldoxime to substituted benzoic acid and ammonia by action of perchloric acid in 10% ethanol by volume . A spectrophotometric method was used for this investigation , by following the decay absorbances of benzaldoximes at the proper analytical wavelengths . The reaction was found to obey a pseudo first order kinetic with respect to oxime . The observed rate constants k were evaluated in the temperature in the range 323-353 K and found to depend on temperature and donor or acceptor property of the substituent as well as its position on the aromatic rings . Finally the activation parameters for Beckmann rearrangement reactions were calculated and discussed .

الخلاصة

يشتمل البحث على دراسة حركية لإعادة ترتب بكمان لانتي بنزالدوكزيم ومعوضـاته الـى حـامض البنزويك او مشتقاته مع الامونيا بفعل حامض البيركلوريك في الايثانول بنسبة حجميـة 10 % . اسـتعملت الطريقة الطيفية الفوتومترية بالدراسة وذلك بمتابعة امتصاصيات البنزالدوكزيمات عنـد الاطـوال الموجيـة المناسبة . وجد ان التفاعل هو من المرتبة الاولى الكاذبة بالنسبة الى الاوكزيم . حسبت ثوابـت السـرع k بدرجات حرارية ضمن المدى 323-353 مطلقة ووجد انها تعتمد على درجة الحرارة وخاصـية الـدفع او السحب للمجموعة المعوضة وكذلك موقعها على الحلقة الاروماتية . واخيراً احتسـبت متغيـرات التنشـيط للتفاعل المذكور اعلاه وتمت مناقشتها .

Introduction

The kinetic of hydrolysis of aliphatic and aromatic Schiff bases[1-5] or Schiff bases derived from β – diketone[6] had been studied extensively by many workers .

Several kinetic investigations on Beckmann rearrangement of ketoximes[7] and other oximes[8-9] had been done in various media to conclude that rate constants depend on temperature , solvent , substituent and type of catalyst .

Azzouz[10] etal had studied thermodynamic functions and kinetic stability of hydrogen bonding of benzaldoxime . This showed that stability of aldoximes were increased

when aldoximes were capable to form an intra molecular hydrogen bond , the type of syn or anti isomer of aldoxime and deuterium isotope effect . Later Azzouz[11] etal had studied kinetic and stability constants of 2-pyridinealdoxime with some positive ions . This led to the comparison of rate constants of benzaldoxime with 2-pyridinealdoxime at different temperatures and concluded that intra molecular hydrogen bonding was accompanied by decreasing the rate constants of 2-pyridinealdoxime . The last investigation was extended later to a kinetic[12] study of rearrangement of hetrocyclic aldoximes in perchloric acid . This showed that rate constants of anti aldoxime were increased in order of :- Furfuraldoxime > thiophenealdoxime > pyrrolealdoxime > pyirdinealdoxime .

The existence of aldoximes in two spatial isomer forms i.e syn and anti forms arised the curiosity of the workers to deal with kinetic of Beckmann rearrangement reactions of anti benzaldoximes . This investigation was a continuation of a similar study on syn benzaldoximes[13] performed earlier .

Experimental

All chemicals used throughout this work were of Fluka or BDH origins . 60% perchloric acid (Fluka) was used as supplied .

All syn aldoximes were synthesized by standard method[14] . They converted to the to their corresponding anti forms by using a gaseous hydrochloric method[15] as follows:-

About 0.1g of syn aldoxime was dissolved in about 100ml of dry benzene . Hydrochloric acid gas was passed through the benzene solution for about 15minutes . The precipitate formed was fillered , washed with benzene to remove the unreacted oxime and dissolved in 20ml of distilled water . The solid antialdoxime was collected after neutralization of the final solutions with 5% $NaHCO_3$, followed by extraction with ether , Table (1) , summarizes the melting points of antialdoximes .

Instrumentation

All UV spectra and kinetic study were carried out by using a double beam spectrophotometer Shimadzu UV-210A .

All IR spectra of solid aldoximes were measured by using PYE Unicam SP 1100 spectrophotometer .

Temperature control during measurements was achieved by connecting a thermostat of type Julabo Paratherm PT 40 PS to the cell housing of the spectrophotometer .

Kinetic measurement

This was carried out by mixing 1ml each of antialdoxime with perchloric acid of concentrations 10^{-4}M and 0.6328M respectively . The decay absorbance of antialdoxime was followed at optimum wavelength λ_{max} . The rate constants (k) was evaluated from pseudo first order plot .

Results and discussion

Table (1) Summarizes the nomenclature of antialdoximes , their melting points and the azomethine C=N stretching vibrations.

Table (1) : Nomenclature , melting points and IR bands for antialdoximes

No.	Nomenclature	Melting points C°	C=N vibrations
1	Benzaldoxime	129	1635(s)
2	o-Nitrobenzaldoxime	154	1650(m)
3	m- Nitrobenzaldoxime	123	1680(m)
4	p- Nitrobenzaldoxime	184	1630(m)
5	o-Chlorobenzaldoxime	101	1625(m)
6	m-Chlorobenzaldoxime	117	1620(s)
7	p-Chlorobenzaldoxime	147	1630(s)
8	o-Hydroxybenzaldoxime	45	1670(s)
9	m-Hydroxybenzaldoxime	60	1660(m)
10	p-Hydroxybenzaldoxime	85	1630(m)
11	o-Methylbenzaldoxime	57	1620(s)
12	m-Methylbenzaldoxime	50	1625(s)
13	p-Methylbenzaldoxime	122	1600(s)

The stretching absorption for azomethine linkages had a range between 1620-1680cm^{-1} . This certainly assigned the presence of C=N in all antialdoximes and confirim their chemical structure beside their melting points .

The kinetic study of Beckmann rearrangement reaction of benzaldoxime with perchloric acid was started by comparing the UV spectra of reactants with products , benzoic acid and ammonia solution . Actually , no spectral interferences were observed at λ_{max} of benzaldoxime . This encourage to measure the decay absorbances of benzaldoximes with time with confidence . Rate constants for pseudo first order kinetics were evaluated from an equation of the form :-

$$\ln A_o / A_t = k_1 t$$

A_o = Initial absorbance of benzaldoximes at time t = 0.

A_t = Remaining absorbance of benzaldoximes after time = t.

k_1 = rate constant (min^{-1}).

t = minute.

Rate constants were measured in the temperature range between 323-353K , typical plot for p-chlorobenzaldoxime seen in Fig. 1

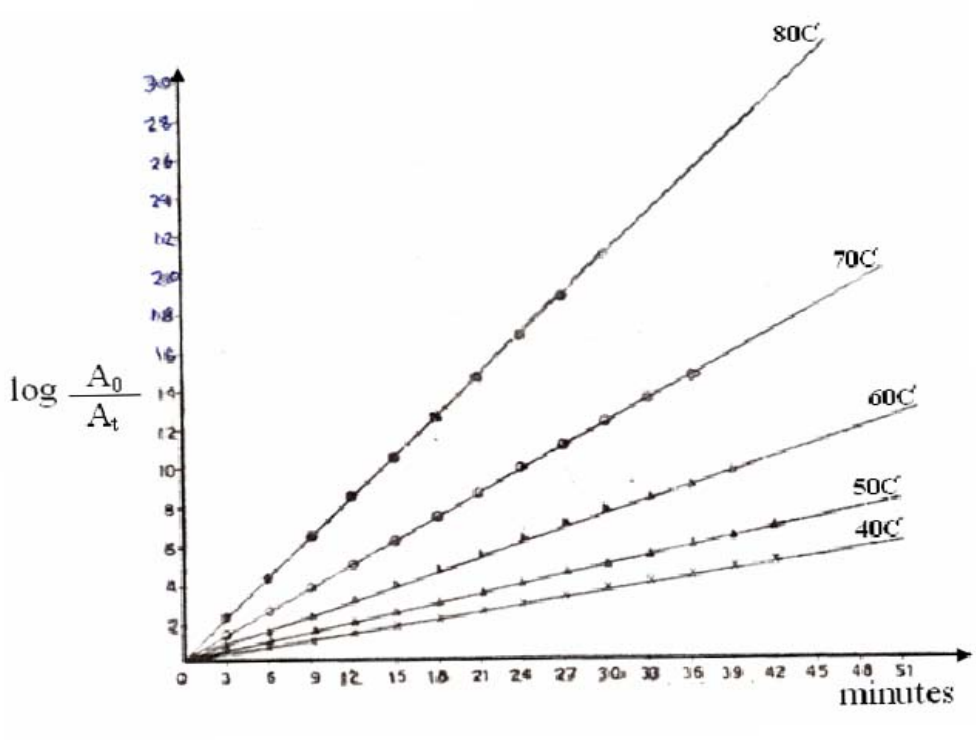

Fig. 1 : Kinetic plots for Beckmann rearrangement of anti-p-chlorobenzaldoxime at various temperature

Table (3) summarizes the analytical wavelengths and rate constants for anti benzaldoximes at five different temperatures . Comparison of rate constant for unsubstituted antibenzaldoxime with substituted antibenzaldoxime at 50C° led to compare the values of sigma constants[16] from Hammett equation as in Table (2) .

Table (2) : Sigma constant for meta and para substituents antibenzaldoxime

substituents	σ_m	σ_p
CH_3	-0.069	-0.170
NO_2	0.71	0.778
OH	0.121	-0.37
Cl	0.373	0.222

The negative signs of sigma constants means that substituents were electron donors as σ_m and σ_p for methyl group and σ_p for hydroxyl group . Conversely the positive signs of sigma constants means the subsituents were an electron acceptor for other all remaining values in Table (2) .

Table (3) : Rate constants for the Beckmann rearrangement reactions of antialdoxime at different temperature with analytical wavelength λ_{max}

Sub. Benzaldoxime	λ_{max}(nm)	10^4 Rate constants (sec^{-1})			
		323K	333K	343K	353K
Hydrogen	251	0.37	0.71	1.25	1.77
o-nitro	244	1.11	1.55	2.02	2.97
m-nitro	247	4.07	7.73	9.68	12.63
p-nitro	297	11.53	28.65	49.73	69.34
o-chloro	252	0.34	0.66	0.99	1.68
m-chloro	248	2.32	4.97	6.54	7.82
p-chloro	254	0.32	0.62	0.97	1.56
o-hydroxy	295	0.27	0.41	0.73	1.09
m-hydroxy	255	1.11	2.08	3.00	5.15
p-hydroxy	266	5.20	8.64	12.07	16.53
o-methyl	254	0.34	0.64	0.91	1.45
m-methyl	254	0.33	0.62	0.89	1.44
p-methyl	258	0.21	0.46	0.81	1.24

For para substitutents the rate constants for the rearrangement reactions were observed to follow the following decreasing order of :-

p-Nitrobenzaldoxime > p-hydroxybenzaldoxime > p-chlorobenzaldxime > p-methylbenzaldoxime > benzaldoxime

p-Nitrobenzaldoxime showed anomalous higher and unexpected rate constants due to its negative σ_p . This could explained[17] by the higher inductive effect of oxygen atom when compare with resonance effect . Similarly m-substituents followed the decreasing rate constants of rearrangements reaction .

m-nitrobenzaldoxime > m-chlorobenzaldxime > m-hydroxybenzaldoxime > m-methylbenzaldoxime

Generally it was observed that electron acceptors as m and p-substituents were accompanied by an increasing rate constants of reactions where as electron donors lead to decreasing rate constants when compared to unsubstituted benzaldoxime. Now when rate constants for ortho substituents were compared to benzaldoxime , the following decreasing order of rate constants were observed :-

o-nitrobenzaldoxime > benzaldoxime > o-chlor or methylbenzaldoxime > o-hydroxybenzaldoxime

These rate constants for rearrangement could be explained for the following substituents effects or a combination of them at ortho position as :-

First electronic behaviour of substitutent , second steric effect[17] , third the hydrogen bonding . Similar results were also obtained at other temperatures of 60C°, 70 C°and 80 C°.

The relationship between rate constants of rearrangement of antibenzaldoxime and its substituents with activation parameters at 363K were seen in Table (4) . These substituents would change the electronic densities around the azomethine[7] linkages in benzaldoximes or the most reactive centers in benzaldoximes . Consequently , this would lead the variation of rate constants of rearrangement .

Table (4) : Comparsion between rate constants and activation parameters for the rearrangement of antibenzaldoximes at 363K .

Sub.benzaldoxime	$k\times10^4$ sec^{-1}	E_a $kJ.mole^{-1}$	$\Delta G^{\pm}$ $kJ.mole^{-1}$	$\Delta H^{\pm}$ $kJ.mole^{-1}$	$\Delta S^{\pm}$ $J.mole^{-1}.K^{-1}$	A sec^{-1}
benzaldoxime	3.00	50.08	105.59	47.06	-165.95	4831.9
o-nitrobenzaldoxime	4.46	33.36	105.75	30.35	-207.75	27.49
m- nitrobenzaldoxime	18.07	33.98	101.57	30.97	-194.37	146.2
p- nitrobenzaldoxime	97.41	53.67	96.47	47.57	-134.68	51247.3
o-methylbenzaldoxime	2.53	51.71	107.76	48.70	-162.98	6995.3
m-methylbenzaldoxime	2.52	48.11	107.51	48.10	-171.88	2106.9
p-methylbenzaldoxime	2.25	55.97	107.84	52.96	-151.91	25591.1
o-chlorobenzaldoxime	2.78	61.99	107.22	58.97	-132.88	23119.1
m-chlorobenzaldoxime	12.62	37.58	102.66	34.57	-187.51	315.4
p-chlorobenzaldoxime	2.70	43.18	107.30	40.17	-184.88	440.5
o-Hydroxybenaldoxime	2.25	50.87	107.84	47.86	-165.24	4698.5
m-Hydroxybenaldoxime	7.34	45.69	104.29	42.68	-169.67	2751.8
p-Hydroxybenaldoxime	20.83	36.16	101.16	33.15	-187.22	331.6

Activation parameters $\Delta G^{\pm}$, $\Delta H^{\pm}$, $\Delta S^{\pm}$ and A were calculated[11-12] by using an equations of the forms :-

$k = Ae^{-Ea}/RT$

$\Delta H^{\pm} = E_a - RT$

$\Delta G^{\pm} = \Delta H^{\pm} - T\,\Delta S^{\pm}$

$K = KT / h\, e^{\Delta S\pm / R}\, e^{-Ea / RT}$

The p-substituted benzaldoximes , Table (4) showes that Ea and $\Delta H^{\pm}$ values were decreased in order of p-CH_3 > p-NO_2 > p-Cl >p-OH .

This trend was changed in meta and ortha substituents as follows :-

m-CH_3 > m-OH >m-Cl >m-NO_2 , o-Cl > o-CH_3 >o-OH > o-NO_2 .

These variation in orders could be explained by a change in electron density arround the azomethine linkages in substituted benzaldoximes . The approximate values of $\Delta G^{\pm}$ for aldoximes means that their followed a similar rearrangement reactions[12] . Moreover , $\Delta G^{\pm}$ and $\Delta S^{\pm}$ parameters were also changed by the variation of substituents .

The negative values of $\Delta S^{\pm}$ indicated that rearrangements involve solvent attack on the protonated oxime[18,19] molecule or formation of cyclic intermediate step . All these activation parameter discussed with frequency factor A support[11-12] the pseudo first order rearrangement reactions of benzaldoximes under action of perchloric acid .

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