

Kinetic Study of Acidic Hydrolysis of Carboxylate Ester with Hydroxamet Ions in Micellar Assemblies

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In present investigations, acid hydrolysis reaction represent the effect of nucleophile, surfactant and temperature on the specific condition. Hydrolysis of carboxylate ester (4-nitrophenylacetate) with hydroxamet ions as nucleophile (acetylhydroxamic acid and salicylhydroxamic acid) in presence of surfactant cationic, anionic and non-ionic (cetyl trimethylammonium bromide (CTAB), sodium lauryl sulphate (SLS) and Brij-35) at 27 and 40 °C. The resultant data show the variation of acid concentration effect the reaction rate and nucleophile represent the various effects in the reaction medium. The various surfactant resultant data represent the order of reaction rate CTAB > SLS > Brij-35 and reaction rate is increases by the increasing of reaction temperature.

Keywords: Kinetic hydrolysis, Surfactants, 4-Nitrophenyl acetate, Acetylhydroxamic acid, Salicylhydroxamic acid.

INTRODUCTION

In present years, there has been a regeneration of interest in the study of acid catalysis for an assortment of reactions mostly in concentrated acid solutions, where due to non-ideal behaviours, thermodynamic laws show large deviations. The area of acid catalysis [1-7] has requisite renewed significance mainly in the area of theoretical chemistry.

The hydrolysis of carboxylate ester useful for the investigation of anthropogenic organic chemicals in the environment both biotic and abiotic chemicals transformations have effect under environmental conditions. For most abiotic environmental processes by which pollutant are altered hydrolysis, photolysis, oxidation and reduction. A major pathway for alteration of organic esters in aquatic environment is hydrolysis. Hydrolysis reactions are generally sensitive to a variety of catalytic influences specific acid and base catalysis, metal oxide surface catalysis and metal ion catalysis [8,9]. Hydrolysis reaction with water is generally the most important reaction for molecules susceptible to nucleophile attack. In hydrolysis of carboxylate ester may process by a number of different mechanisms depending on the substrate structure the pH and presence of catalyzing specified [10-12].

Toxic chemicals are used as a pesticide, insecticides and chemical warfare agent. Such as methyl parathion, parathion,

paraoxon, *etc.* are some of the most frequently used pesticides in agriculture. These esters are effective acetylcholinesterase and butyrylcholinesterase inhibitors. Because of their biological and environmental signify impact, there degradation has been extensively investigated using different hydrolyzing nucleophile [13-21]. Nucleophilic hydrolysis and oxidation are the mostly favoured reaction to detoxify them. Nucleophiles have been extensively employed as potent electrolyzing agent for organized assembly and biomimetic models. Micelles and other associated colloid system act as self assemble micro-reactor, concentration or separating and diluting reactants of chemical reactions. Most of the catalytic processes proceed with the attack of nucleophile on the acyl carbon and phosphate group. Therefore, such processes are potentiated by performing the reaction in aggregates such as micelles or vesicles which assist in bringing together nucleophilic reagent and hydrophobic substrate. The aqueous surface dispersion such as micelles, micro-emulsions, vesicles, *etc.* together with the ability to maintain the rate enhancement of electrolytic reaction. The nucleophile like hydroxamate ions, hydroxamic acid and different type of surfactant have been applied for reaction system. In the present study, we have investigated nucleophilic catalysis of carboxylate ester hydrolysis in acidic, anionic, non-ionic cationic micellar media.

EXPERIMENTAL

The ester (4-nitrophenyl acetate), nucleophiles acetylhydroxamic acid (AHA), salicylhydroxamic acid (SHA) and surfactant cetyl trimethylammonium bromide (CTAB), sodium lauryl sulphate (SLS) and Brij-35 were purchased from Sigma Aldrich. Borax buffer and NaOH were purchased from SD Fine Chemicals, Mumbai, India. All the solutions were prepared in ideal conditions for the kinetic study of ester. Electrical conductivity was measured by using CM ISO Elico, India conductivity meter equipped with CD-06 platinum conductance electrode in $27 \pm 0.1^\circ\text{C}$. The pK_a of nucleophile were determined by pH metrically using Pico+LabIndia. For the kinetic study, Shimadzu UV-1601PC Japan spectrophotometer is employed for observing the appearance of living *p*-nitrophenoxide ion at 400 nm. Borax buffer was used (pH 7.7).

Detection method: The hydrolysis of ester in presence of nucleophile was measured with increasing the absorbance of *p*-nitrophenoxide ion at 400 nm. The absorbance/time results fit the first order rate equation in $\ln [(A_0 - A_\infty)/(A - A_\infty)] = kt$. The hydrolysis of 4-nitrophenyl acetate has been carried out with nucleophile acetylhydroxamic acid and salicylhydroxamic acid in presence of HCl buffer and micellar medium. The concentration of ester was always maintained at 1.0×10^{-4} mol dm^{-3} in all kinetic measurements.

RESULTS AND DISCUSSION

Effect of acid: Acid hydrolysis of 4-nitrophenyl acetate has been performed in the presence of nucleophile in variation of HCl concentration. For this reaction, ester concentration maintained (1.0×10^{-4} M) surfactant (1.0×10^{-3} M), nucleophile (1.0×10^{-3} M) and the variation of HCl concentration from 0.1 to 5.5 mol dm^{-3} used. The pseudo first-order rate constant are summarized in Table-1. Kinetics rate data for this illustrated reaction protocol showed the rate of hydrolysis increased in acidic medium upto 3.5 M HCl and further ascended the acidity results in decrease of the reaction rate. Moreover, the results show that the reactivity of salicylhydroxamic acid was more than acetylhydroxamic acid in same condition and both nucleophile higher rates at 3.5 M HCl above this concentration the rate was decreased. This result was obtained due to the formation conjugated acid species. The conjugated acid catalyzed rate of reaction showed to have positive ionic strength in high acidic concentration and in nucleophilic concentration, the same is predictable to be less.

Effect of nucleophile: Kinetic rate data of substrate (4-nitrophenyl acetate) by varying the nucleophile concentration in the presence of cationic surfactant in acidic medium. For the reaction protocol, surfactant concentration (1.0×10^{-3} M) HCl = 0.1 M, temp 27°C and nucleophilic concentrations vary from 1.5 to 7.0 Mm. Kinetic rate results (Table-2) show the pseudo first order rate of reaction in presence and absence of surfactant (Fig. 1). The nucleophilic reactivity in micelle depends upon the binding of substrate interaction with anionic nucleophile [22]. The rate increased in micellar medium is due to the favourable electrostatic attraction of the positive charged head group of cationic micelles with the negatively charged anions of nucleophiles [23]. Thus, the rate of reaction increased with increasing the concentration of nucleophiles. It is also observed that the k_{obs} value for the reaction of 4-nitrophenyl acetate increases with the increasing concentration of salicylhydroxamic acid and acetylhydroxamic acid, in presence and absence of cationic surfactant. The variation of k_{obs} values of the reaction depend on the head group of surfactant, for this fact the presence of cationic surfactant was found to have high rate of reaction. The high k_{obs} value indicates that the surfactant increases the aggregation numbers mainly due to the increase in the electrical surface potential of micelles and partially due to an increase of hydrophobicity of palisade layer of micelle.

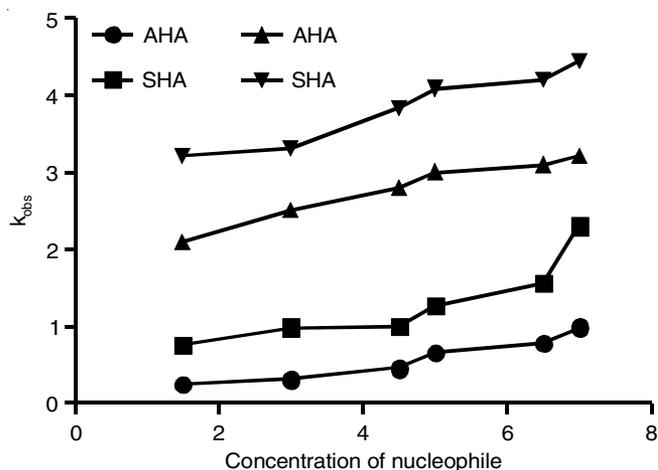


Fig. 1. Effect of nucleophile in presence and absence of surfactant

Effect of surfactant: The rate of kinetics of the hydrolysis of 4-nitrophenyl acetate by nucleophiles with varying concentrations of different surfactants at 27 and 40°C . The kinetic

TABLE-1
KINETICS DATA FOR THE EFFECT OF ACIDIC MEDIUM FOR THE HYDROLYSIS OF CARBOXYLATE ESTER WITH NUCLEOPHILE (AHA & SHA) IN DIFFERENT SURFACTANTS

HCl (mol dm^{-3})	pH	$10^5 k_{\text{obs}} (\text{s}^{-1})$					
		AHA			SHA		
		CTAB	SLS	Brij 35	CTAB	SLS	Brij 35
0.1	1.00	1.81	1.78	1.60	2.41	2.01	1.82
0.2	0.70	1.90	1.80	1.70	2.46	2.08	1.88
0.3	0.55	2.10	2.02	1.98	2.55	2.11	1.91
0.4	0.45	2.30	2.09	2.01	2.61	2.15	2.06
0.5	0.30	2.36	2.12	2.09	2.66	2.21	2.90
0.8	0.15	2.45	2.18	2.16	2.70	2.32	2.10
1.0	0.00	—	—	—	—	—	—

Reaction condition [PNPA] = (1.6×10^{-4} M), [Nu] = (1.6×10^{-3} M), [Surfactant] = (1.0×10^{-3} M), [Temp] = 27°C .

TABLE-3
KINETICS DATA FOR THE HYDROLYSIS OF CARBOXYLATE ESTER WITH
NUCLEOPHILE IN VARIOUS CONCENTRATIONS OF SURFACTANTS

Surf. (mM)	$10^5 k_{\text{obs}} (\text{s}^{-1})$											
	AHA						SHA					
	CTAB		SLS		Brij-35		CTAB		SLS		Brij-35	
	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C	27 °C	40 °C
0.0	0.25	0.50	0.25	0.50	0.25	0.50	0.78	1.0	0.78	1.0	0.78	1.0
1.0	1.81	3.21	1.98	3.09	1.60	3.01	2.41	4.99	2.01	4.02	1.82	3.98
2.0	2.48	4.50	2.31	4.36	2.11	4.22	4.11	8.23	3.84	7.32	3.59	7.20
3.0	3.58	6.89	3.32	6.60	2.78	5.11	5.01	9.98	4.64	9.50	4.21	8.40
10	2.41	4.85	2.11	4.24	1.99	2.01	4.21	8.44	4.10	8.10	4.00	8.10
20	–	–	–	–	–	–	3.79	6.97	3.34	6.60	3.01	6.10

Reaction condition [PNPA] = $(1.6 \times 10^{-4} \text{ M})$, [Nu] = $(1.6 \times 10^{-3} \text{ M})$.

TABLE-2
EFFECT OF NUCLEOPHILE FOR THE HYDROLYSIS OF
CARBOXYLATE ESTER WITH NUCLEOPHILES IN
PRESENCE AND ABSENCE OF SURFACTANTS

Nu. (mM)	$10^5 k_{\text{obs}} (\text{s}^{-1})$			
	Nil		Surfactant (CTAB)	
	AHA	SHA	AHA	SHA
1.5	0.24	0.75	2.10	3.21
3.0	0.30	0.98	2.5	3.30
4.5	0.45	1.0	2.8	3.85
5.0	0.65	1.25	3.0	4.10
6.5	0.78	1.55	3.10	4.21
7.0	0.98	2.30	3.22	4.45

Reaction condition [PNPA] = $(1.6 \times 10^{-4} \text{ M})$, [Surfactant] = $(1.0 \times 10^{-3} \text{ M})$, [Temp.] = 27 °C.

rate data of substrate (4-nitrophenyl acetate) at various concentration of cationic, anionic and non-ionic surfactant are summarized in Table-3. The results show that the cationic, anionic and non-ionic surfactant play significant role for the hydrolysis of 4-nitrophenyl acetate with both nucleophiles. The nucleophilic reactivity in micellar medium depends upon the binding of surfactant head group with anionic nucleophile [24]. The rate of reaction was high and increases in micellar medium as compared to aqueous medium due to the favourable electrostatics attraction of surfactant with nucleophile [25]. The kinetic rate initially increases with increasing surfactant concentrations. The k_{obs} values for the reaction with salicylhydroxamic acid and acetylhydroxamic acid increased with increase in the concentration of CTAB, SLS and Brij-35 upto 3.0 Mm and then decreases. However, kinetic rate of CTAB is more reactive than SLS and Brij-35. The reason for the increasing k_{obs} value with associated with the increasing of surfactant concentration which resulted in the increase aggregating number of micelle and led to increase in electrical surface potential of the micelle and also the polarity due to increase in hydrophobicity of the palisade layer of micelles. From the resultant data of kinetic study, the reactivity order of surfactant is found to be CTAB > SLS > Brij-35.

Conclusion

The acid hydrolysis of 4-nitrophenyl acetate decreases in rates at higher acidity, due to the hydrophobicity of palisade layer of micelles. The experimental data showed that salicylhydroxamic acid has higher rate of reactions as compared with acetylhydroxamic acid in acidic micellar media. In this study

we report, that raising the concentration of nucleophile increase the reaction rate in presence and absence of surfactant. In the presence of surfactant reaction rate higher than absence of surfactant on both nucleophiles. The surfactant concentration initially increases the rate of reaction due to interaction surfactant and surface and after the saturation, the rate suddenly decreases. The increase in temperature also effect the reaction rate.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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