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-SHORT COMMUNICATION-

THE ROLE OF SOLVENT ON THE KINETICS AND MECHANISM OF THE HYDROLYSIS OF SALICYLIDENE BENZOYL HYDRAZONE

BY

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ملخص

لقد تمت دراسة تاثير مذيبات مختلفة على ميكانيكية و كيناتيكية التميؤ لمركب سالسيليدين بنزول هايدرازون تحت درجات حرارة مختلفة (١٧-٤٥°مئوية) وباستخدام قياسات طيفية في مجال الاشعة فوق البنفسجية والمرئية .

ABSTRACT

The effect of various solvents on the kinetics and mechanism of the hydrolysis of Salicylidenebenzoyl hydrazone (SBH) has been studied at five different temperatures (17-45° C) using U.V. and visible spectrophotometry.In both protic and aprotic solvents, the hydrolysis rates follows first order kinetics. The role of solvent on the reaction rate, thermodynamic parameters and mechanism have been reported and discussed.

INTRODUCTION

In a previous work [1], the effect of molecular stucture and pH on the hydrolysis of substituted benzylidenebenzoyl hydrazones(SBH) was studied. As a continuation of this work, it was decided to investigate the effect of different solvents on the kinetics and mechanism of the hydrolysis of SBH.

EXPERIMENTAL

Reagents and apparatus:

The Salicylidenebenzoyl hydrazone was prepared and purified by the conventional method[2].Stock 0.01M solutions were prepared in pure solvent. The modified universal buffer series of Britton and Robinson[3] was used for the hydrolysis medium.The buffer consisted of a mixture of boric acid, phosporic acid and acetic acid.

A Pye-Unicam SP 8-100 spectrophotometer equipped with kinetic facilities and fitted with a thermostated cell holder $\pm(0.1^{\circ}C)$ was used for the kinetic study.

Rate Measurements:

After reaching the required temperature, the hydrazone and the buffer were mixed so as to keep the concentration of the hydrazone equal $5X10^{-5}M$ in the presence of 5% (V/V) solvent. The course of the reaction was then followed for each solvent, by measuring the decrease in the absorbance of the hydrazone at various times and at the maximum wavelength corresponding to 285 nm.

RESULTS AND DISCUSSION

The variation in absorbance with time for the hydrolysis of salicylidenebenzoyl hydrazone in different solvents is shown in Figure (1). It can be seen from Figure(1) that a good linear correlation was obtained when a plot of $\ln(A_t - A_\infty)$ versus time was performed(A_t is the obsorbance at time t and A_∞ is the absorbance at time infinity.This indicates that the hydrolysis of salicylidenebenzoyl hydrazone in 5% (V/V) solvent to buffer mixture is considered as first order kinetics. In all runs, the rate constant was obtained from the slope of the linear plot.

The effect of solvent nature on the rate constant of hydrolysis was studied and the results obtained are listed in Table (1). It can be seen fromn Table (1) that the rate constant, k, increases gradually by increasing the dielectric constant, D, of the protic solvents, whereas dimethyl sulphoxide does not follow this variation. On the other hand, Figure (2) shows a linear plot between log k and 1/D for the hydroxylic solvents with a deviation of the point corresponding to the formation of complexes between dimethyl sulphoxide and water. Yagil suggests that each dimethyl sulphoxide molecule coordinates with two water molecules by hydrogen bonding[4].

Figure (1): A plot of $\ln(A_t - A_\infty)$ vs. time for the hydrolysis of salicylidenebenzoyl hydrazone in different solvents at pH = 1.92(27°C).a,methanol; b,iso-propanol c,dimethyl sulphoxide; d,trifluoro ethanol e,t-amyl alcohol.

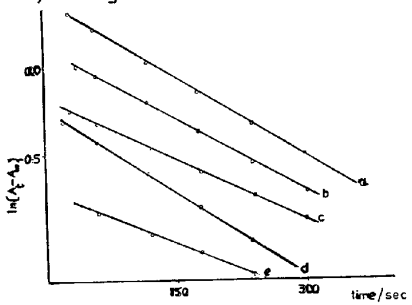


Figure (2): A plot of log k vs. $\frac{1}{D}$ at pH 1.92 and 27°C.

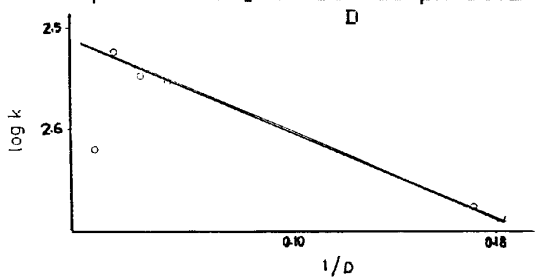


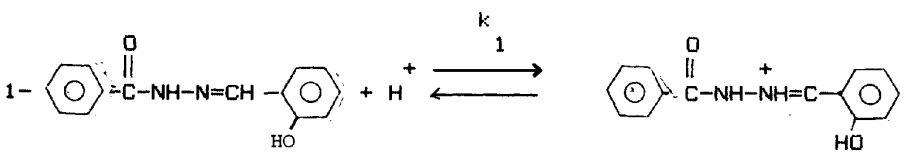
Table (1): Effect of solvent on the rate constant of the hydrolysis of salicylidenebenzoyl hydrazone at pH 1.92 (27°C)

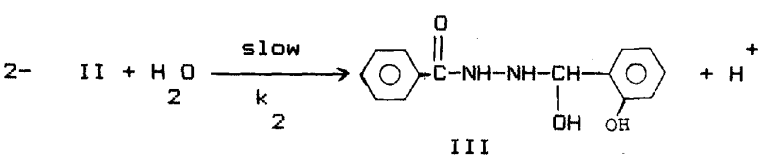
Solvent	$10^3 .k\ (sec^{-1})$	dielectric constant
tri-fluouro ethanol	3.4	——
methanol	3.0	31.6
ethanol	2.6	24.3
iso-propanol	2.4	19.5
t-amyl alchol	2.1	5.8
dimethyl sulphoxide	2.4	46.5

From Table (1),it is possible to conclude that the effect of hydroxylic solvents on the rate constant reflects the difference in solvation proporties of the solvents. It is known that the polar solvent molecules stablize the polar transition state more effeciently than the non-polar one [5].

The different parameters of activation ($\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$)for the kinetic hydrolysis of the salicylidenebenzoyl hydrazone with different solvents are presented in Table (2). The parameters indicate that the hydrolysis is enhanced with increasing the dielectric constant of the hydroxylic solvents. The highest $\Delta S^{\#}$ value corresponding to trifluoroethanol compared to other solvents, indicates a less random distribution of solvent molecules around the activated complex. Moreover, Table (2) shows that the increase in the rate of hydrolysis and the decrease in the energy of activation with changing the solvent can be written in the following sequence: triflouro-ethanol > methanol > ethanol > isopropanol > ter-amyl alcohol .

The mechanism of hydrolysis of unsubstituted and substituted benzylidene benzoyl hydrazones has been postulated previously [1]. Therefore, the mechanism of hydrolysis of salicyldiene benzoyl hydrazone can be written as follows :





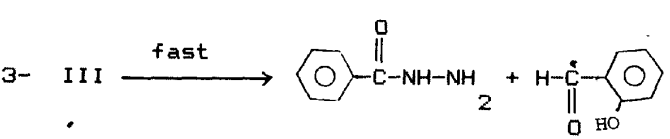


Figure (3): A plot of $\Delta H^{\#}$ vs. $-\Delta s^{\#}$ for the hydrolytic decomposition of salicylidenebenzoyl hydrazone at pH 1.92 (27°C).

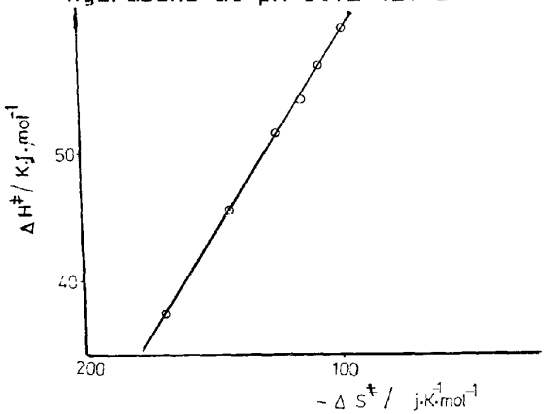


Table (2): The effect of solvent nature on the secondary rate constants, activation energies and thermodynamic parameters for the hydrolysis of salicylidenebenzoylhydrazone at pH 1.92(27°C)

Solvent	k_s $M^{-1}.S^{-1}$	E_a KJ.mol^{-1}	$-\Delta G^{\#}$ KJ/mol	$\Delta H^{\#}$ KJ/mol	$-\Delta S^{\#}$ J.mol^{-1}.K^{-1}
tri-fluoro ethanol	0.26	40	87.7	37.4	168
methanol	0.23	48	88.0	45.4	142
ethanol	0.20	57	88.3	54.1	114
iso-propanol	0.19	59	88.5	56.8	106
t-amyl alcohol	0.16	62	88.9	59.9	97
dimethyl sulphoxide.	0.18	54	88.5	51.7	123

Table(3):Effect of % ethanol in the solvent - buffer mixture on values of first and second rate constants for the hydrolysis of salicylidene benzoyl hydrazone at pH 1.92 (20°C).

% ethanol	$10^{3}.K_{-1}$ S	k_{s} $S^{-1}\ M^{-1}$
5.0	2.2	0.17
10.0	1.6	0.12
20.0	0.8	0.07
30.0	0.7	0.05
40.0	0.4	0.03

In this study, the following observations led to support the assumption that the attack of water molecules on species II is the rate determining step:

1) Table (1) shows that the rate of hydrolysis of salicyliden-benzoyl hydrozone in ethanol is higher than in dimethyl sulphoxide. This was attributed to the decrease in the conc-entration of available water molecules around the activated complex as a result of the complexation with dimethyl sulphoxide .

2) It was also found that changing the %(V/V) solvent in the solvent/buffer mixture affects the rate of hydrolysis as shown in Table (3). This indicates that the value of the rate constant is dependent on the percentage of water.

The plot of enthalpies of activation and entropies for the hydrolysis of salicylidenbenzoyl hydrozone in protic and apro-tic solvents is shown in Figure (3). A straight line is obtain-ed with a slope (isokinetic temperature) of 310 K. The linear plot obtained in Figure 3 implies that the salicylidenebenzoyl hydrozone hydrolysed by the same mechanism in the investigated solvents[6-9].

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