

دراسة حركية على تقيؤ مركبي بيروليدين بنزويل هيدرازون

والثيوفيتيليد بنزويل هيدرازون

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ملخص

لقد تمت دراسة تأثير مكونات الوسط الحمضي على حركية وميكانيكية تقيؤ مركبي بيروليدين بنزويل هيدرازون و الثيوفيتيليد بنزويل هيدرازون . كما قمنا بقياس ثابت سرعة التفاعل وطاقة التنشيط وبعض ثوابت الديناميكا الحرارية لهذا التفاعل في محلول منظم يحتوي على أيون رباعي الاوكسالات عند درجة حرارة ٣٥°م .

قمنا بمقارنة هذه النتائج بنتائج أخرى نشرت سابقاً وتتعلق بتقيؤ مركب الفيرفيراليد بنزويل هيدرازون ومدى تأثير الذرة الغير متجانسة في المركبات الثلاثة على عملية التقيؤ .

في وجود المحلول المنظم الذي يحتوي على أيون رباعي الاوكسالات كوسط للتميؤ ، تم حساب ثابت سرعة التفاعل المحفز بالنسبة لكل من أيونات $H_2C_2O_4$ ، $HC_2O_4^-$ ، H^+ وتم استنباط معادلة تربط بين ثابت سرعة التفاعل الظاهري وبين تراكيز الأيونات المختلفة الموجودة في المحلول المنظم .

Kinetic Studies On the Hydrolysis of Pyrrolidene Benzoylhydrazone And Thiophenylidene Benzoylhydrazone

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ABSTRACT

The influence of the nature of acidic medium on the kinetics and the mechanism of the hydrolysis of pyrrolidene benzoylhydrazone (PBH) and thiophenylidene benzoylhydrazone (TBH) has been studied.

The observed rate constants, activation energy and thermodynamic parameters for the hydrolysis of PBH and TBH in tetraoxalate buffer solutions at 35°C have been measured. These results were compared with that reported for furfurylidene benzoylhydrazone FBH and the effect of heteroatom on the hydrolysis has been investigated.

In presence of tetraoxalate buffer as a hydrolysis medium for TBH, the catalytic rate constants with respect to H^+ , $HC_2O_4^-$ and $H_2C_2O_4$ were calculated. An equation relating the observed rate constant to the concentration of all species in the buffer mixture has been constructed.

KEY WORDS: Kinetic Studies, Hydrolysis of Pyrrolidene and Thiophenylidene Benzoylhydrazones.

INTRODUCTION

Many studies have been done on the hydrolysis of aliphatic and aromatic hydrazones in acidic and basic media ⁽¹⁻¹⁰⁾. However, few studies have been done on the hydrolysis of heterocyclic hydrazones ⁽¹¹⁾. In this work, we wish to report the results of the kinetic data for the hydrolysis of pyrrolidene benzoylhydrazone, PBH, and thiophenylidene benzoylhydrazone, TBH, as a continuation to our earlier work ⁽¹¹⁾ on the hydrolysis of furfurylidene benzoylhydrazone, FBH. The effect of the heteroatom of the heterocyclic ring on the rate of hydrolysis has been investigated. Moreover, the effects of buffer nature on the kinetics and the mechanism of the hydrolysis of TBH have been discussed.

EXPERIMENTAL

Materials

Pyrrolidene benzoylhydrazone, PBH, and thiophenylidene benzoylhydrazone, TBH, were prepared and purified by the conventional methods⁽¹²⁾. 10^{-3} M of hydrazone solutions were prepared by dissolving the appropriate amounts in absolute ethanol.

Hydrochloric acid-potassium chloride buffer series⁽¹³⁾ and potassium tetraoxalate buffers⁽¹⁴⁾ were used as the hydrolysis media. The ionic strength was kept constant at 0.145 by the addition of KCl. The concentration of hydrogen ions was evaluated from pH measurements and the activity coefficients of the ions⁽¹⁴⁾.

Apparatus

Kinetic runs for the hydrolysis of PBH and TBH were spectrophotometrically performed using a Pye-Unicam SP8-100 spectrophotometer fitted with a thermostated cell holder. All pH measurements were carried out using a Corning pH-meter, model 12.

Procedure

Each reaction run was performed by mixing 4.75 ml of the buffer and 0.25 ml of 10^{-3} M of the hydrazone solution at a fixed temperature. The mixture was shaken and transferred to the stoppered quartz cell (1 cm) and the change in absorbance with time, at the selected wavelength, was recorded. The wavelengths used in the rate studies of PBH, TBH, and FBH were 325, 314, and 305 nm respectively. The observed rate constants for the hydrolysis, K_{obs} , were obtained from the slopes of the plots of $\ln(A_t - A_\infty)$ versus time.

RESULTS AND DISCUSSION

The hydrolysis of PBH and TBH in aqueous medium containing 5% ethanol has been found to follow first order plots similar to that previously reported for the hydrolysis of furfurylidene benzoylhydrazone, FBH⁽¹¹⁾.

Straight lines were obtained by plotting $\log k_{obs}$ vs $-\log [H^+]$ for the hydrolysis of PBH, TBH and FBH using hydrochloric acid-potassium

chloride buffer as the hydrolysis medium at 35°C. Figure 1 represents the results

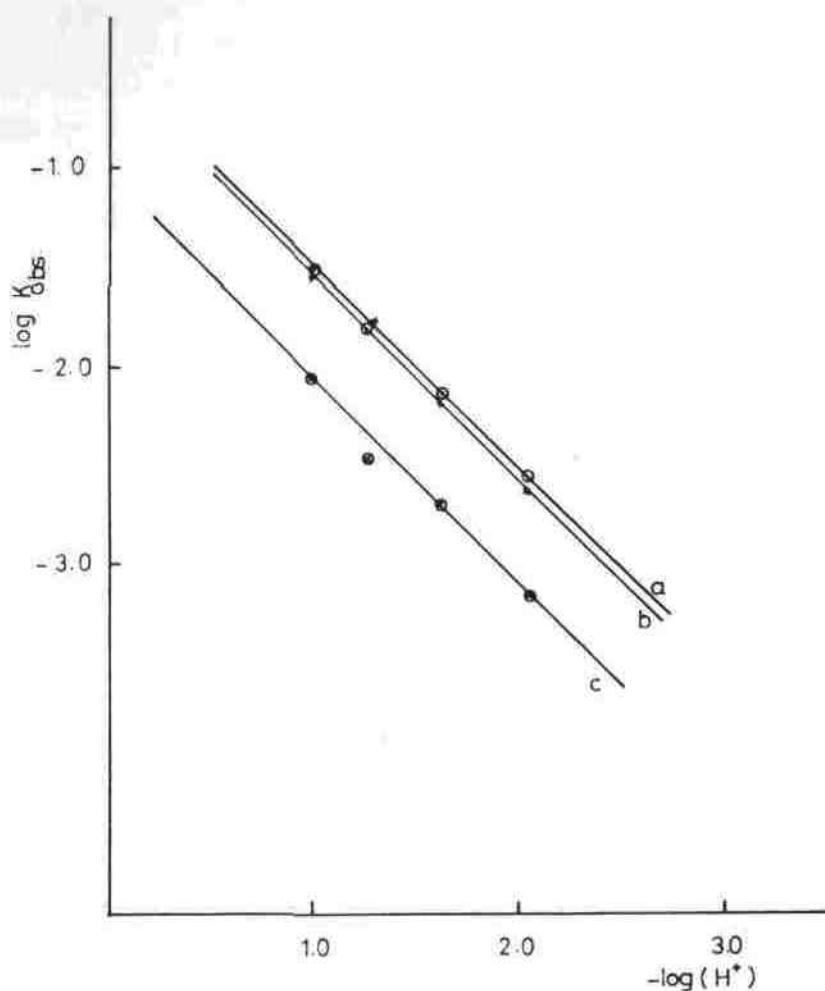
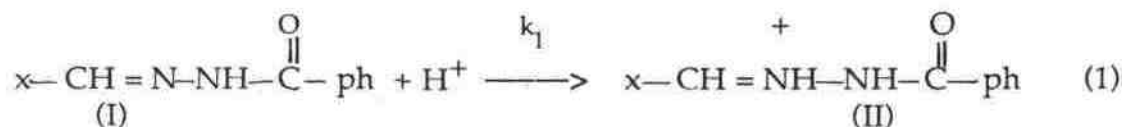
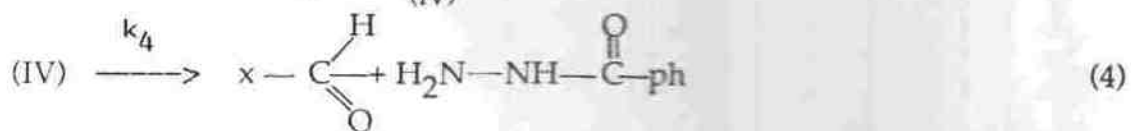
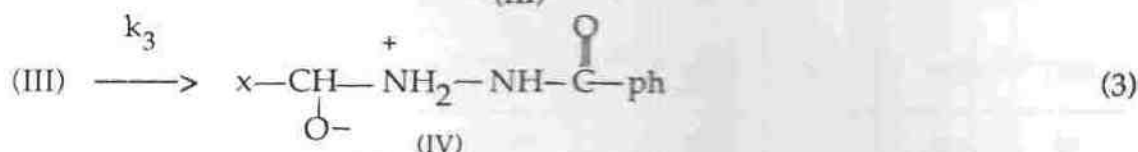
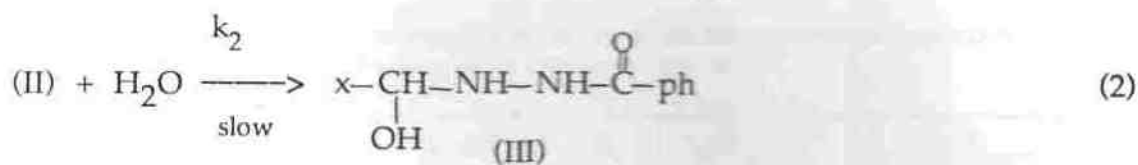


Fig. (1): A plot of $\log k_{obs}$ versus $-\log [H^+]$ in presence of hydrochloric acid-potassium chloride buffer solution at 35°C
 a- PBH b- TBH c- FBH

obtained for PBH and FBH for comparison, where the lines for PBH and TBH are almost closed. The slopes of such lines are unity which indicate a specific acid catalyzed mechanism as listed in scheme 1^(7,10).

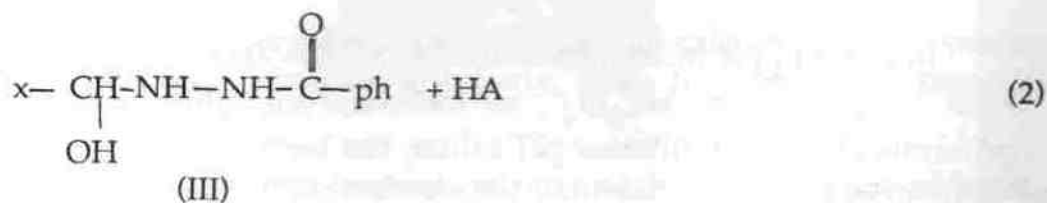
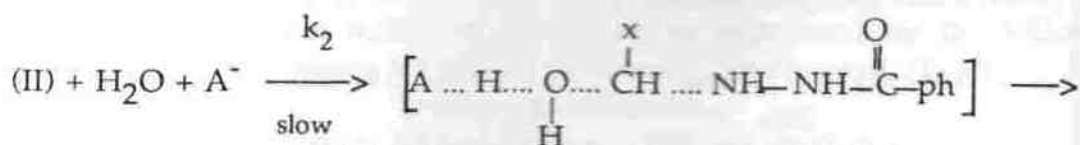
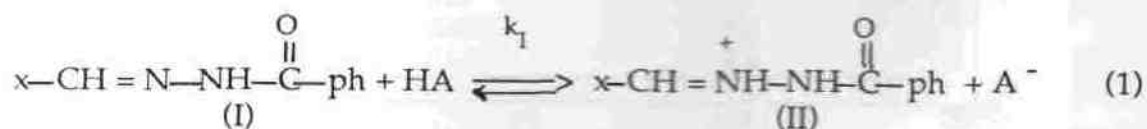


where $x =$, ,



Scheme 1

For studying the effect of the nature of the acidic medium on the hydrolysis mechanism of the investigated hydrazones, the potassium hydrogen tetraoxalate buffer was used as hydrolysis medium. It was found that, the plots of $\log k_{\text{obs}}$ versus $-\log [H^+]$ were linear, as shown in Figure 2 with slopes around 1.3 suggesting a general acid-base catalysed mechanism as reported in scheme. 2.



Scheme 2

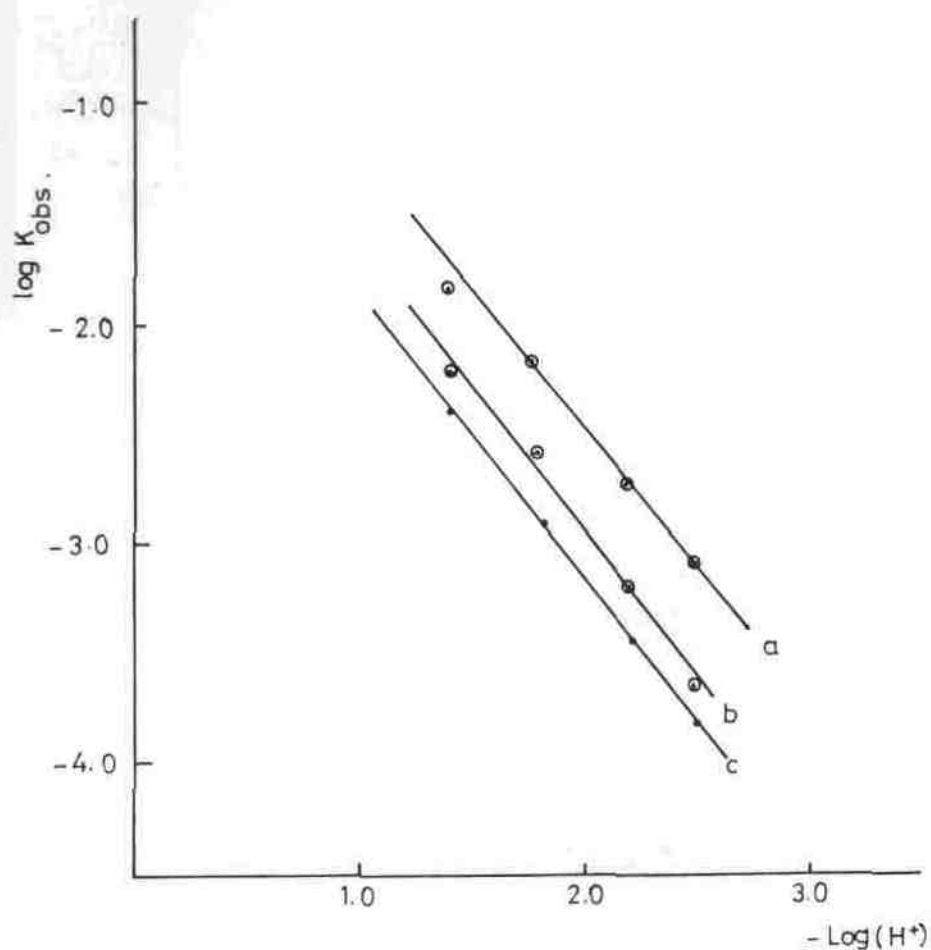
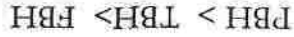


Fig. (2): A plot of $\log k_{\text{obs}}$ versus $-\log [H^+]$ for the potassium hydrogen tetraoxalate buffer at 35°C
 a- PBH b- TBH c- FBH

In order to get more information about this assumption, the effect of anion concentration, HC_2O_4^- , on the observed rate constants for the hydrolysis of TBH, at different pH values, has been studied. The results are listed in Table 1. The variation of the observed rate constants at zero buffer concentration, k_0 , with pH values are reported in Table 2.

Upon the analysis of the plot of $\log k_{\text{obs}}$ versus pH and from data in Table 1, the rate constants with respect to H^+ , HC_2O_4^- and $\text{H}_2\text{C}_2\text{O}_4$ were found to be 0.044, 0.013 and 0.067 respectively.



Activation parameters were obtained from Arrhenius plots and the appropriate transition state theory equations. Thermodynamics parameters of activation (ΔG^\ddagger , ΔH^\ddagger and ΔS^\ddagger) for the hydrolysis of PBH, TBH and FBH are listed in Table 3. Analysis of such data shows that the observed rate constants for the hydrolysis of the studied hydrazones decrease in the following order:

It also can be seen from Table 1, that the calculated rate constants from the proposed equation are fairly close to those experimentally obtained.

$$k^{obs} = 0.044 [H^+] + 0.013 [HC_2O_4^-] + 0.067 [H_2C_2O_4]$$

Therefore, the observed first order rate constant for the hydrolysis of TBH in tetraoxalate buffer at 35°C, can be expressed by the following equation:

$10^3 k_o/s^{-1}$	1.20 0.80 0.40 0.16
pH	1.6 1.8 2.0 2.4

Table 2: Variation of the observed rate constant for the hydrolysis of TBH at zero buffer concentration at 35°C

pH	$10^3 [H_2C_2O_4]/M$	$10^3 [HC_2O_4^-]/M$	$10^3 k^{obs}/s^{-1}$	$10^3 k^{calc}/s^{-1}$
1.6	25	65	10.7	3.6
	33	87	11.8	4.4
	42	109	13.9	5.3
	50	131	15.5	6.1
	1.0	15	1.1	0.42
	1.3	20	1.9	0.55
2.4	1.5	23	2.2	0.57
	1.8	29	2.8	0.74
	2.0	34	3.2	0.83
	2.2	40	3.8	0.95
	2.3	43	4.1	1.00
	2.4	46	4.4	1.05

Table 1: Effect of anion concentration of the buffer on the observed rate constant for the hydrolysis of PBH and TBH at 35°C

Table (3): The observed rate constants, activation energies and thermodynamic parameters for the hydrolysis of PBH, TBH and FBH using tetraoxalate buffer at 35° C (pH = 2.0).

Compound	$10^3 k_{\text{obs}}/\text{s}^{-1}$	E_a/kJmol^{-1}	$\Delta H^\ddagger/\text{kJmol}^{-1}$	$\Delta G^\ddagger/\text{kJmol}^{-1}$	$-\Delta S^\ddagger/\text{J}\cdot\text{mol}^{-1}\text{K}^{-1}$
PBH	6.7	39.3 ± 0.04	36.7	88.33	167.5
TBH	2.7	55.4 ± 0.07	52.8	90.60	122.7
FBH ^a	2.2	65.9 ± 0.17	63.3	91.10	90.3

a = ref. (11)

This observation can be attributed to the fact that the Π - electrons density at position 2 of the heterocyclic ring have the values of 1.03, 0.912 and 0.772 for PBH, TBH and FBH respectively (15). The increase in the electron donating character of PBH compared to TBH and FBH, increases the electron density on the nitrogen atom of the azomethine linkage which in turn increases the concentration of the protonated species and leads to a higher observed rate constant for the hydrolysis.

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