

Effect of Surfactants upon the Acid Catalyzed Hydrolysis of Phenyl Urea

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The kinetics of acidic hydrolysis of phenyl urea in micellar media have been studied. The cationic (cetyl trimethyl ammonium bromide, cetyl pyridinium chloride), anionic (sodium lauryl sulphate) and non-ionic (Triton -X-100, Brij-35) surfactants have been used. The results indicate that the presence of micelles enhance the rate of reaction. Kinetic studies show that the reaction obeyed first order kinetics. The rate surfactant profiles can be explained well by pseudo phase ion exchange model.

Key Words: Surfactants, Hydrolysis, Micellar media, Phenyl urea.

INTRODUCTION

The micellar catalysis of organic reaction has been widely studied¹⁻³. The hydrolysis of carboxylic acid esters and amides in acid mainly proceeds according to an addition-elimination mechanism^{4,5}. Surprisingly very limited work has been reported on micellar catalysis of hydrolysis of urea specially phenyl urea. In the present investigation, the acidic hydrolysis of phenyl urea in presence of surfactant cationic cetyl trimethyl ammonium bromide (CTAB), cetyl pyridinium chloride (CPC), anionic sodium lauryl sulphate (SLS), Non-ionic Triton -X -100 and Brij-35 in acidic water methanol solutions (9:1) at 80°C in 0.01 M H₂SO₄ is carried out.

EXPERIMENTAL

Phenyl urea was used as received (97.5 %, Lancaster, UK). Rate constants were measured by means of UV spectroscopy in water-methanol (9:1) mixture on a UV 2100 Scanning Chemito make Spectrophotometer. The UV Scanning spectrophotometer using 1 cm path length quartz cuvettes . The concentration of phenyl urea was 4.9×10^{-4} mol L⁻¹. The reaction mixture was thermo stated at fixed temperatures at 70, 80 and 90°C (MacMake automatic thermostat). The acid strength 0.01 M H₂SO₄ was used throughout the experiment. Different strength of surfactant like

CTAB (E. Merck) CPC, Brij-35, SLS, TX-100 (all purchased from SD Fine Chem. Co., India) were used in different increasing molar concentration. After a definite time interval absorbance were recorded by means of UV-Vis spectrophotometer. The acid hydrolysis of phenyl urea follows the pseudo-phase first order reaction rates.

RESULTS AND DISCUSSION

In the acid hydrolysis of phenyl urea as suggested by O'Connor *et al.*^{7,8} the elimination of the amine from the unprotonated or n-protonated urea is promoted by an intermolecular proton transfer *via* water. The N-protonated besides the O-protonated is already considered to be possible in relatively weakly acid solution.

The rate of hydrolysis of phenyl urea is not directly proportional to the hydronium ion concentration, but rises with the acid strength only in solution of low acidity, whereas it passes through a maximum and decreases again in stronger acid solutions in accordance with the results of O'Connor *et al.*^{7,8}.

The pseudo-first order rate constants ($K\psi$) in surfactant environment (CTAB, CPC, SLS, Brij-35 and TX-100) have been investigated, $K\psi$ increases with increasing concentration of the surfactant (Table-1, Fig. 1) owing to show low solubility of phenyl urea in reaction mixture. The cationic anionic as well as non-ionic micelle enhanced the rate of hydrolysis, but in case of TX-100 has no significant effect. The micellar catalysis effect has been found to following order: CPC > Brij-35 > CTAB and SLS. This rate acceleration in micellar solution arises from substrate in the micellar phase and in the bulk phase, and the distribution of the substrate between these two phases. Basically, these rate effects can be attributed to electrostatic and hydrophobic interaction between the substrate and the surfactant aggregate. Micellar effects upon reaction rates are generally analyzed in terms of the pseudo phase ion exchange model. Despite its short out comings, it fits a great deal of data^{9,10}. The variation of the rate constant with surfactant is generally treated on the assumption that substrate 'S' is distributed between the aqueous and micellar pseudo-phases, designated by subscripts 'W' and 'M', respectively **Scheme-1** and can react in each pseudo-phase with the first order rate constants being k_w and k_M .

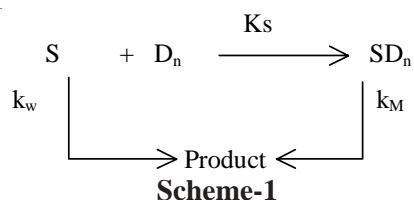


TABLE-1
EFFECT OF SURFACTANT UPON THE RATE CONSTANT OF
PHENYL UREA AT 0.01M AT 80°C

$M \times 10^4$	CTAB $\times 10^4$	CPC $\times 10^4$	SLS $\times 10^4$	Brij-35 $\times 10^4$
0.0	5.36	5.36	5.36	5.36
0.27	5.39		5.35	30
0.57	5.95	6.65		13
0.90	6.25	6.69		22
1.6	7.10	7.7	5.33	
1.8	7.15	8.1		170
2.7	16	40	5.75	
5.4	26.03	201	8.6	
6.9	35.02		9.8	
10.9	120		11.8	
13.7			12.0	

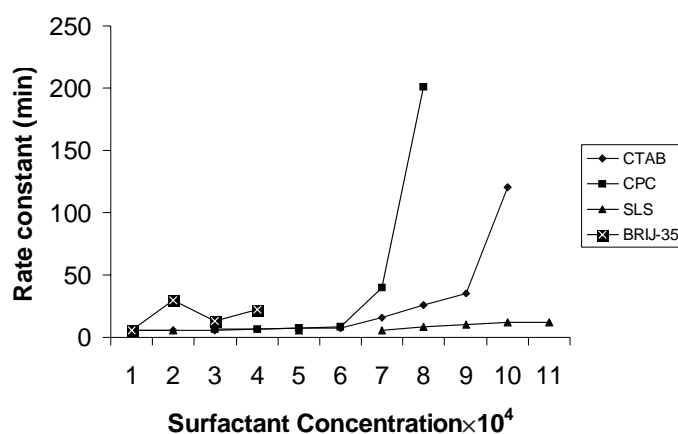


Fig. 1. Effect of surfactant upon acidic hydrolysis of phenyl urea

The concentration of micellized surfactant is designed and its concentration is that of the total concentration (D) less that of monomeric surfactant, which will be approximately that of the critical micelle concentration under kinetic conditions (eq.1)

$$D_n = [D] - \text{CMC} \quad (1)$$

K_s is the equilibrium for substrate binding. This model (**Scheme-1**) leads to the relationship:

$$\frac{1}{K_w - K_\psi} = \frac{1}{K_w - K_m} + \frac{1}{K_w - K_m} \frac{N}{K_s([D_T] - \text{CMC})}$$

where, K_ψ is the observed pseudo-first-rate constant, N is the micellar aggregation number and K_s represents substrate-binding constant. By plotting $1/(K_w - K_\psi)$ against $1/[D_T] - \text{CMC}$ it is possible to calculate K_m and K_s by correlation rate data analysis (Table-2). The CMC value of the CTAB,

CPC, SLS were taken from literature¹¹ and for Brij-35 from literature¹². The quantitative explanation offered above, for the observed enhancement, would mean that the reaction occurs mostly in the micelles phase. The rate is enhanced 20-fold in presence of CTAB, 35-fold in presence of CPC, 2-fold in presence of SLS and 30-fold in presence of Brij-35. The catalytic effect of non-ionic surfactant (TX -100) on the reaction seems to be less significant.

TABLE-2
CORRELATION RATE DATA FOR PHENYL UREA

Surfactant	$D_n \text{ range} \times 10^{-4}$	K_s/N	Correlation Coefficients
CTAB	0.27 - 1.8	138.8	0.962
CPC	0.57 - 2.7	18.8	0.998
SLS	5.40 - 10.9	2500.0	0.926
Brij-35	0.27 - 1.8	307.6	0.924

Micellar enhancement of bimolecular reactions is due to the increased reactant concentration in the micellar phase. The present result indicates that the reaction takes place between the substrate solubilized into a micelles and the nucleophile residing at the Stern layer of the micelle, without being bound strongly to it the micelles-water interface.

TABLE-3
ACTIVATION PARAMETERS FOR ACIDIC HYDROLYSIS OF
PHENYL UREA IN MICELLAR MEDIA

Surfactant conc. mol/L (10^{-4})	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger	Correlation Coefficient
CTAB (10.9)	125	105	93.5	0.960
CPC (5.5)	156	215	91.5	0.950
SLS (13.8)	25.5	172	76.6	0.920
Brij-35 (0.9)	368.8	809	127.5	0.990

ΔH^\ddagger and ΔG^\ddagger are KJ mol^{-1} ; ΔS^\ddagger in $\text{KJ}^{-1} \text{mol}^{-1}$

These values are fairly typical for the A-2 reactions. Mainly the three principal activation parameters, ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger are of little values as a criterion of reaction mechanism in solution. Here ΔS^\ddagger may be used as differentiating between A-1 and A-2 mechanism. However, two particulate A-1 and A-2 mechanisms the binding constant of micelles can play active role in reaction mechanism. Hence according to different models such as PPIE, gives high binding constant specially with SLS (Table-2). These values and binding constant prove that reaction mechanism has been performed after micellization. It is well known that micellization process of any organic reaction happened after CMC. It means that the loss of translational and rotational freedom of the attacking water molecule in transition state

which leads to positive contribution to ΔS^\ddagger therefore these values shows that reaction takes place A-1 mechanism of pseudo first order kinetics.

In the overall view of activation parameters for the substrate phenyl urea at 70, 80 and 90°C in CTAB, CPC (both are cationic), SLS (anionic) and Brij-35 (non-ionic) gives ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger values increasing CTAB, CPC, SLS, Brij-35 gradually with high correlation coefficient. From the Table-3, one can concluded that Brij-35 given high values for ΔH^\ddagger , ΔS^\ddagger , ΔG^\ddagger in comparison to CTAB, CPC and SLS. It seems that in non-ionic the reaction becomes smooth with high free energy and correlation coefficient values.

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