SOLVENT EFFECTS ON ρ VALUES OF THE HAMMETT EQUATION FOR THE HYDROLYSIS OF BENZYLIDENE BENZOYLHYDRAZONES

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ملخـــص

يتنـاول البحث التـالي دراســة ومناقشة وتدوين تأثيرات المذيبات (المثيل الكحولي ، الاثيل الكحولي ، البيوثيل الكحولي ، وثنائي مثيل أكسيد الكبريت) على قيم (ρ) أحد ثوابت معادلة هاميت ، وذلك لمادة بنزيليدين بنزويل هايدرازون ومشتقاته . وقد تم انجاز هذا البحث باستعمال جهاز أطياف الاشعة فوق البنفسجية .

Abstract

The effect of solvents on ρ values of the Hammett equation which characterizes the hydrolysis of Benzylidene Benzoylhydrazone (BBH) and its derivatives (m–NO_2 , m–CH_3 , m–OCH_3 , and m–Cl) , have been studied with four solvents (MeOH , $EtOH^{(1)}$, n–BuOH , and DMSO) by U.V. – spectrophotometry . The effects of solvents on ρ values , one of the Hammett equation parameters , have been reported and discussed .

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Introduction

The effects of solvents on the ρ values have been discussed by Wynne – Jones , [2] who have reported the relative acid strengths of some acids in some hydroxylic solvents as water , methanol , and ethanol ; he suggested the inverse proportionality of ρ values to the dielectric constants of the solvent used . Furthermore , Kilpatrick and his co-workers [3] confirmed Wynne-Jones's results on the dissociation of acids in aqueous dioxane ; however , they indicated that this relationship was limited to solvents with dielectric constants larger than $\sim$ 25 .

Tokura et al .[4] have treated the effects of solvents on ρ values as a two – variable problem within a linear free – energy relationship framework . They assumed that the standard activation free energy is a continuous function of o , a substituent variable , and ξ , a solvent variable . It is proposed that the solvent effects on ρ values can be explained in terms of the interaction or cross-term of σ and ξ .

The present work deals with the solvent effects on the Hammett constants of the hydrolysis of benzylidene benzoylhydrazone .

The existence of a linear dependence of σ values , a substituent constant , on the rate constant , log k/k_o , and the mechanism of the hydrolysis of benzylidene benzoylhydrazones have been reported .

Experimental

Reagents and apparatus :

The benzylidene benzoylhydrazones (X – BBH , where X = H , m – CH_3 , m – OCH_3 , m – Cl , and m – NO_2) were prepared and purified by the conventional method.[5] Stock 0.001 M solutions were prepared in pure solvent . The modified universal buffer series of Britton and Robinson [6] were used as hyrolysis media .

A Pye-Unicam Sp 8 – 100 spectrophotometer equipped with a thermostated cell holder $\pm$ (0.1°C) was used for the kinetic study .

Rate Measurements :

The hydrazone and the buffer were mixed at room temperature to keep the concentration of the hydrazone equal 5×10^{-5}M in the presence of 5% (v/v) solvent . The course of the reaction was followed for each solvent and each hydrazone , by measuring the decrease in the absorbance of the hydrazone at various times and at the maximum wavelength corresponding to each hydrazone .

X-BBH	λ max (nm)
X = H	295
m-CH_3	295
m-NO_2	280
m-OCH_3	292
m-C1	290

Results and Discussion

As founded previously [1] the rate of hydrolysis of X-BBH was found to be first order as indicated from the polt of $\ell n (A_t - A_\infty)$ versus time .

It can be shown from Table (1) that the rate constants of the hydrolysis of BBH and its derivatives are affected by the nature of the substituent as well as the nature of the solvent used . In fact , the electron releasing substituents stabilize the transition state and increase the values of the rate constants , meanwhile , the electron withdrawing substituents destabilize the transition state and decrease the values of the rate constants .

It can be noticed from Table (1) that for the same substituent , the rate constant increases with increasing the polarity of the medium .

The observation that the rate constant of DMSO is lower than in MeOH (although its dielectric constant is higher) , can be attributed to the fact that each dimethyl sulfoxide molecule coordinates with two water molecules by hydrogen bonding . [7]

The polt of σ , a substituent constant , and log k/k_o , for the hydrolysis of BBH and its derivatives in four different solvents , is shown in the Figure . A straight line is obtained with a slope representing a ρ value . This plot implies that as the solvent polarity decreases , the role of the substituent increases and ρ values increase , and this is consistent with Tokura's results . [4]

It can be noticed from Table (2) that the polarity of solvent increases with an increase in the percentage mole ratio of water . It means that 5 v % n – BuOH is the most polar aqueous medium among other aqueous media .

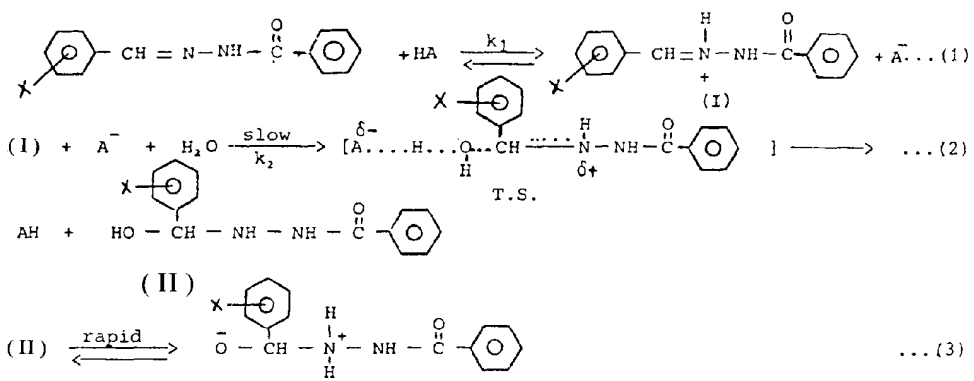
It is so interesting that the rates of hydrolysis of the hydrazones in DMSO – water follow the same trend ; i.e , similar to other hydroxylic solvents .

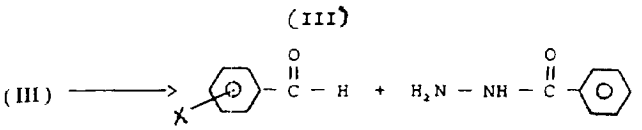
Table (2) shows that the polarity of the medium goes in the following order:

5 v% n – BuOH > 5 v% DMSO > 5 v% EtOH > v% MeOH .

Table (3) has shown [8] that as the percentage of water decreases , the dielectric constant values decrease .

The mechanism of hydrolysis of unsubstituted and substituted benzylidene benzoylhydrazones that has been postulated [9,10] is written as follows :





...(4)

It has been shown , from the previous mechanism , that the attack of water is involved in the rate determining step . Therefore , as the concentration of water increases there is a decrease in the partial positive charge on nitrogen in the transition state which causes a decrease in ρ values and hence , a decrease in the role of the substituent . This confirms the fact that as the solvent polarity increases , there is a decrease in ρ values and a decrease in the role of the substituent and vice versa .

Acknowledgement

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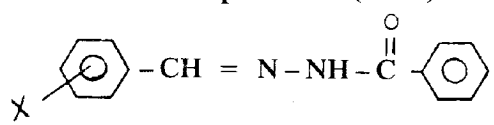
Figure :

A plot of log k/k$_o$ vs. σ for the hydrolysis of benzylidene benzoylhydrazones in four different solvents at pH = 1.92 (27°C) .

a : n-butyl alcohol
b : dimethyl sulfoxide
c : ethyl alcohol
d : methyl alcohol .

Table (1)

Rate constants of the hydrolysis of BBH and its derivatives and ρ values in various solvents at pH = 1.92 (27°C) .



Solvent	X=H 10^3 k/s^{-1}	X = m–NO_2 10^3.k/s^{-1}	X = m–CL 10^3.k/s^{-1}	X = m–CH_3 10^3.k/s^{-1}	X = m–OCH_3 10^3.k/s^{-1}	ρ
Methanol	3.50	1.40	2.00	4.20	2.60	–0.830
Ethanol	2.70	1.30	1.70	3.10	2.40	–0.600
Dimethyl Sulfoxide	2.44	1.20	1.97	2.60	2.20	–0.425
n-Butanol	1.88	1.20	1.55	2.20	1.70	–0.270

Table (2)

Percentage mole ratio of H_2O , ρ values for different solvent mixtures

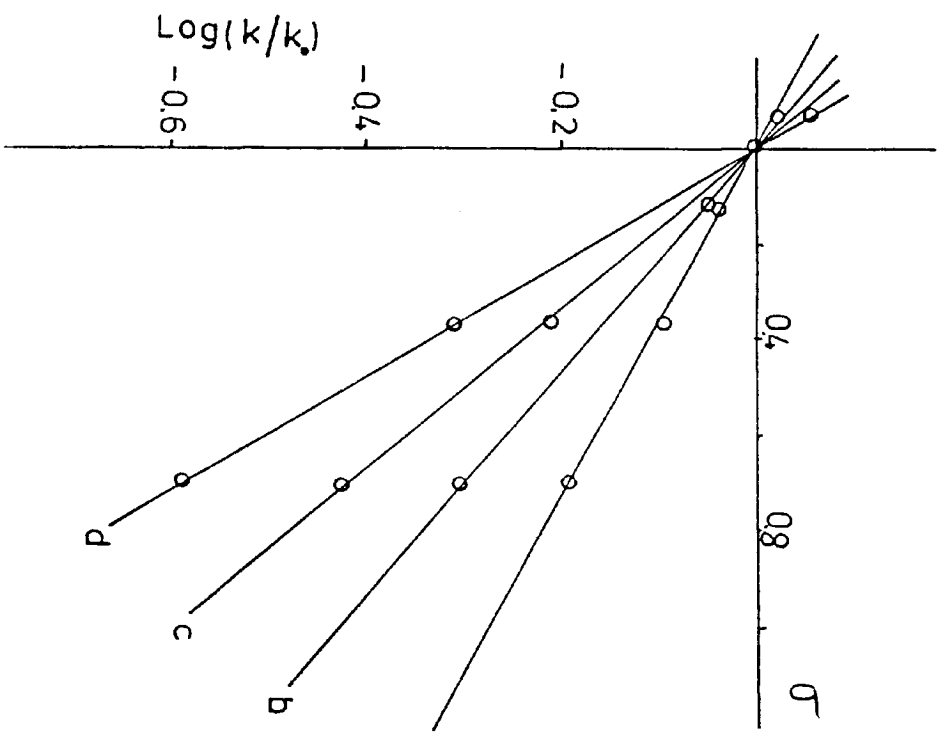
Solvent 5 v%	% mole ratio of H_2O	ρ
n-Butanol	98.97	−0.270
Dimethyl sulfoxide	98.68	−0.425
Ethanol	98.42	−0.600
Methanol	97.72	−0.830

Table (3)

Effect of percentage of alcohols on the dielectric constants of the aqueous media at room temperature[8] .

Solvent	v%	D
Methanol	20	71.50
	40	63.49
Ethanol	20	72.70
	40	66.50

Table (4)

Values of σ for the groups used in this study [11]

Substituent	σ_m
CH_3	-0.07
H	0.00
OCH_3	0.12
Cl	0.37
NO_2	0.71