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Comparison of rate constants for the Beckmann rearrangement reactions of syn and anti substituted benzaldoxims in perchloric acid

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ABSTRACT

Anti substituted benzaldoximes were prepared by a standard method, and their structures were confirmed by physical method, namely UV-IR spectra and melting points. The study deals with kinetic study for the Beckmann rearrangement reactions of anti isomers of benzaldoxime and its substitutents in perchloric acid as acidic catalyst. The reaction order was found to be of type pseudo first with respect to aldoxime. A spectrophotometric method was used for the investigation of kinetic study. Rate constants for the Beckmann rearrangement reactions of anti isomeric of benzaldoximes were evaluated at temperatures range between (323-363)K and discussed. Finally a relative rate constants k_{syn}/k_{anti} were evaluated at a temperature ranges mentioned and show mostly a relative values greater than unity in all aldoximes with exception of 3-nitrobenzaldoxime. The cause for the last result was explained and discussed.

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INTRODUCATION

A Beckmann rearrangement of oximes had widely been studied and different mechanisms were postulated[1]. Several kinetic investigations on Beckmann rearrangement of ketoximes had been done in various media to determine the rate determining step of reaction, which seemed to depend[2] on the temperature isolvent, substituent and the type of catalyst employed.

Azzouz[3] etal had studied a kinetic study for the Beckmann rearrangement of syn benzaldoximes to benzoic acids and ammonia in the presence of catalytic perchloric acid. This investigation was later extended to study the same reaction with 2-pyridine aldoxime[4] and hetrocyclic aldoxime[5]. The authors concluded that rate constants of these syn aldoximes depend on the strength of intramolecular hydrogen bonding available in these aldoximes and in the orders of :-

Thiophenealdoxime > furfurylaldoxime > pyirdinealdoxime > pyrrolealdoxime.

The rate constants for the same antialdoximes follow a different orders of

furfurylaldoxime > thiophenealdoxime > pyrrolealdoxime > pyirdinealdoxime.

The lack of rate constants for the Beckmann rearrangement of anti substituted benzaldoximes and their comparison with syn substituted benzaldoximes at a ranges of temperatures between (323-363) K were prompted this work.

EXPERIMENTAL

All chemical used throughout this work were of Fluka or BDH origins.60% perchloric acid (Fluka) was used as supplied. All syn aldoximes were synthesised by using a standard method[6]. i.e by converting the syn aldoximes to their corresponding antiforms by using a gaseous hydrochoric method[6] 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 15 minutes. The precipitate formed was filtered, washed with benzene to remove the unreacted oxime and dissolved in 20ml of distilled water.

The solid antioxime was collected after neutralization of the final solutions with 5% $NaHCO_3$ followed by extraction with ether. TABLE 1 summarizes the UV and IR spectra with melting points of antibenzaldoximes. For a sake of comparison of melting points between a pair of syn and antialdoximes, the melting points for syn aldoximes was also added to TABLE 2.

RESULT AND DISCUSSION

At the beginning of this investigation, it was though of great importance to confirm the chemical structures of antialdoximes under study. Therefore, the following divisions of results were through necessary:-

TABLE 1 : IR for solids and UV spectra of 10^{-4}M antialdoximes in ethanol

No.	Name of antialdoxime	IR bands cm^{-1}	UV bands $\lambda_{(nm)}$ (Σ_{max}) ethanol
1	Benzaldoxime	3300(b), 2980(m), 1635(s), 975(b)	250(2000)
2	2-Nitrobenzaldoxime	3280(b), 3000(w), 1650(m), 970(s)	236(10000)
3	3-Nitrobenzaldoxime	3260(b), 2900(m), 1635(m), 960(s)	233(12800)
4	4-Nitrobenzaldoxime	3140(b), 2900(m), 1630(s), 950(s)	240(1950)
5	2-Hydroxybenzaldoxime	3500(m), 3100(w), 1690(s), 925(m)	227(16250) 275(18500) sh305(9250)
6	3-Hydroxybenzaldoxime	3300(b), 2900(w), 1660(m), 960(s)	226(11000) 260(13000)
7	4-Hydroxybenzaldoxime	3360(b), 2905(m), 1630(m), 940(b)	225(12000) 262(14750)
8	2-Chlorobenzaldoxime	3300(b), 2940(m), 1625(m), 960(vs)	250(10620) 285(8000) sh325(5500)
9	3-Chlorobenzaldoxime	3140(b), 2880(b), 1620(s), 950(b)	251(24750) sh383(9250)
10	4-Chlorobenzaldoxime	3240(b), 2910(m), 1630(s), 945(s)	245(8750) sh280(6250)
11	2-Methylbenzaldoxime	3160(s), 3060(b), 1620(s), 965(vs)	253(30000)
12	3-Methylbenzaldoxime	3160(b), 3060(m), 1625(s), 970(vs)	255(16250)
13	4-Methylbenzaldoxime	3400(b), 2990(m), 1630(s), 950(vs)	256(20730)
14	4-Methoxybenzaldoxime	3200(w), 3000(b), 1630(s), 970(vs)	265(23000)

IR spectra

The IR spectra of solid antialdoximes showed the following absorptions:-

1. The stretching vibrations for OH groups of oximes of different intensities were observed in the range between (3140-3400)cm^{-1}.
2. The stretching vibrations of C-H groups in oximes under study of different intensities and in a range between (2880-3060)cm^{-1}.
3. The stretching vibration of azomethine linkage C=N of strong or medium intensities in a range between (1630-1690)cm^{-1}.
4. The stretching vibration of N-O group of oximes linkage of different intensities and in a range between (925-975)cm^{-1}.

All these stretching vibrations were summarized in TABLE 1 and in agreement[8] with chemical structures of antialdoximes under study

UV spectra

The UV spectra of antialdoximes were measured in ethanol solvent as in TABLE 1. These showed band or bands for π□$\rightarrow\pi^*$ transitions with molar extension coefficient of more than 1000 in unit of Liter.$mole^{-1}cm^{-1}$, TABLE 1 illustrates the following types of transitions:-

1. Single transition for the whole π-system was observed in aldoximes numbered 1-4, 11-13.
2. Single transition as above with a shoulder were observed in aldoximes numbered 9 and 10.
3. Double transitions for aldoximes numbered 6, 7 and 14. These could assigned one for phenyl group and the other for C=N in aldoximes.
4. Double transitions identical to previous number were accompanied by the appearance of third shoulder for aldoximes numbered 5 and 8. These shouldered were arised from intramolecular[9] hydrogen bonding of types O-H—O, O-H—Cl in the aldoximes stated respectively.

Melting points

Melting point was related to association of molecules by any association method[10] as hydrogen bonding. TABLE 2 shows the following facts:-

1. For 4-substituent aldoximes, the melting points of

aldoximes were increased in the following order:- 4-NO_2 > 4-Cl > 4-OCH_3 > 4-OH.

2. For 3-substituent aldoximes, the melting points of aldoximes were increased in the following sequence:- 3-NO_2 > 3-Cl > 3-CH_3 > 3-OH.
3. For 2-substituent aldoximes, the melting points of aldoximes were depened on the process of association by hydrogen bonding and steric effect[11]. The melting point of 2-substituted were increased in the following order:- 2-NO_2 > 2-Cl > 2-CH_3O > 2-OH.
4. Upon comparison of melting points between a pair of syn and anti aldoxime isomers found in TABLE 2. In general, this Table showed that melting points of any anti isomer is greater than its syn isomer with exclusions of aldoximes numbered 5, 8, 9, and 10. The last could happen by occurrence of hydrogen bonding in aldoximes mentioned. In other words, probably the hydrogen bonding were accompanied by depression[12] of melting point of aldoxime.

For any pair of syn and anti isomers of aldoxime, the greater melting point of anti isomer could be explained by the greater planarity[7] of aldoximes as observed previously on benzaldoxime and its substituents. Basu and Cumper[13] had confirmed the planarity statement by measurement of dipole moments of isomer 3-nitrobenzaldoximes. Their result showed that dipole moments of syn and anti isomers of 3-nitrobenzaldoxime had a values of 3.6 and 3.93 in Debye unit. The last supported the greater planarity of anti isomer of aldoxime.

TABLE 2 : Comparison of melting points between syn and anti isomers between substituted benzaldoximes and λ_{max} of anti isomers in ethanol

No.	Nomenclature	m.p c̊ of isomers		λ_{max} of anti isomers
		syn	anti	
1	Benzaldoxime	35	129	251
2	2-Nitrobenzaldoxime	95	154	244
3	3-Nitrobenzaldoxime	119-120	123	247
4	4-Nitrobenzaldoxime	115-116	184	297
5	2-Chlorobenzaldoxime	110	101	252
6	3-Chlorobenzaldoxime	70	117	248
7	4-Chlorobenzaldoxime	103-104	147	254
8	2-Hydroxybenzaldoxime	61	45	295
9	3-Hydroxybenzaldoxime	73	60	255
10	4-Hydroxybenzaldoxime	94	85	266
11	2-Methylbenzaldoxime	49	57	254
12	3-Methylbenzaldoxime	60	70	254
13	4-Methylbenzaldoxime	80-81	122	258
14	2-Methoxybenzaldoxime	84	93	253
15	4-Methoxybenzaldoxime	61-62	133	267

Kinetic study

The kinetic[3] study of Beckmann rearrangement reactions of syn benzaldoxime and its substituent had been studied previously in our laboratory. This showed that reaction was converted to benzoic acid and ammonia. This encourage us to repeat the same study with anti benzaldoxime and its substituent in the same manner.

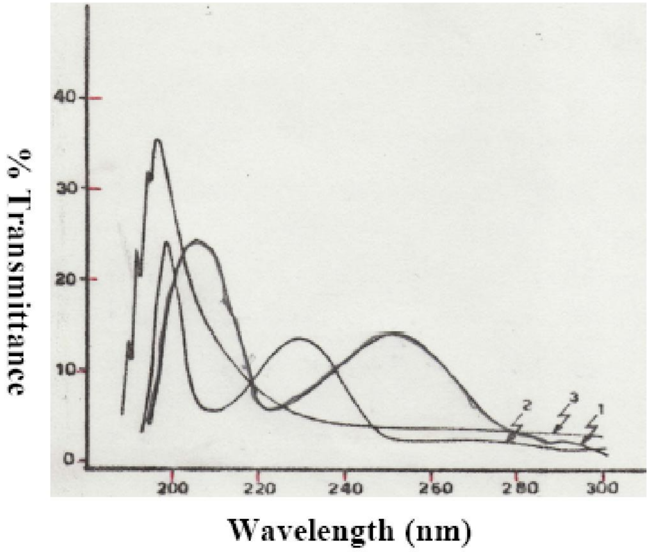

Figure 1 : Absorption spectra in 10% ethanol for:- (1) 10^{-5}M anti benzaldoxime, (2) 10^{-5}M benzamide, (3) 10^{-5}M benzoic acid

The absorption spectra of 10^{-5}M antibanzaldoxime, rearranged benzamide and the benzoic acid final product was seen in Figure 1. This spectra showed no spectral interferences between spectra at wavelength of 251nm for the antibenzaldoxime. Hence this wavelength was used as a mointer for kinetic study of antibenzaldoxime. Similarly, other substituted antibenzaldoxime were kinetically studied by observing their λ_{max} with time at TABLE 2. Rate constants were evaluated from an equation:-

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

where A_o = Initial absorbance of benzaldoximes, A_t = Remaining absorbance of benzaldoximes, k_1 = rate constant (min^{-1}), t = minute

The observed rate constants for a pseudo first order reactions of antibenzaldoxime were collected in TABLE 3. By comparing the k_{syn}/k_{anti} relative values of rate constants for the rearranged antibenzaldoxime and its substituent with other rearranged syn isomers[3], one can observe in TABLE 3 that all relative values at five different temperature range between (323-363)K were more than unity, with exception of anti 3-nitrobenzaldoximes. The cause of this anomalous result, led the authors to search or a suitable answered. One of this important factor was the planarity[7] of anti 3-nitrobenzaldoximes which had a relationship with association or polymerization of the molecule. The problem of association of molecules had observed previously to influence on some physical parameters as dissociation[14] constants of substituted benzoic acids and the heats of sublimation[7] of a syn, anti isomers of benzaldoximes and in the same manner on the rate constants[15] of anti 3-nitrobenzaldoxime under study.

TABLE 3 : Comparison of rate constants k_{syn} and k_{anti} for Beckmann rearrangements of substituted benzaldoximes and their k_{syn}/k_{anti} values at different temperatures.

Sr. No.	Temperature K	Nomenclature	10^4 k_{syn} sec^{-1}	10^4 k_{anti} sec^{-1}	k_{syn}/k_{anti}	Sr. No.	Temperature K	Nomenclature	10^4 k_{syn} sec^{-1}	10^4 k_{anti} sec^{-1}	k_{syn}/k_{anti}
1	323	Benzaldoxime	19.1261	11.5254	1.66	34	353		1.8043	1.5557	1.16
2	333		34.7631	28.6451	1.21	35	363		3.2082	2.7049	1.19
3	343		57.7191	49.7339	1.16	36	323	2-Hydroxybenzaldoxime	0.2797	0.2666	1.05
4	353		72.7095	69.3414	1.05	37	333		0.4656	0.4149	1.12
5	363		107.9517	97.4117	1.11	38	343		0.7604	0.7380	1.03
6	323	2-Nitrobenzaldoxime	6.4375	1.1132	5.78	39	353		1.1272	1.0899	1.03
7	333		10.4120	1.5492	6.72	40	363		2.3927	2.2507	1.06
8	343		14.3865	2.0171	7.13	41	323	3-Hydroxybenzaldoxime	1.9062	1.1134	1.71
9	353		20.4829	2.2918	8.94	42	333		3.1085	2.0776	1.45
10	363		30.7972	4.4695	6.89	43	343		4.9205	2.9983	1.64
11	323	3-Nitrobenzaldoxime	1.0378	4.0698	0.25	44	353		7.0981	5.1463	1.38
12	333		1.6200	7.7288	0.20	45	363		10.0426	7.3397	1.37
13	343		2.4663	9.6768	0.25	46	323	4-Hydroxybenzaldoxime	5.8622	5.1981	1.13
14	353		3.6694	12.6336	0.29	47	333		8.8623	8.6440	1.02
15	363		5.0880	18.0665	0.28	48	343		12.3815	12.0732	1.02
16	323	4-Nitrobenzaldoxime	19.1261	11.5254	1.66	49	353		16.8374	16.5288	1.02
17	333		34.7631	28.6451	1.21	50	363		21.1291	20.8288	1.01
18	343		57.7191	49.7339	1.16	51	323	2-Methylbenzaldoxime	0.6911	0.3374	2.05
19	353		72.7095	69.3414	1.05	52	333		0.9904	0.6394	1.55
20	363		107.9517	97.4117	1.11	53	343		1.3928	0.9124	1.53
21	323	2-Chlorobenzaldoxime	0.4890	0.3361	1.45	54	353		2.2545	1.4483	1.56
22	333		0.7527	0.6581	1.14	55	363		4.0048	2.5360	1.58
23	343		1.1351	0.9877	1.15	56	323	3-Methylbenzaldoxime	0.4435	0.3260	1.36
24	353		2.3875	1.6788	1.42	57	333		0.7041	0.6173	1.14
25	363		3.2180	2.7810	1.16	58	343		1.0460	0.8873	1.18
26	323	3-Chlorobenzaldoxime	5.4045	2.3232	2.33	59	353		1.6895	1.4381	1.17
27	333		9.3290	4.9720	1.88	60	363		2.9891	2.5207	1.19
28	343		14.2936	6.5393	2.19	61	323	4-Methylbenzaldoxime	0.2322	0.2098	1.11
29	353		19.1340	7.8237	2.45	62	333		0.4772	0.4627	1.03
30	363		24.0151	12.6152	1.90	63	343		0.8386	0.8097	1.04
31	323	4-Chlorobenzaldoxime	0.4777	0.3219	1.48	64	353		1.3562	1.2370	1.10
32	333		0.6547	0.6241	1.05	65	363		2.4901	2.2516	1.11
33	343		1.0062	0.9684	1.04						

Majer[7] etal had used the molar extension coefficient for measuring planarity of substituted benzaldoxime. This encourage the workers to measure UV spectra of similar compounds as anti 2, 3 and 4-nitrobenzaldoximes in ethanol solvent. Their results showed the following absorptions of λ_{max} (nm) with their molar extension coefficients Σ_{max} (Liter.mole^{-1}.cm^{-1}) values of 236(10000), 233(12800) and 240(1950) respectively. These results clearly confirmed the anti 3-nitrobenzaldoxime was more planer[7] and had lesser degree polymerizations compare to its 2 and 4 isomers. This decreased degree of polymerization process in 3-nitrobenzaldoxime means a less energy to ever needed to over come on polymerization process before Beckmann rearrangement reaction in 3-nitrobenzaldoxime. Certainly, this accompanied by an increasing rate constants for the observed rate constants of Beckmann rearrangement of anti 3-nitrobenzaldoxime among other antialdoxime found in TABLE 3. This last resulted to a decrease of k_{syn}/k_{anti} for 3-nitrobenzaldoxime at all temperature range between (323-363)K.

CONCLUSIONS

1. Anti substituted benzaldoxime and its substituents were prepared by standard method[6] and converted to it isomeric aldoxime by using a hydrochloric acid gas method[7]
2. The structures of these antialdoximes were confirmed by the measurement of their melting points UV and IR spectra.
3. The kinetic study for a Beckmann rearrangement of antialdoximes to their benzoic acid or its substituent and ammonia were performed by using, perchloric acid.
4. A spectrophotometric method was used for kinetic study at optimum wavelength of aldoxime.
5. Pseudo first order reaction was observed for the rearrangement reactions of antialdoximes. Rate constants observed in the range (323-363)K were evaluated from kinetic equation of order stated.
6. Relative rate constants k_{syn}/k_{anti} observed in this investigation for all aldoximes had a values greater than unity at all temperatures with exception of 3-nitrobenzaldoxime.
7. The reason for lower k_{syn}/k_{anti} value for 3-nitrobenzaldoxime among other aldoxime in TABLE 3 was explained by a fact, greater planarity[7] of anti 3-nitrobenzaldoxime and a its lesser degree of polymerization process.

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