KINETIC STUDY OF THE CARBOXYLATE ESTER WITH HYDROXAMATE ION IN CATIONIC AND NON-IONIC MICROEMULSION SYSTEM

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Abstract

In current year a kinetic study of nucleophilic substitution reaction in microemulsion has witnessed a significant growth of interest. The kinetic study of P-nitrophenyl acetate with Hydroxamate ion (SHA) has been studied in cationic and non-ionic microemulsions prepared from combination by weight percent of cationic (CTAB and CPC), non-ionic surfactant (Triton x-100), co-surfactant n-butanol, oil-phase n-hexane and water. Conductivity behaviour depends mainly on the weight percent and composition of aqueous phase. In the room temperature (27°C) pseudo first-order rate constant increase with the increasing weight percentage of water (W_0), comparative above room temperature (40°C) the reaction rate is very fast. Kinetic model of nucleophilic substitution reactions, have been discussed.

1. INTRODUCTION

Hydroxamate ions are α-effect nucleophiles, whose reactivity is higher than that predicted by Bronsted relations between nucleophilicity and basicity.[1-3] The chemistry of hydroxamic acids has received considerable attention in view of their pharmacological, toxicological and pathological properties. Antibacterial antifungal, antitumor and ant-inflammatory activities of hydroxamic acid are connected with their ability to inhibit various enzymes.[4-16] Structural chemistry of hydroxamic acid contains still unresolved problems, like the reason for their relatively high acidity and the structure of corresponding anions .[17] The α-nucleophiles exhibit an enhanced reactivity toward a variety of electrophilic centers in comparison to normal nucleophiles. They have proved to be very efficient in promoting acyl, phosphoryl and sulfuryl transfer processes.[18] Extensive efforts using α-nucleophiles have been made for the detoxification of organophosphorus compounds.[19-27] Organophosphorus compounds, which are known toxic substances, are used as pesticides, insecticides and chemical warfare agents. These compounds are extremely potent inhibitors of acetylcholinesterase, the enzyme responsible for regulating the concentration of the neurotransmitter acetylcholine at cholinergic synapses.[28] In these regions; we have been studying the electrolytic cleavage of carboxylate ester using hydroxamate ion microemulsion media.

Today microemulsions still offer worthwhile scientific challenges for researchers. Many novel applications of microemulsions will probably emerge in the coming years. Microemulsions[29-38] has recently attracted a great deal of attention of researchers from scientific and applicative viewpoints. One of the most salient features of the system is the formation of distinctive order microstructures. Therefore it is of great interest to investigate them from various viewpoints. Microemulsions are transparent optically isotropic and thermodynamically stable mixtures of oil and water stabilized by surfactants and usually with a co-surfactant; they are frequently droplet-type dispersions, either of oil-in-water (O/W) or water-in-oil (W/O).

In present work the hydrolysis of p-nitrophenyl acetate with SHA in the presence of cationic and non ionic surfactant. The result provides new approach and direction for the design of more effective deacylation reaction.

EXPERIMENT

The substrate p-Nitrophenyl acetate (PNPA), surfactant cetyltrimethylammonium bromide (CTAB), cetylpyridinium chloride (CPC) and Triton x-100 were purchased from sigma Aldrich. The nucleophile salicylhydroxamic acid (SHA) (Merk), medium chain alcohol n-butanol (Merk), was used as co-surfactant. Aliphatic oil such as n– hexane (merk) was used. All the solutions were prepared by triple distilled water. Microemulsions were prepared by mixing the appropriate composition and stirred vigorously until clear. The basic composition of microemulsion depends on the percentage composition of the water, surfactant, co-surfactant and oil. Electrical conductivity of microemulsions was measured by using dcm-200 conductivity meter equipped with CD-06 platinium conductance electrode in 27°C±0.1°C.

The pKa of nucleophile were determined by ph metrically using systronic type-335 pH meter. The kinetic reactions were studied spectophotometrically using UV-300 spectrophotometer by monitoring the appearance of the living p-nitrophenoxide ion on 400nm and 27°C & 40°C. Phosphate buffer was employed pH (7.7). Reactions of PNPA with nucleophile were determined spectrophotometrically. For all the kinetics runs the absorbance/time result fit very well to the first order rate equation in $(A\infty - At) = \ln (A\infty - Ao) - kt$. Spectrophotomeric data was show that the increasing in absorbance at 400nm with the formation of p-nitrophenoxide ion during the time of reaction. (Fig. 2) representing graph for the hydrolysis of PNPA with SHA in presence of surfactant at pH (7.7), Temp. 27°C & 40°C. The spectrum show on increasing in absorbance at 400nm with the formation of p-nitrophenoxide ion during the reaction.

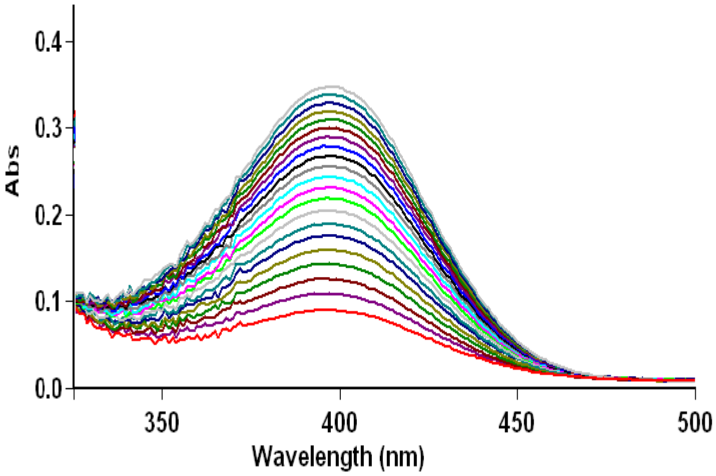

Fig. 4.1 UV-Vis spectra, repeat scans every 0.1 min. up to 1 min. showing the increasing absorbance of *p*-nitrophenoxide ion at 400 nm due to the hydrolysis of *p*-nitrophenyl acetate (PNPA) with (SHA)

in the presence of Surfactant. **Reaction conditions:** pH = 7.7, Temp. = 27°C and 40°C, [PNPA] = 1.0×10^{-4}M, [SHA] = 1.0×10^{-3}M.

RESULT AND DISCUTION

For kinetic studies first we were prepared different types of microemulsion system. All microemulsions were prepared by mixing of n-hexane, surfactants (CTAB, CPC & Triton x-100) n-butenol as co-surfactant and titrating the slurry with water, agitating mildly to give clear solution (Table 1). Microemulsions enclosed large weight percentage of water and there for known as O/W microemulsion, in which microemulsions of n-hexane (oil) are dispersed in aqueous buffer, presence of surfactants (cationic and non-ionic) help to stabilised this mcroemulsions**.**

Table - 1 Composition by weight percent of cationic and non-ionic microemulsions. For all microemulsion pH maintained as per-reaction condition required using phosphate buffers. ME 1-8 were prepared with surfactant in same composition.

ME	W_0	Surfactant (%)			n-Butanol(%)	n-Hexane(%)
		Triton x-100	CTAB	CPC		
1	5	20	19.9	14.2	4	1
2	5.5	19	18.9	13.6	4	1
3	6	18	17.9	13	4	1
4	6.5	17	16.9	12.4	4	1
5	7	16	15.9	12	4	1
6	7.7	15	14.9	11.5	4	1
7	8	14	13.9	11.1	4	1
8	8.5	13	12.9	10.7	4	1

In the present study reaction has been carried out at water content W_0 values to investigate the different catalytic properties of water pool of microemulsion. Water pool ratio W_0 has been calculated by using eq. [1]

$$\mathbf{W_0 = H_2O / Surfactant} \qquad \textbf{[1]}$$

The pH of microemulsion solution was detected by directly using a glass electrode in to the microemulsion solutions. The pH value of microemulsion was same as that of aqueous solution, which indicates the pH value of the water content is close to that of initial buffer system. Conductivity is one of the important indication of structure variation and properties of microemulsions. For all the microemulsion system we have measured electric conductivity. We observed that conductivity increasing with the increasing of water content (W_0) (Fig-1). Rate constant for the hydrolysis of p-nitrophenyl acetate (PNPA) by SHA were determined at 27°C and 40°C (Table 2 & 3). All the reaction were carried out under the reaction condition [PNPA] = 1.0 x 10^{-4} M, [HA] = 1.0 x 10^{-3} M, pH = 7.7 at 27°C and 40°C. Rate constant indicate nucleophilic dependent reaction. All the kinetic data (Table 2 & 3) positively support for the hypothesis that SHA is working as nucleophillic catalyst for the reaction of PNPA.

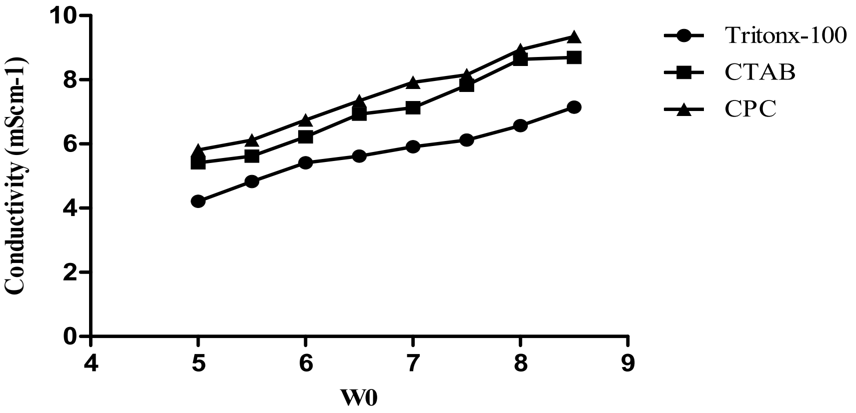

Fig.1. Summary of comparative conductivity data of microemulsions.

ME	W_0	Rate Constant					
		Triton X-100		CTAB		CPC	
		10^3kobs(s^{-1})	K_2(M^{-1} S^{-1})	10^3kobs(s^{-1})	K_2(M^{-1} S^{-1})	10^3kobs(s^{-1})	K_2(M^{-1} S^{-1})
1	5	1.01	1.90	3.44	5.40	5.89	9.20
2	5.5	1.11	3.01	4.07	6.42	6.58	10.12
3	6	1.18	3.60	4.89	7.86	7.49	11.31
4	6.5	1.30	4.02	5.27	9.07	8.23	12.34
5	7	1.67	4.78	5.99	10.13	8.84	13.47
6	7.5	1.86	5.23	6.84	11.78	9.69	15.15
7	8	2.15	5.96	7.88	12.89	10.11	17.83
8	8.5	2.53	6.23	8.73	15.23	11.73	21.29

[PNPA] = 1.0×10^{-4} M, [SHA] = 1.0×10^{-3} M, pH = 7.7 at 27°C

Table 2. Summary of the kinetic rate data for the nucleophilic reaction of PNPA with salicylhydroxamate ion in O/W microemulsion media at 27°C.

[PNPA] = 1.0×10^{-4} M, [SHA] = 1.0×10^{-3} M, pH = 7.7 at 40°C

ME	W_0	Rate Constant					
		Triton X-100		CTAB		CPC	
		10^3kobs(s^{-1})	K_2(M^{-1} S^{-1})	10^3kobs(s^{-1})	K_2(M^{-1} S^{-1})	10^3kobs(s^{-1})	K_2(M^{-1} S^{-1})
1	5	2.11	3.86	6.09	12.10	9.12	15.22
2	5.5	2.32	5.43	8.15	15.21	11.23	19.87
3	6	2.43	5.67	8.94	15.54	13.11	21.13
4	6.5	2.73	7.99	10.13	19.01	15.24	24.13
5	7	3.21	8.89	11.89	21.65	16.23	27.97
6	7.5	3.87	10.25	12.54	22.43	17.39	30.14
7	8	4.33	11.22	14.23	23.12	19.97	33.26
8	8.5	5.07	12.13	16.33	27.34	21.66	38.39

Table 3. Summaries of the kinetic rate data for the nucleophilic reaction of PNPA with salicylhydroxamate ion in O/W microemulsion media at 40°C.

The resulting data suggest electrostatic interaction concentration of hydroxide ion at a positively charged micro droplets surface (cationic surfactant) accelerates hydrolysis of ester compared with aqueous solution at the same pH, a non charged surface (non-ionic surfactant) slow accelerate the reaction compared with cationic surfactant. The conductivity data of all the microemulsion increasing with increasing the water content (W_0). There with the effect of medium measured by the conductivity water concentration ($W_0 = H_2O$/Surfactant) is slightly increasing with in increasing the rate of ester hydrolysis.

The kinetic effect of microemulsions can be divided in to two contribution (i) non electrostatic which relates to hydrophobic interaction with reagents and is commonly modelled by the effect of nonionogenic surfactants (ii) electrostatic which relates to interaction of hydroxide ion with a charged micro droplet surface.[39]

The (Table 2 and 3) represent the kinetic data for nucleophilic reactivity of the PNPA with SHA in room temperature and above room temperature (27°C & 40°C). Kinetic study of all reaction was carried out under the specific reaction condition. [PNPA] = 1.0×10^{-4}M, [HA] = 1.0×10^{-3}M, PH 7.7 at 27°C & 40°C. In kinetic study of anionic nucleophilic reaction with microemulsions, using kinetic models. The variation of the rate constant for nucleophillic attack by hydroxamate ion in microemulsion based on the cationic and non ionic surfactants. Kinetic studies of the reaction of PNPA have been calculated spectrophotometrically under pseudo first order condition at 27°C & 40°C.

The overall first order rate is given by

$k_{obs} = k^0_{obs} + k_{Nu}[Nu^-]$ (2)

$k^0_{obs} = k_{H2O} + k_{OH^-}[OH^-]$ (3)

In viewing of the fact that hydroxamate ions are α-effect nucleophiles.[40-41] So the competition with other nucleophile i,e OH^- and H_2O is not usual and K_{obs} is simply given by

$k_{obs} = k_{Nu^-}[Nu^-]$ (4)

Ionization state of hydroxamic acid effect the catalysis power of hydroxamate ion, eq. (5) may written to describe k_{obs}

$k_{obs} = k_2 [HA]_T \alpha_{HA}^-$ (5)

Where K_2 is the rate constant, $[HA]_T$ the analytical concentration hydroxamic acid, α_{HA}^- is the fraction of hydroxamate ion ionized ($\alpha_{HA}^- = Ka/Ka + H^+$). (Table 2 & 3) show the summarized data of second order rate constant together with pseudo first order rate constant. Kinetic rate data of nucleophilic reaction show pseudo-first order rate constant increasing with increasing W_0 for ME-1 to ME-8. The rate of reaction of triton-x 100 with SHA is slowly increases compare to cationic microemulsion (CTAB & CPC). Cationic micreoemulsions are more reactive then non ionic microemulsion system. The order of reaction in all microemulsion is CPC > CTAB > Tritonx-100. According to the pre defined theory above the room temperature rate of reaction is increasing with increasing the temperature. The order of reaction rate data of all microemulsions are same as pseudo-first order rate data (CPC > CTAB > Triton X-100). During the nucleophilic reaction in the microemulsion solution the substrate molecule situated in to hydrophobic droplets and anionic nucleophile exist in water content. This evidence is support by the decreasing in rate of reaction of PNPA and SHA with decreasing in water content (W_0).

CONCLUSION

The conductivity and ion-transport behaviour of O/W microemulsion was determined by the weight percentage. For all microemulsion conductivity data are representing that the microemulsion solution stable for nucleophilic reaction. The nucleophilic reaction of PNPA with SHA is increasing with increasing the water content (W_0). On the view of surfactant behaviour the cationic surfactant are more reactive than the non ionic surfactant CPC>CTAB>Tritonx-100. The reaction rate is decreasing with increasing the concentration of surfactant. For all microemulsion was stable above room temperature and show the increasing the rate of reaction with increasing the temperature according to pre defined theory.

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