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Neighbouring Group Participation in Micellar Catalysed Hydrolysis of Schiff Bases

K.R. SANKARAN* and R. LAKSHMI
Department of Chemistry
Annamalai University, Annamalainagar-608 002, India

The rate of alkaline hydrolysis of Schiff bases in 30% aq. acetonitrile exhibits second order kinetics—first order in each reactant. The presence of neighbouring hydroxyl group in the benzaldehyde portion enhances the rate of hydrolysis, probably due to stabilisation of transition state. Such a neighbouring group effect seems to be most pronounced in anionic micelles of NaLS than in cationic micelles of CTAB. The greater Hammet negative reaction constant, P, in NaLS medium (–0.96) than in CTAB (p = –0.59) is suggestive of greater electronic influence of substituents on the rate of hydrolysis in NaLS than in CTAB.

INTRODUCTION

As the formation and decomposition of Schiff base linkages play an important role in enzymatic reactions the mechanism for the formation of several Schiff bases and kinetic investigations has been dealt with in detail in the past.[1–9] Above pH 9, the rate of the reaction has been found to be pH independent and the rate limiting step is the attack of water on the free Schiff base or of hydroxide ion on its conjugative acid.

In spite of exhaustive study of the hydrolysis of Schiff bases, the influence of neighbouring hydroxyl groups or substituents on the rate of hydrolysis of Schiff bases in the absence and presence of cationic and anionic detergents has not formed part of earlier works. Hence the present study on the influence of neighbouring hydroxyl groups on the rate of hydrolysis of Schiff bases has been undertaken and from the influence of substituents on the rate of hydrolysis, a suitable mechanistic scheme can be proposed.

EXPERIMENTAL

The respective Schiff bases of benzaldehyde or salicylaldehyde were prepared by the following procedure.[10] 0.10 mol of aniline was added with efficient stirring to 0.10 mol of benzaldehyde in a 500 mL flask. The mixture was set aside for 15 minutes and then poured into 95% ethanol. Crystallisation started after a few minutes and completed by cooling in ice. The product was filtered and dried in vacuum.

The reactions were carried out under pseudo first order conditions in 30% aq. acetonitrile at 30 ± 0.2°C at constant ionic strength maintained by using 0.18 mol dm^{-3} NaCl. The reactions were followed by measuring the decrease in absorbance for Schiff bases at 350 nm using a UVIDEC-340 spectrophotometer. From the decrease in absorbance measured, the specific rates (k_1 in S^{-1}) were calculated using integrated rate equation. These values agree with those obtained from the slopes of linear graphs of logarithm of change in absorbance versus time.

The pK_a values determined following the procedure of Cordes and Jencks[2b] for benzilidene aniline were 9.6, 9.4 and 9.8 in aqueous medium, in NaLS of concentration 8.0×10^{-3} mol dm^{-3} and in CTAB of concentration 6.0×10^{-4} mol dm^{-3} respectively. There is not much change in pK_a value in detergent solution for salicylidene aniline also (11.4, 11.2 and 11.8 in aqueous, in NaLS of concentration 8.0×10^{-3} mol dm^{-3} and in CTAB of concentration 6.0×10^{-4} mol dm^{-3} respectively). The product of the reaction is the respective aldehyde.

RESULTS AND DISCUSSION

The kinetics of hydrolysis of Schiff bases, benzalidene aniline, *o*-hydroxy benzalidene aniline and some substituted aniline derivatives have been studied in 30% aq. acetonitrile medium with 0.18 mol dm^{-3} OH^- concentration at 30 ± 0.2°C. The ionic strength of the medium is maintained by using 0.18 mol dm^{-3} NaCl solution.

The reaction exhibits total second order kinetics, first order with respect to each reactant. The rate of alkaline hydrolysis of *o*-hydroxybenzalidene aniline is affected by change in either NaLS or CTAB concentration. The rate constant varies from 0.96×10^{-3} s^{-1} to 2.74×10^{-3} s^{-1} when [NaLS] is varied from 0.40×10^{-3} mol dm^{-3} to 1.20×10^{-3} mol dm^{-3} whereas the rate constant changes from 1.45×10^{-3} mol dm^{-3} to 2.87×10^{-3} mol dm^{-3} when CTAB is varied from 1.00×10^{-3} mol dm^{-3} to 2.00×10^{-3} mol dm^{-3}. Similar results have been obtained in the hydrolysis of benzalidene aniline at pH 9.0.[8, 9]

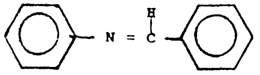
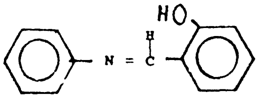
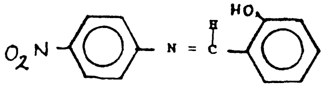
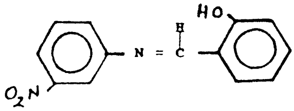
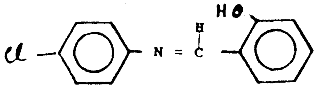
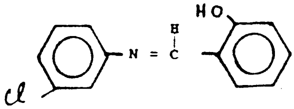
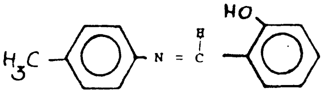
Table-1 summarises the specific rates for the alkaline hydrolyses of Schiff bases, benzalidene aniline, *o*-hydroxybenzalidene aniline and Schiff bases with substituent at aniline moiety both in the absence and presence of NaLS and CTAB. The intoduction of an *ortho*-hydroxyl group adjacent to —CH=N—increases the rate of hydrolysis by 5-fold even in the absence of detergent. The presence of CTAB enhances the rate of *o*-hydrolysis benzalidene aniline markedly, probably due to stabilisation of tetrahedral intermediate. But the rate enhancement due to the presence of *o*-hydroxyl group is more marked in NaLS, probably due to greater solubilization of Schiff base in this medium. pK_a of the Schiff bases remains almost the same in this medium. The electron donating group like *p*-CH_3 on aniline moiety enhances the rate significantly in NaLS while electron-withdrawing groups like *p*-NO_2 retard the rate more in NaLS suggesting that polar influence on the rate of hydrolysis is significant in the presence of NaLS. When Hammett correlations were attempted with logarithm of K_2 versus Hammett substituent constants[6] fairly good linear graphs were obtained in the presence

CTAB with reaction constant 'p' equal to –0.59. In the absence of detergent and in the presence of NaLS, the reaction constants calculated are –0.87 and –0.96 respectively; such a negative 'p' value suggests an electron-deficient transition state which may be more stabilised by anionic micelle formed by NaLS.

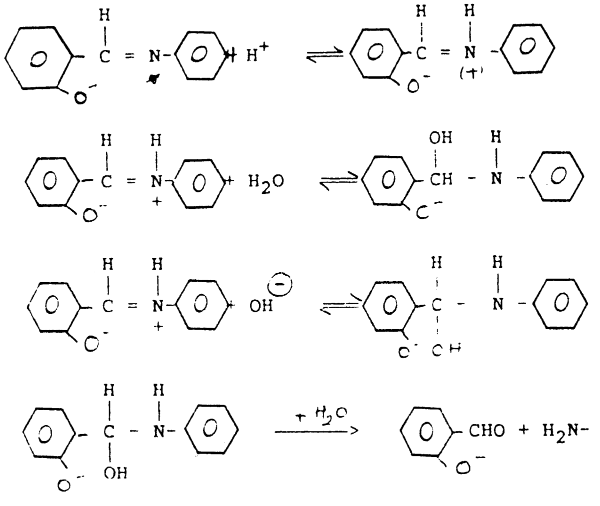
TABLE-1

SUBSTITUENT EFFECT ON THE RATE OF HYDROLYSIS OF SCHIFF BASE IN THE ABSENCE AND PRESENCE OF CATIONIC (CTAB) AND ANIONIC MECELLES (NaLS)

[SB] = 1.2×10^{-3} mol dm^{-3}; [OH$^-$] = 0.18 mol dm^{-3}; Temp. = 30 ± 0.2°C

	Compound [SB]	$10^4 k_1$ s^{-1} (in the absence of detergent)	$10^4 k_1$ s^{-1} (in the presence of CTAB)	$10^4 k_1$ s^{-1} (in the presence of NaLS)
		1.58	5.10	9.20
A		9.20	18.40	27.40
B		3.40	7.52	9.90
C		2.89	8.32	8.45
D		17.40	18.70	32.10
E		2.60	14.20	28.500
F		25.80	29.30	88.20

In the mechanistic Scheme proposed for the alkaline hydrolysis of schiff base, in very highly alkaline,



(1)

(2)

(3)

(4)

the step (2) or (3) is probably rate-limiting. Such a step will involve an electron-deficient carbon which seems to be more stabilised by neighbouring phenoxide group in NaLS than in CTAB.

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