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Kinetic Studies of the Hydrolysis of Furfurylidene Benzoylhydrazone

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Summary. The hydrolysis of furfurylidene benzoylhydrazone, *FBH*, in hydrochloric acid medium has been found to follow specific acid catalysis, whereas the hydrolysis in universal buffer medium has been found to follow general acid-base catalysis. Mechanisms for the hydrolysis in different acidic media have been postulated. The observed rate constants, secondary rate constants, activation and thermodynamic parameters for the hydrolysis of furfurylidene benzoylhydrazone have been reported. The effect of change in percentage of ethanol in the ethanol-buffer mixture on the rate of hydrolysis has been discussed.

Keywords. Kinetic studies; Hydrolysis; Furfuryl benzoylhydrazone.

Kinetische Untersuchungen zur Hydrolyse von Furfurylidenbenzoylhydrazon

Zusammenfassung. Es wurde festgestellt, daß die Hydrolyse von Furfurylidenbenzoylhydrazon (*FBH*) in HCl-Medium einer speziellen Säurekatalyse gehorcht, wohingegen die Hydrolyse in universellen Puffer-Medien nach einer generellen Säure-Base Katalyse abläuft. Es werden Mechanismen für die verschiedenen sauren Medien postuliert. Die beobachteten Geschwindigkeitskonstanten, die sekundären Geschwindigkeitskonstanten, Aktivierungs- und sonstige thermodynamische Parameter für die Hydrolyse von Furfurylidenbenzoylhydrazon werden berichtet. Der Effekt wechselnder Ethanolkonzentration auf die Hydrolysengeschwindigkeitskonstante in Ethanol-Puffer-Mischungen wird diskutiert.

Introduction

Several studies concerning the hydrolysis of simple azomethines derived from aliphatic or aromatic amines have been reported [1–7]. On the other hand, the effects of substituents, *pH*, solvent and temperature on the rate of hydrolysis of benzylidene benzoylhydrazone have been investigated [8, 9]. However, a literature survey revealed the absence of hydrolysis studies on furfurylidene benzoylhydrazone.

In this paper, the effect of the nature of acidic media on the kinetics and mechanism of hydrolysis of furfurylidene benzoylhydrazone have been studied to show the similarities and differences in its hydrolysis from that of benzylidene benzoylhydrazone.

Experimental

The furfurylidene benzoylhydrazone, *FBH*, was prepared and purified by the conventional method [10]. A stock solution of 10^{-3} *M FBH* was prepared in absolute ethanol. The modified universal buffer series of Britton and Robinson [11] or standard hydrochloric acid concentrations were used as the hydrolysis media giving a *pH* range 1–4.

Kinetic runs for the hydrolysis of *FBH* were performed in 5% (*v*/*v*) ethanol-water mixtures at 30 °C. Disappearance of *FBH* was followed by UV spectrophotometry in a Pye-Unicam Sp 8-100 spectrophotometer fitted with a thermostated cell holder. A Corning *pH*-meter, model 12, was used for the *pH* measurements. After being properly thermostated at the required temperatures, aliquots (9.5 ml) of buffer or standard hydrochloric acid were transferred to a test tube containing (0.5) ml of 10^{-3} *M FBH*. The mixture was then shaken vigorously and transferred to 1 cm quartz cell and the change in UV absorption at the selected wave length (306 nm) was recorded. The disappearance of *FBH* was followed to 85% completion. The infinity readings were taken after ten half lives.

Results and Discussion

The hydrolysis of *FBH* in ethanol-water mixture has been found to follow a first order plot as reported previously [8, 9] for the hydrolysis of substituted benzylidene benzoylhydrazones. The rate constant – *pH* profile for the hydrolysis of *FBH* was found to be dependent on the nature of acidic medium used, as shown in Fig. 1. When hydrochloric acid was used as a source of hydrogen ions, the rate constant decreased sharply by increasing the *pH* value, whereas when universal buffers (mixture of phosphoric acid, boric acid and acetic acid) were used, the rate constant showed a small decrease with increasing *pH* value.

It can be seen also from Fig. 1 that for both acidic media the rate of hydrolysis becomes very slow at a *pH* above 3.5.

The results in Fig. 1 indicate that the kinetics and mechanism of *FBH* are dependent on the source of the hydrogen ion [12]. In order to get more information

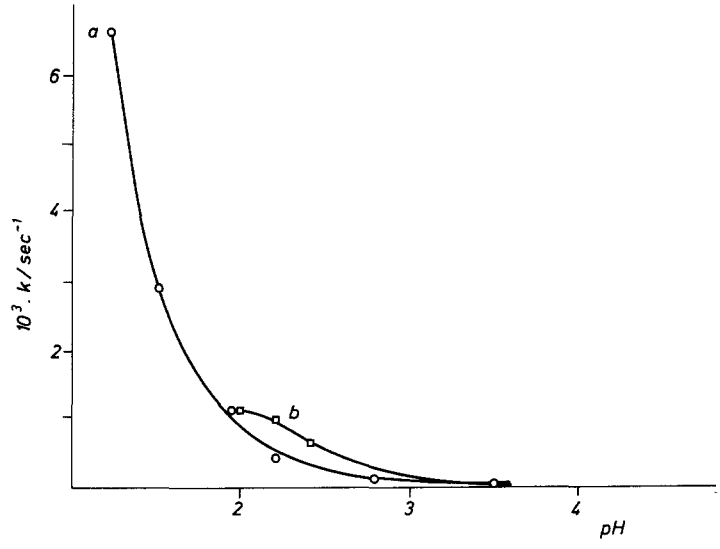


Fig. 1. A plot of the observed rate constant vs. *pH* for the hydrolysis of furfurylidene benzoylhydrazone at 30 °C; *a* hydrochloric acid medium, *b* universal buffer medium

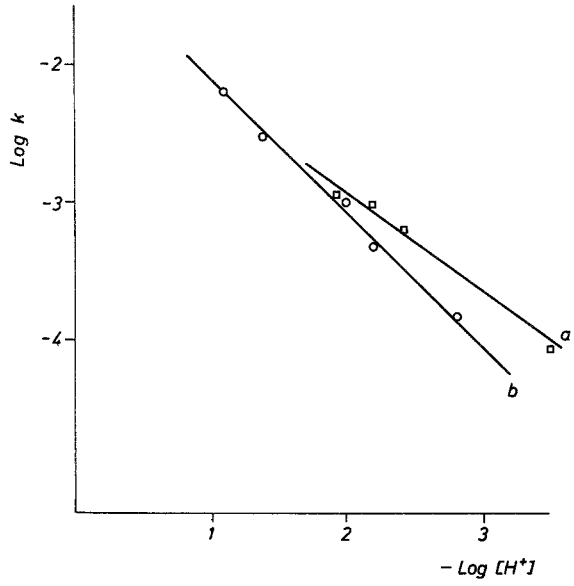
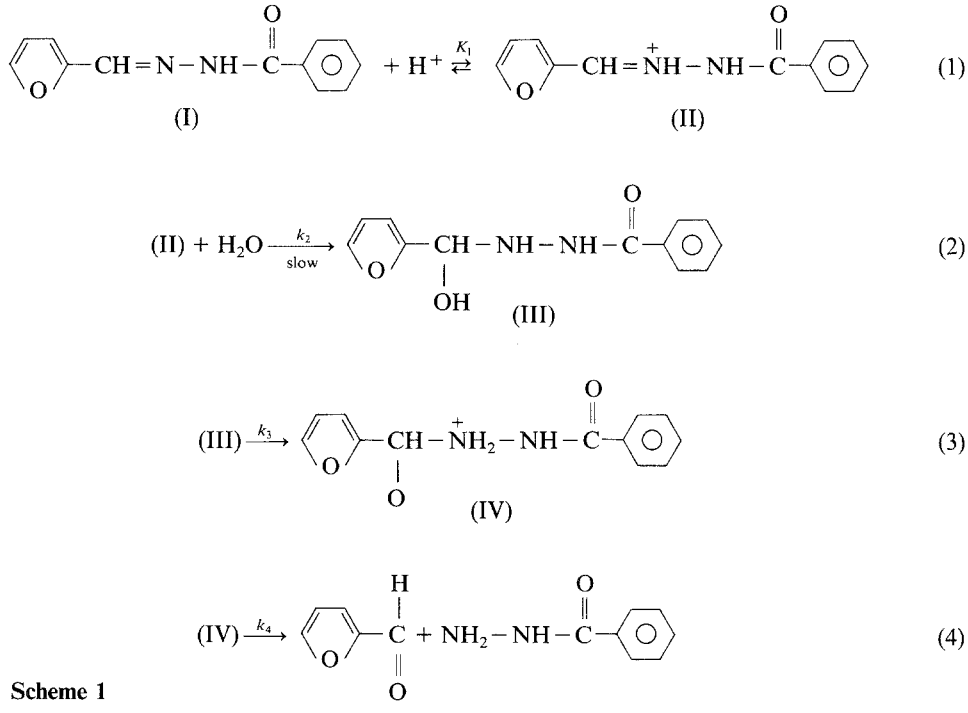


Fig. 2. A plot of log $k_{obs.}$ vs. $-\log [H^+]$ of the media for the hydrolysis of furfurylidene benzoyl hydrazone; *a* universal buffer medium, *b* hydrochloric acid medium

about this, a plot of logarithms of rate constants versus logarithms of hydrogen ion concentration is shown in Fig. 2. The slope of the linear plot obtained when hydrochloric acid was used is about 0.97, indicating specific acid catalysis, whereas the slope of the line obtained with universal buffer is about 0.7, suggesting general acid catalysis.

Therefore the specific acid catalysis mechanism shown in Scheme 1 is postulated for the hydrolysis of *FBH* in hydrochloric acid medium [5, 13].



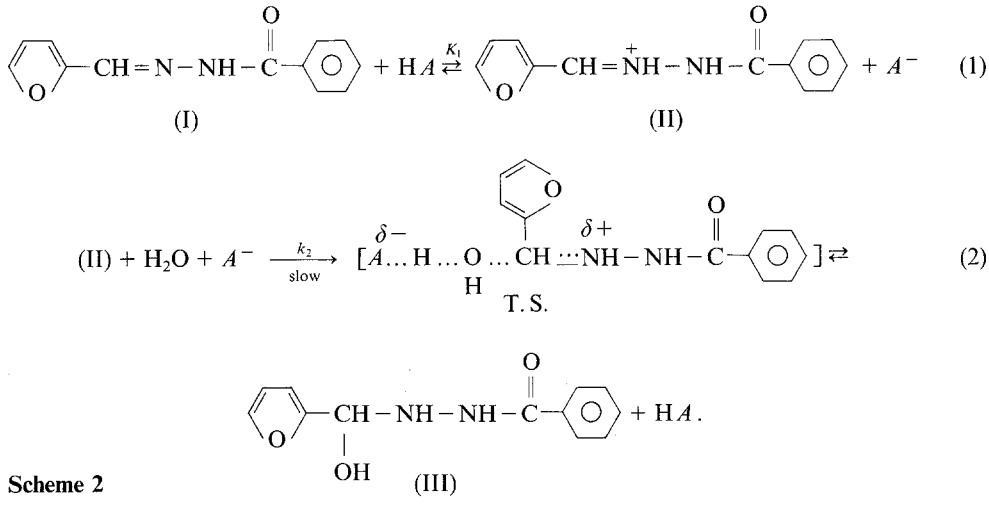
Scheme 1

According to the mechanism of Scheme 1 the rate of the hydrolysis reaction follows the equation:

$$-\frac{d(II)}{dt} = k_2[II] = k_2 K_1 [I][H^+]$$
$$= k_{ob.}[I][H^+].$$

It can be seen from the rate expression that the observed kinetics greatly depend on equilibrium constant, hydrogen ion, and the hydrazone concentrations.

On the other hand, a general acid-base catalysis mechanism is postulated in Scheme 2 for the hydrolysis of *FBH* in universal buffer acidic media which is similar to the mechanism proposed by many workers for similar systems [8, 19, 15].



Scheme 2

Steps (3) and (4) in Scheme 2 are similar to those shown in the mechanism proposed for specific acid catalysis. The rate of the hydrolysis reaction follows the equations,

$$-\frac{d(II)}{dt} = k_2[II][A] = k_2 K_1 [I][HA],$$
$$-\frac{d(II)}{dt} = k_{ob.}[I][HA].$$

Activation parameters were obtained from the plot of logarithm of the observed rate constants versus the reciprocal of absolute temperatures. Thermodynamic parameters of activation ($\Delta G^{\#}$, $\Delta H^{\#}$, and $\Delta S^{\#}$) were calculated from the appropriate transition state theory equations. Table 1 shows a comparison between the results obtained for the hydrolysis of *FBH* with those obtained for the hydrolysis of benzylidene benzoylhydrazone [8]. It can be seen from Table 1 that the rate constant for the hydrolysis of benzylidene benzoylhydrazone is about two fold higher than that of *FBH*. This observation can be attributed to the fact that oxygen is a highly electronegative atom which holds a large electron density around its vicinity (localization of electrons) [16]. This makes the furan ring to induce a withdrawal of electron density from the conjugated system and to act as an elec-

Table 1. The observed rate constants, secondary rate constants activation energies, and thermodynamic parameters for the hydrolysis of furfurylidene benzoylhydrazone and benzylidene benzoylhydrazone at $pH = 1.92$ (30 °C)

Compound	$10^3 \cdot k_{ob.}/s^{-1}$	$k_s^*/s^{-1} M^{-1}$	E_a/kcal mol^{-1}	$\Delta G^{\#}$/kcal mol^{-1}	$\Delta H^{\#}$/kcal mol^{-1}	$\Delta S^{\#}$/cal mol^{-1} K^{-1}
Furfurylidene benzoylhydrazone	1.1	0.09	15.2	21.8	14.6	23.7
Benzylidene benzoylhydrazone [1]	2.7	0.23	14.5	20.9	13.9	23.5

* $k_s = k_{obs.}/[H^+]$

Table 2. Effect of % water in the ethanol – water mixture on the values of the observed rate constants for the hydrolysis of *FBH* at $pH = 1.92$ (30 °C)

% Water	$10^3 \cdot k/s^{-1}$
95	1.1
90	0.98
80	0.76
70	0.50

tron – withdrawing species which results in a positive partial charge at the neighboring nitrogen atoms.

On the other hand, the $\Delta S^{\#}$ values for both hydrazones are the same (s. Table 1), which indicates similar steric requirements. Such $\Delta S^{\#}$ values are consistant with a water involvement in the rate determining step [17]. Moreover, it was also found that changing the solvent percentage (*v*/*v*) in the solvent-water mixture affects the rate of hydrolysis as shown in Table 2. The decrease in water percentage (*v*/*v*) decreases the rate of hydrolysis which is in agreement with the suggestion that water is involved in the rate determining step.

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