KINETICS AND MECHANISM OF THE HYDROLYSIS OF BENZYLIDENE BENZOYLHYD - RAZONE DERIVATIVES .

BY

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ملخـــص

لقد قمنا بدراسة ميكانيكية وحركة تفاعل التمؤ (Hydrolysis) لسلسلة من مشتقات بنزيليدين بنزويل هايدرازون عند درجات حرارية مختلفة بين درجات حرارة ٢٥ ـ ٤٠ °م بواسطة اطياف الأشعة الفوق بنفسجية والمرئية .

كما وجدنا أن تفاعلات التمؤ (Hydrolysis)تتبع حركة الرتبة الأولى (First Order Kinetics)ولقد فرضت ميكانيكية التفاعل التي تحتوي على هجوم جزيء الماء على الهدف البروتوني والذي اعتبر كمساعد قاعدي عام .

إن هذه الميكانيكية قد عُزِّزَت بواسطة تأثير تركيز الأيون السالب في المعدِّل (Buffer) ، عند درجة حموضة ثابتة على ثابت السرعة الملاحظة .

وقد توصلنا الى النتائج التالية :

١ ـ وجدت قيمة "β" التابعة لبرونستد (Bronsted) في تفاعل التمؤ (Hydrolysis) .

٢ ـ لقد تم مناقشة وتقييم عوامل ارهينياس (Arrhenius) ، والعوامل الحرارية وكذلك العلاقة المتبادلة لهامت (Hammett) .

٣ ـ لقد تم تحديد قيم (pka) للحامض المرافق التابع لبنزويل هايدرازون ومشتقاته .

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Abstract

The kinetics and mechanism of hydrolysis of a series of substituted benzylidene benzoylhydrazones (X – BBH) have been studied at five different temperatures in the range 25 – 45°c by U.V. -visible spectrophotometry . The hydrolysis reactions were found to follow first - order kinetics . A mechanism has been postulated in which the attack of water on the protonated substrate is subject to general base catalysis . This mechanism has been supported by the effect of anion concentration of buffer , at constant pH , on the observed rate constant . The Bronsted β-value for the hydrolysis reaction is 0.73. Hammett correlations , Arrhenius and thermodynamic parametres have been evaluated and discussed . The pK_a values for the conjugate acids for benzylidene benzoylhydrazones derivatives (X - BBH) have been determined

Introduction

Numerous studies concerning the hydrolysis of simple azomethines derived from aliphatic or aromatic amines have been reported [1 – 9] .
Different mechanisms of hydrolysis have been proposed depending on the pH values [4,8,10,12] . Recently Temerk et al [8] proposed a specific acid catalysis mechanism for the hydrolysis of some N^1– (4 – substituted benzylidene) salicylohydrazides without reporting experimental evidences of their mechanism.

In the present work , more studies have been done about the mechanism of hydrolysis of some benzylidene benzoylhydrazones and a comparison has been made to show the differences and similarities between our results and those of Temerk et al [8] . Moreover , the effects of pH , substituents and temperature on the kinetics of hydrolysis of (X – BBH) have been studied to throw more light about the mechanism of hydrolysis .

Experimental

Materials :

The benzylidene benzoylhydrazone derivatives (X – BBH ; X = H ; p – OCH_3 ; m–NO_2 , m–CL , m–CH_3) , were prepared and purified by the conventional method [13] . Stock solutions (0.001 M) were prepared in absolute ethanol . The modified buffer series of Britton and Robinson [14] and Potassium

tetraoxalate [15] were used as the hydrolysis media .

Instrumentation and Kinetic Procedure :

The rates of hydrolysis of benzylidene benzoylhydrazones were measured spectrophotometrically using a pye–Unicam Sp8–100(spectrophotometer) with a thermostatically controlled cell holder accurate to within ±0.1 °C . Also a Corning pH – meter , model 12 was used for pH measurements . After being properly thermostated at the required temperatures , the buffer (9.5 ml) and the hydrazone solution (0.5 ml) were mixed . The mixture was shaken and transferred to the stoppered quartz cell (1cm) and the change in U.V. absorption with time at the selected wavelength was recorded . The following wavelengths were used in the rate studies of BBH , 295 nm ; m−CH_3 −BBH , 292 nm ; p−OCH_3 −BBH , 328 nm ; m−Cl−BBH , 290nm; and m−NO_2 −BBH , 280 nm . The rates of hydrolysis of hydrazones were followed to 80% completion . The U.V spectrum of the reaction mixture was determined in each case after ten − half − lives . It was found to be identical with that of the expected hydrolysis product namely substituted benzaldehydes and bezoylhydrazine under the same conditions .

pK_a Determinations :

The pK_a values were determined spectrophotometrically using the half height method [4] .

Results And Discussion

The hydrolysis of benzylidene benzoylhydrazone (BBH) and its derivatives in 5 % (v / v) ethanol buffer mixtures are considered as a first order reaction as indicated from the linearity of the plot of ln ($A_t - A_\infty$) versus time . It was observed that the rates of hydrolysis above pH 4 were very slow . Therefore , the rates of the hydrolysis reactions were studied using Britton and Robinson buffer in the pH range (1−3.1) . It was found that the observed rate constants increase with decreasing the pH value as shown in Figure 1 . The slopes of the linear plots were found around 0.64 , suggesting a general acid − base catalysis mechanism for the hydrolysis of hydrazones.

In order to study the mechanism of hydrolysis of (BBH) , potassium tetraoxalate buffer has been used as a hydrolysis medium . At each pH value , the ratio of acid to anion was held constant and the ionic strength was maintained constant at 0.145 by addition of potassium chloride while the total concentration of the buffer was changed . Table 1 shows the effects of anion concentration , at a fixed pH value , on the observed rate constants for the hydrolysis of BBH . It can be seen that the observed rate constant increases linearly with increasing the anion concentration , which confirm a general acid −base catalysis mechanism for the hydrolysis of BBH . The observed rate constants at zero buffer concentration , k_0 , were obtained by extrapolating the plots of the observed rate constants versus the anion concentration , at different pH values , to zero buffer concentration . Hence , the k_0 values become dependent only on the H^+ according to the equation , $k_{obs.} = k_H+[H^+]$.

The plot of log k_0 versus pH values is shown in Figure 2 . From the slope of the plot,it is found that the order with respect to $(H)^+$ is one and the k_H+ is 0.065 $M^{-1}S^{-1}$.

From the above results it is evident that the mechanism of hydrolysis is general acid .. base catalysis and in contrast to that proposed by Temerk et al [8] . On the other hand , the results of Temerk were analyzed by plotting their log k_{obs} . versus pH values , as shown in Figure 1 , where it is found that the slope of the linear plot to be around 0.64 which agrees with our proposed mechanism . Moreover , Temerk et al [8] reported that no measurable reaction was observed beyond pH 3.90 , which is in contrast to our observation that the reaction proceeds in basic medium but at much slower rate than in acidic medium . It was found , that the half life of the hydrolysis of BBH to be around three hours at pH 13 and 50℃. Further studies about this observation are in progress .

Activation parameters were obtained from Arrhenius plots and the appropriate transition state theory equations . Thermodynamic parameters of activation ($\triangle G^{\neq}$, $\triangle H^{\neq}$ and $\triangle S^{\neq}$) for the hydrolysis of various hydrazones are depicted in Table 2 . It seems from analysis of the data in Table 2 that the rate of hydrolysis depends on the molecular structure of hydrazone in the following order :

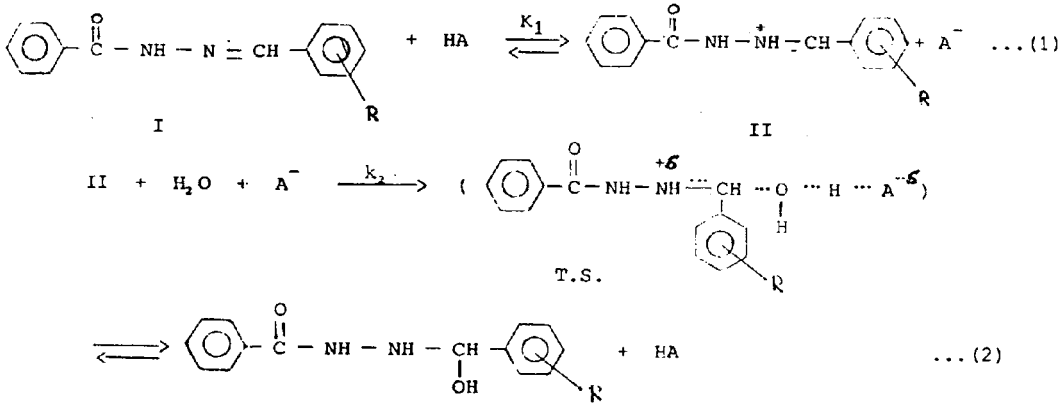
$$p-OCH_3 > m\text{–}CH_3 > H > m\text{–}Cl > m\text{–}NO_2 .$$

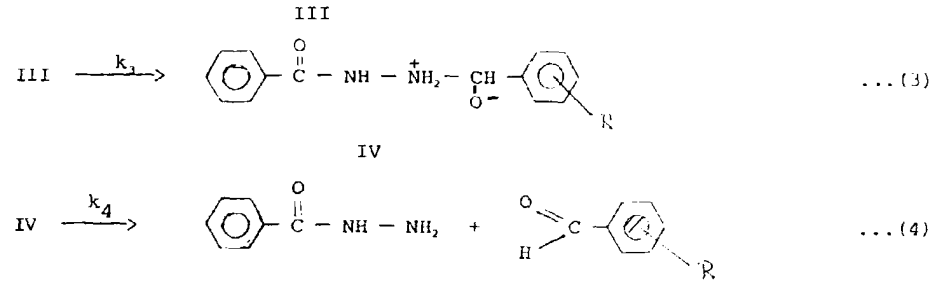
The high negative $\triangle S^{\neq}$ for the (p–OCH_3 – BBH) would indicate that the activated complex is randomly linked to solvent molecules . The linear correlation between the activation enthalpies and entropies implies that all the hydrazones are hydrolysed by the same mechanism and the changes in rates are governed by changes in both enthalpies and entropies of activation [16 , 17] . These observations were found in agreement with those presented by Temerk[8].

The Hammett plot of log k_{rel} . versus σ is shown in Figures 3 at 32.5 and at 45°c as well as Temerk results at 27°c . It can be seen that as the temperature is increased by 12,5°c , the absolute ρ values decrease from –0.57 to –0.43 . This decrease may be attributed to the fact that the effect of substitution on the rate constant is diminished as the temperature approaches the isokinetic temperature [16] . In the present work , the small ρ value indicates a low sensitivity of the hydrolysis of C = N – Group to polar effect of substituents which has been observed also for schiff base hydrolysis [18] .

Values of pK_a for the conjugate acids of a series of substituted benzylidene benzoylhydrazones together with their observed rate constants are listed in Table 3. The logarithms of the observed rate constants for the substituted benzylidene benzoylhydrazones fall near a Bronsted line of slope 0.73 when plotted against their pK_a values . The β value obtained which is 0.73 indicates that the transition state would resemble the products , i.e. the carbinolamine hydrogen would be closer to the catalyst than to the oxygen , as the proton transfer would be more than half completed [19 , 20] .

In light of the above discussion the following mechanism is postulated .





The mechanism shows that the protonated substrate is undergoing hydrolysis and its concentration decreases with increasing pH resulting in an increase in the rate constant at high hydrogen ion concentration , which is supported by the results in Table 1 . It can be seen also from the proposed mechanism that the increase in the electron – donating of the substituents increases the electron density on the nitrogen atom of the azomethine linkage which in turn causes a shift in the equilibrium of step (1) in the forward direction . This increases K_1 and is reflected in a net increase in the reaction rate constant . This behaviour is quite obvious in the methoxy substituted compound as shown in Table 2 .

Evidences for the rate determining step to be the attack of water on the protonated hydrazones come from the followings :

1 – The entropies of activation listed in Table 2 are typical for reactions involving water in the rate determining step [21] . Water will suffer loss of translational and rotational freedom when tied to the protonated species leading to a negative entropy of activation .

2 – It was observed [22] that the rate increases as the water content in the medium of the hydrolysis of various hydrazones is increased .

Step 3 in the mechanism involves a proton transfer and a proton transfer is expected to be fast [7] .

Table (1)

Effect of anion concentration of the buffer on the observed rate constants for the hydrolysis of BBH

(t = 30 °C)

pH	$10^3 . [H_2C_2O_4]/M$	$10^3 . [HC_2O_4^-]/M$	$10^3 . k_{obs.}/S^{-1}$
1.6	25	.65	7.9
	33	.87	9.6
	42	109	13.0
	50	131	14.3
2.0	8	.62	3.5
	10	.78	4.1
	12	93	4.9
	14	108	5.5
	17	123	6.0
2.4	1.0	.15	0.95
	1.1	.17	1.06
	1.3	.20	1.19
	1.5	23	1.38
2.7	0.36	6.6	0.53
	0.43	8.0	0.63
	0.50	9.0	0.73
	0.60	11.0	0.83

Table (2)

Observed rate constants , activation energies and thermodynamic parameters of activation for the hydrolysis of hydrazones (5×10^{-5}M) at pH 1.92

(25 °C)

Structure	$10^3 k_{obs.}$ /S^{-1}	E_a Kcal / mple	$\triangle G^{\#}$ Kcal / mole	$\triangle H^{\#}$ Kcal / mole	$-\triangle S^{\#}$ cal K^{-1} mole^{-1}
BBH	2.7	14.54 ± 0.04	20.95	13.95	23.49
m−Cl−BBH	1.7	15.24 ± 0.07	21.21	14.65	22.03
m−NO_2−BBH	1.0	17.24 ± 0.04	21.52	16.65	16.34
m−CH_3−BBH	3.1	13.67 ± 0.17	20.88	13.08	26.17
p−OCH_3−BBH	5.6	11.37 ± 0.04	20.52	10.78	32.70

Table (3)

Observed rate constants and pK_a values for the protonated substituted benzylidene benzoylhdrazones using universal buffer at pH 1.9 and (25 °C)

Substituent	$10^3 . k_{obs.} / S^{-1}$	pK_a
m−NO_2	1.0	3.07
m−Cl	1.7	2.92
H−	2.7	2.81
m−CH_3	3.1	2.33
p−OCH_3	5.6	2.12

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Figure (1) :

A plot of log $k_{obs.}$ for the hydrolysis of substituted benzylidene benzoylhydrazones as a function of pH at 32.5 °C

A = BBH

B = m−NO_2 − BBH

C= BSH [Ref. 8] .

Figure (2) :

A plot of log k_0 for the hydrolysis of Benzylidene benzoylhydrazone as a function of pH at 30 °C (k_0) observed rate constant at zero buffer concentration) .

Figure (3) :

A plot of log $k_{rel.}$ against Hammett constant $\bar{\sigma}$.

A = 45 °C $\rho = -0.43$

B = 32.5 °C $\rho = -0.57$

C= 27 °C $\rho = -0.87$ [Ref. 8]

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