Int. J. Chem. Sci.: 11(2), 2013, 761-772
ISSN 0972-768X
www.sadgurupublications.com

A KINETIC AND MECHANISTIC STUDY ON EFFECT OF VARIATION OF MICELLES ON REDOX REACTIONS OF α-AMINO ACIDS BY PERMONOSULPHURIC ACID

P. RAJKUMAR* and K. SUBRAMANI

PG & Research Department of Chemistry, Islamiah College, VANIYAMBADI – 635752 (T.N.) INDIA

ABSTRACT

The oxidation of α-amino acids by permonosulphuric acid (PMS) at 27 ± 0.2°C in micellar medium has been attempted. The reaction is first order each, in PMS and α-amino acids. The rate of electron transfer from α-amino acids to PMS increases with an increase in the concentration of micelles. The unbound amino acids yield about 100% carbonyl compounds in presence of micelles. It rules out the synchronous C-C and N-H bond fission. With increase in micelles concentration, an increase in the rate has been observed. The product and stoichiometry corresponds to the reaction of 1 mole of α-amino acids for about 1 mole of PMS. The added CTAB enhances the rate of oxidation of a reaction much more than NaLS.

Key words: Permonosulphuric acid (PMS), Oxidation reaction, Mechanism, α-Amino acids, Sodium laurylsulphate (NaLS), Cetyltrimethylammonium bromide (CTAB).

INTRODUCTION

The kinetics studies[1-3] employing permonosulphuric acid (PMS) is an efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds. Oxidation is an important process in organic chemistry and introduction of PMS as economic and effective reagent for oxidation under mild and aqueous conditions constitutes a standing challenge. PMS is an oxidant both in acid and alkaline media for the oxidation of a large number of compounds such as nitrates[4], hydroxylamine[5], bromides[6], EDTA[7] and organic compounds[8] such as amines[9,10], which is non-hygroscopic, non-photosensitive and stable colourless solid, which is freely soluble in water, acetic acid, N, N-dimethyl formamide[11,12] etc. The little work has been done on PMS as oxidant in micellar medium[13,14].

Aqueous solutions of micelles have been known to exhibit unusual properties. At low concentrations, the surfactant molecules behave just like ordinary electrolytes, but after

*Author for correspondence; E-mail: rajkum.phd@gmail.com

attaining a certain concentration, surfactant chains tend to self-associate, resulting in the formation of aggregates (micelles, micro emulsions and vesicles)[15,16]. The utilization of surfactants as reaction media affects reaction rates, yield of products, mechanism, regioselectivity, and stereochemistry[17]. The micellar catalysis or inhibition factor is highly sensitive to the concentration of added counter ions.

Kinetic and mechanistic studies of a variety of redox reactions in the presence of micelles have been carried out to understand the role of micelles as well as to speed up the removal of contaminant[18-20]. The details of effect of micelles on oxidation of α-amino acids by permonosulpuric acid in the presence and/or the absence of surfactants are not yet known. In this paper, kinetics of oxidation of some α-amino acids by PMS in micelles have been presented. The cation radical is formed due to the oxidation of OH group by PMS is nearly a synchronous fashion of electron transfer resulting in a C-C and N-H bond fission[21].

EXPERIMENTAL

Materials and kinetic procedure

All the glass apparatus were of Pyrex glass and stoppers were well ground. The loss of solvent, tested in standard flask and in reaction bottles, was found to be negligible. Burettes, pipettes and standard flask were standardized by usual procedure. The temperature was controlled by an electrical operated thermostat[22]. It was provided with sufficient thermal lagging, suitable heaters, stirrer and proper cooling arrangements for continuous work. The temperature was maintained to ± 0.2^{o}C using Jackson thermometer working in conjugation with sunvic electric relay. A sensitive thermometer reading to one tenths of a degree was used to measure the temperature accurately. The bath liquid, water was covered with a layer of thermocol bits to minimize heat loss due to radiation and also water loss due to evaporation.

The kinetics studies were carried out by allowing reactions in glass stoppered Corning glass vessels. All ingredients of the reaction mixture were taken in separate flasks and the latter were suspended in a temperature controlled water bath. The solution of temperature pre-equilibrated permonosulphuric acid of desired concentration was withdrawn and then immediately discharged into the reaction mixture. The liberated iodine was titrated against thiosulphate solution using starch as an indicator. The progress of the reaction was followed by estimating the amount of unconsumed [PMS] iodometrically in aliquots (5 mL) withdrawn from the reaction mixture at regular time intervals for about 75% of the reaction. The order of the reaction with respect to each reactant was determined by the relation

between initial rates. The α-amino acids were commercial products (Merck, Ltd., Mumbai, India) of the highest purity available and were used as such. The surfactants used in the present work are sodium laurylsulphate (NaLS)[23] and cetyltrimethylammonium bromide (CTAB)[24]. The surfactants were purified by adopting earlier procedure[25]. The chemicals were purchased from BDH (UK) and SD Fine chemicals (INDIA) and E.Merck (INDIA). Double distilled water was used as a solvent. H_2SO_4 was standardized by using standard sodium bicarbonate solution with methyl orange as an indicator.

The thermo spectrophotometer fitted with recording and thermostating arrangement was used to follow the rate of the reaction. The excess of the reductant was used in kinetic runs. It gives pseudo first order rate constant. The individual kinetic runs were strictly first order to PMS. Furthermore, the pseudo-first-order rate constant does not depend on the initial concentration of PMS. The reaction rate increases linearly with an increase in the concentration of the α-amino acids. For all the kinetic experiments, conversions were followed at least for four half lives and the specific rates from successive half-life values agreed with in ± 7% and the average values did not differ from those obtained from a plot of logarithmic change in absorbance against time. The pseudo-first order constants calculated using integrated rate equations,

$$k = 2.303/t \log [a/a - x] \quad \ldots(1)$$

Where a initial concentration of oxidant and (a - x) concentration of oxidant at time t, are expressed in sec^{-1}.

PMS oxidant with free ligand was calculated from the volumetric titration at 502 nm. Thus, the reaction is first order with respect to the α-amino acids.

Critical micelle concentration determination

The conductometric technique was used to determine the critical micelle concentration (CMC) values of NaLS and CTAB solutions in different experimental conditions, i.e., NaLS only, CTAB only, NaLS, CTAB + α-Amino acids (Glycine, Alanine, Isoleucine, N-Benzoyl glycine and N-Acetyl glycine), Micelles + PMS. The CMC are summarized in Table 1.

Table 1: CMC values of micelles under different experimental conditions at 27 ± 0.2°C

Reaction solution[a]	CMC × 10^4 (mol dm^{-3})
Water	10.0
Permonosulphuric acid	9.1
Sulphuric acid	8.5

Table 2: First order rate constants for PMS oxidation of α-amino acids and in the presence of NaLS and CTAB at 27 ± 0.2°C

10^2 [α-Amino acids] (mol dm^{-3})	$10^4 k_1$ (s^{-1})	10^4 $k_{calculated}$	$10^4 k_1$(s^{-1}) NaLS	$10^4 k_{calculated}$ NaLS	$10^4 k_1$(s^{-1}) CTAB	$10^4 k_{calculated}$ CTAB
Glycine						
0.5	0.9631	1.0269	0.9749	0.9928	1.0867	1.2346
1.0	1.9271	1.8369	1.9803	1.8882	2.0330	2.2483
1.5	2.8628	2.7920	2.8828	2.9268	3.0521	3.3982
2.0	3.8257	3.7861	3.8557	3.9826	4.0998	4.3246
2.5	4.7566	4.6870	4.9238	4.8264	5.0021	5.2267
Alanine						
0.5	0.8872	0.9020	0.8935	0.9256	0.9549	0.9489
1.0	1.7355	1.8256	1.7620	1.8362	1.9271	1.9568
1.5	2.6474	2.7362	2.6486	2.7298	2.8428	2.9342
2.0	3.4524	3.3980	3.4540	3.5268	3.8201	3.9860
2.5	4.3353	4.4862	4.4078	4.4908	4.7500	4.8826
Isoleucine						
0.5	1.1518	1.2068	1.2350	1.3842	1.4002	1.5092
1.0	2.3949	2.4990	2.4835	2.5998	2.7989	2.9902
1.5	3.4524	3.5260	3.6880	3.7268	4.2562	4.4023
2.0	4.6737	4.7880	4.9202	4.8927	5.6591	5.5682
2.5	5.7579	5.8228	6.2402	6.3456	7.0052	7.1982
N-Acetyl glycine						
0.5	2.0858	2.2862	2.1002	2.3002	2.3486	2.6634
1.0	4.0998	4.3562	4.1862	4.2346	4.6822	4.8956
1.5	6.0231	6.3642	6.0998	6.2982	6.9645	6.9840
2.0	8.0442	8.2678	8.1222	8.4678	9.2876	9.5678
2.5	10.1354	10.4982	10.1985	10.3482	11.5967	11.9824
N-Benzoyl glycine						
0.5	2.5528	2.8626	2.6632	2.9924	2.9820	3.0468
1.0	5.0964	5.2864	5.1998	5.5528	5.8924	6.0246
1.5	7.5887	7.8924	7.7782	7.9926	8.7642	8.9924
2.0	10.0244	10.5090	10.2956	10.5264	11.6842	12.0268
2.5	12.5198	12.8252	12.6084	12.9028	14.5826	14.8982

[PMS] = 0.08 mol dm^{-3}, [H_2SO_4] = 0.25 mol dm^{-3}, [NaLS] = [CTAB] = 1.00 x 10^{-3} mol dm^{-3}, Temperature = 27 ± 0.2°C

Table 3: Stoichiometric data for PMS oxidation of α-amino acids in the presence of micelles at 27 ± 0.2°C

10^3 [Compound] (mol dm^{-3})	10^2 $[PMS]_{initial}$ (mol dm^{-3})	10^2 $[PMS]_{final}$ (mol dm^{-3})	Δ 10^3 [PMS] (mol dm^{-3})	[Compound]: Δ [PMS]
Glycine				
1.0	1.0	0.89	1.10	1.00 : 1.10
2.0	2.0	1.80	2.00	1.00 : 1.00
4.0	2.0	1.60	4.00	1.00 : 1.00
Alanine				
1.0	1.0	0.91	1.00	1.00 : 1.00
2.0	2.0	1.81	1.90	1.00 : 0.95
4.0	2.0	1.61	3.90	1.00 : 1.02
Isoleucine				
1.0	1.0	0.88	1.20	1.00 : 1.20
2.0	2.0	1.78	2.20	1.00 : 1.07
4.0	2.0	1.59	4.10	1.00 : 0.97
N-Acetyl glycine				
1.0	1.0	0.90	1.00	1.00 : 1.00
2.0	2.0	1.82	1.80	1.00 : 0.97
4.0	2.0	1.65	3.50	1.00 : 1.14
N-Benzoyl glycine				
1.0	1.0	0.89	1.10	1.00 : 1.10
2.0	2.0	1.79	2.10	1.00 : 1.05
4.0	2.0	1.62	3.80	1.00 : 1.05

$[H_2SO_4]$ = 0.25 mol dm^{-3}, [NaLS] = [CTAB] = 1.00 x 10^{-3} mol dm^{-3}, Temp. = 27 ± 0.2°C

RESULTS AND DISCUSSION

The oxidation kinetics was carried out at different initial concentrations of reactants at 27 ± 0.2°C. The concentration of α-amino acid was varied in the range (0.5-2.5) × 10^2 mol dm^{-3} at fixed concentrations of other reaction ingredients. A plot of initial rate versus [α-Amino acid] yielded a straight line passing through the origin confirming first order

dependence. The concentration of NaLS and CTAB was varied in the range of (1×10^{-3}, 10×10^{-3}, 1×10^{-4}, 5×10^{-3}, 5×10^{-4}) $\times 10^2$ mol dm^{-3} at concentrations of other reaction ingredients. A plot of initial rate versus [Micelles] yielded a straight line passing through the origin confirming first order dependence. The second order plots were also drawn for comparable concentrations of both; α-amino acids and micelles.

Table 2 summarizes the kinetic data for the oxidation of α-amino acids by PMS in presence of anionic and cationic micelles at 27 ± 0.2°C. The reaction exhibits total second-order dependence on [PMS] as well as [α-Amino acids]. Based on the oxidation of PMS with α-amino acids, the following rate law has been deduced.

$$\text{Rate} = k_2 [\alpha\text{-Amino acids}] [\text{PMS}] \quad \ldots(2)$$

The stoichiometric studies for the PMS oxidation of α-amino acids (free ligands) were carried out with the oxidant in excess. The temperature was maintained at 27 ± 0.2°C. After 100 h, when the reactions was nearing completion, the unreacted PMS was determined both; iodometrically and spectrophotometrically from the change in absorbance measured at 350 nm. The stoichiometric results indicate that 1 mole of α-amino acids consumes about 1 mole of PMS (Table 3).

Tables 4 and 5 summarize the kinetic data for the variation of NaLS and CTAB in the oxidation of amino acids by permonosulphuric acid at 27 ± 0.2°C. The rate of the reaction is increased by the addition of both; NaLS and CTAB. A plot of specific rate constant versus micellar concentration is sigmoidal in shape. The catalytic effect is more in CTAB than NaLS. If the concentration of NaLS and CTAB was increased rate of the reaction also increases.

Table 4: Variation of [NaLS] in the oxidation of α-amino acids by permonosulphuric acid at 27 ± 0.2°C

α-Amino acids	10^2 [NaLS] mol dm^{-3}	$10^4 k_1$ (s^{-1}) NaLS	$10^4 k_{calculated}$ NaLS
Glycine	0.0001	0.0974	0.0970
	0.0005	0.4856	0.4978
	0.001	0.9749	0.9750
	0.005	4.8750	4.8726
	0.01	9.7100	9.7250

Cont…

α-Amino acids	10^2 [NaLS] mol dm^{-3}	10^4 k_1 (s^{-1}) NaLS	10^4 $k_{calculated}$ NaLS
Alanine	0.0001	0.0893	0.0895
	0.0005	0.1785	0.1778
	0.001	0.8935	0.8966
	0.005	4.4672	4.5680
	0.01	8.9005	8.8341
Isoleucine	0.0001	0.1235	0.1350
	0.0005	0.2410	0.2389
	0.001	1.2350	1.2009
	0.005	6.1752	6.2745
	0.01	12.3650	12.3980
N-Acetyl glycine	0.0001	0.2102	0.21998
	0.0005	0.4200	0.4375
	0.001	2.1002	2.2980
	0.005	10.5010	10.6378
	0.01	21.0020	21.1467
N-Benzoyl glycine	0.0001	0.2663	0.2558
	0.0005	0.5326	0.5860
	0.001	2.6632	2.5998
	0.005	13.3160	13.4128
	0.01	26.6326	26.6780

[PMS] = 0.08 mol dm^{-3}, [H_2SO_4] = 0.25 mol dm^{-3}, Temperature = 27 ± 0.2°C

Table 5: Variation of [CTAB] in the oxidation of α-amino acids by permonosulphuric acid at 27 ± 0.2°C

α-Amino acids	10^2 [CTAB] mol dm^{-3}	10^4 k_1 (s^{-1}) CTAB	10^4 $k_{calculated}$ CTAB
Glycine	0.0001	0.1086	0.1090
	0.0005	0.2173	0.2256
	0.001	1.0867	1.0845
	0.005	5.4307	5.3670
	0.01	10.9010	11.0028

Cont…

α-Amino acids	10^2 [CTAB] mol dm^{-3}	10^4 k_1 (s^{-1}) CTAB	10^4 $k_{calculated}$ CTAB
Alanine	0.0001	0.0954	0.0899
	0.0005	0.1998	0.1256
	0.001	0.9549	0.8992
	0.005	4.8002	4.9018
	0.01	9.5490	9.6451
Isoleucine	0.0001	0.1402	0.1327
	0.0005	0.2810	0.2984
	0.001	1.4002	1.4289
	0.005	7.1010	7.0094
	0.01	14.0986	14.1278
N-Acetyl glycine	0.0001	0.2345	0.2346
	0.0005	0.4690	0.4524
	0.001	2.3486	2.2994
	0.005	11.7989	11.7894
	0.01	23.4710	23.5014
N-Benzoyl glycine	0.0001	0.2982	0.3014
	0.0005	0.5962	0.5816
	0.001	2.9820	2.9946
	0.005	14.9100	14.9803
	0.01	29.8289	29.7657

[PMS] = 0.08 mol dm^{-3}, [H_2SO_4] = 0.25 mol dm^{-3}, Temperature = 27 ± 0.2°C

Dependence of rate on the concentration of α-amino acid in NaLS and CTAB

The oxidation studies were carried out by varying [α-Amino Acid] in the range 0.5 to 2.5 x 10^2 mol dm^{-3} by keeping other variable constant. The near constancy in the k_2 values and the slope of nearly unity is obtained from a linear graph of logarithm of specific rate verses logarithm of [α-Amino acid] concentration in each case suggesting first order dependence of rate on [α -Amino acid] (Figs. 1 & 2).

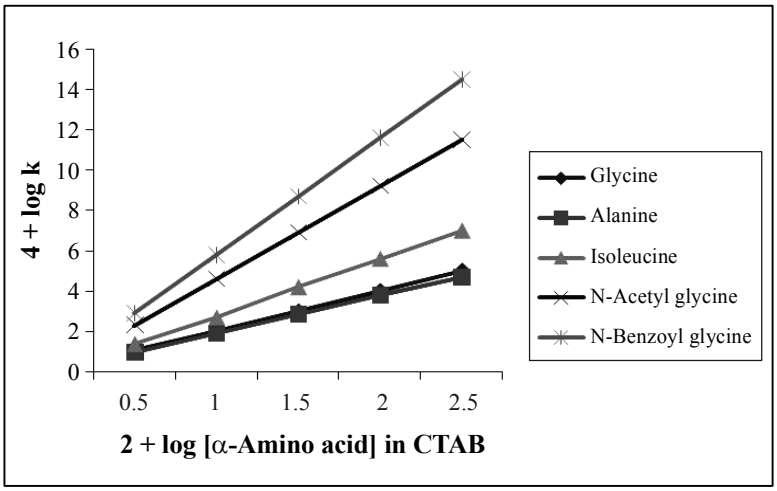


Fig. 1: Dependence of rate on [α-Amino acid] in NaLS

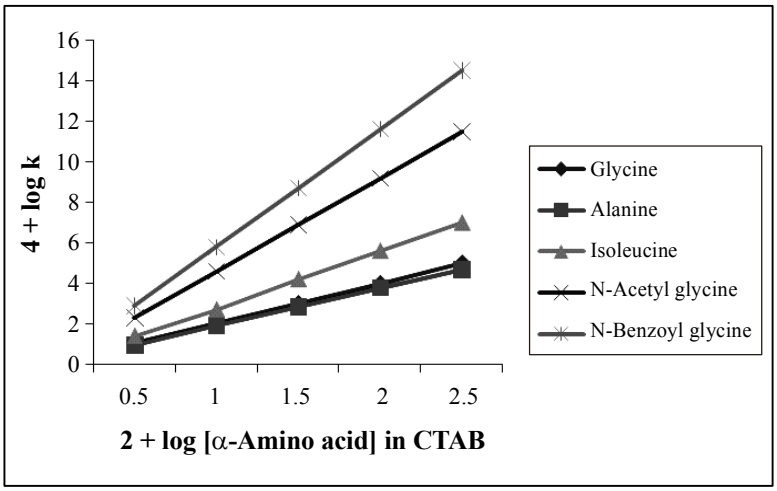
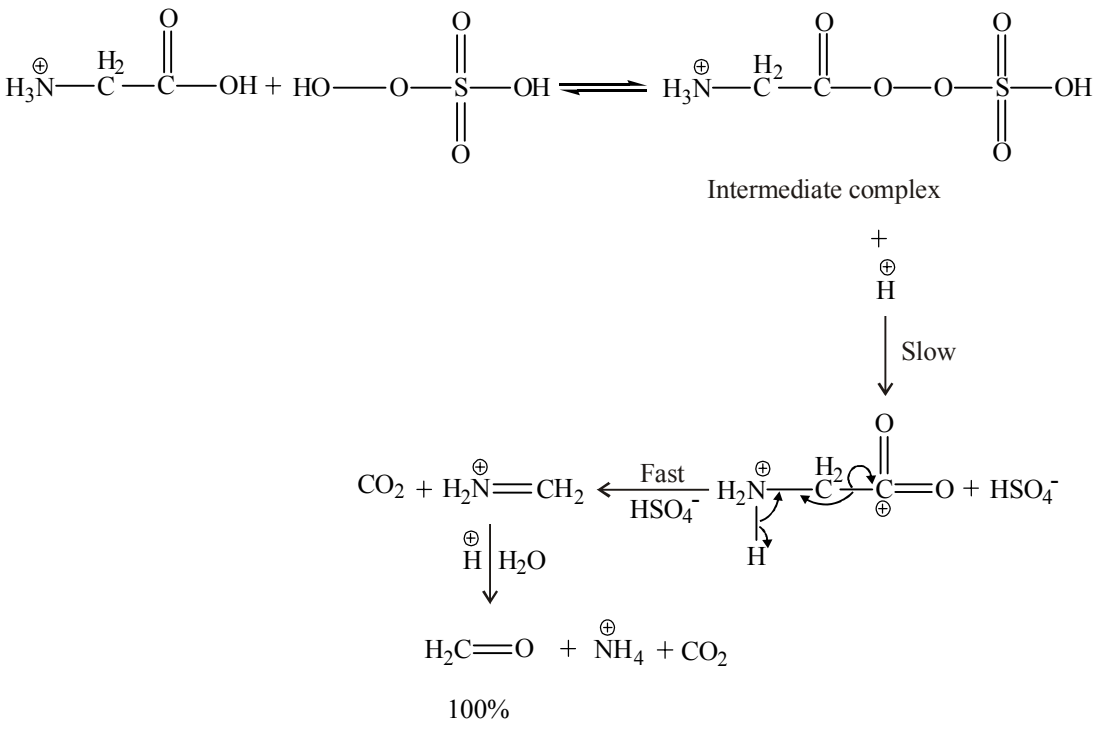


Fig. 2: Dependence of rate on [α-Amino acid] in CTAB

Mechanism

A reaction scheme has been proposed, where the electron transfer possibly occurs within the intermediate complex. The initial act of one electron transfer to PMS may occur by inner sphere path in the slow step. There is 100% decrease in absorbance of 502 nm. The rate of permonosulphuric acid oxidation of unbound α-amino acids is different. The formation of binuclear complex with high association constant K, between PMS acetate and α-amino acids is possibly due to the ligation of PMS acetate to free carbonyl end.



Scheme

CONCLUSION

The kinetics of one electron transfer route seems to be unavailable for PMS with α-amino acids in micellar medium, PMS oxidizes α-amino acids. It rules out the synchronous C-C and N-H bond fission. Oxidation of these acids increases with increase of concentration. With increase in micellar concentration, an increase in the rate was observed. The added CTAB enhances the rate of oxidation of a reaction much more than NaLS. The 1 mole of α-amino acids consumes 1 mole of PMS. The micelles act as a positive catalyst. The reaction proceeds Via free radical mechanism as indicated by acrylonitrile polymerization.

ACKNOWLEDGEMENT

Authors express sincere thanks to PG & Research Department of Chemistry, Islamiah College Vaniyambadi for providing the necessary facilities for the successful completion of this research work and express sincere gratitude to Thiruvalluvar University, Vellore for providing an opportunity for completing the research work successfully.

REFERENCES

1. L. M. Bhardwaj, D. N. Sharma and Y. K. Gupta, Inorg Chem., **15**, 1695 (1976)
2. S. Kapoor and Y. K. Gupta, J. Inorg. Nucl. Chem*.,* **39**, 1019 (1977)
3. S. H.Goh, R. B. Heslop and J. W. Lethbridge, J. Chem. Soc. (A)., 1302 (1966)
4. J. O. Edwards and J. J. Muller, Inorg. Chem., 696 (1962).
5. N. Vijay, D. Mala, C. L. Khandelwal and P. D. Sharma, Indain J. Chem., **47A**, 859 (2008).
6. I. Cresser and J. O. Edwards, Topics Phos. Chem*.*, **7**, 402 (1972).
7. P. Keashwani and Y. K. Gupta, Indian J. Chem., **21A**, 961 (1982).
8. C. P. Patnaik, S. N. Mahapatro, A. K. Panigrahi and R. S. Panda, Bull. Chem. Soc. Jpn., **60**, 3391 (1987).
9. Y. Ogata, K. Tomizawa and T. Morikawa, J. Org. Chem., **44**, 352 (1979).
10. Y. Ogata, K. Tomizawa and T. Ikeda, J. Org Chem., **43**, 2417 (1978).
11. A. G. Dash, R. K. Nanda and P. Mohanti, Indian J. Chem*.,* **12 A**, 162 (1984).
12. F. R. F. Fan and E. S. Gould, Inorg. Chem*.*, **13**, 26 (1974).
13. M. N. Arumugam, K. Santhakumar, K. Kumaraguru, S. Arunachalam, Int. J. Chem. Kinet*.*, **38**, 98 (2006).
14. Maqsood Ahmad Malik, F. M. Al-Nowaiser, Naushad Ahmad and Zaheer Khan, Int. J. Chem. Kinet., **42**, 704 (2010).
15. C. A. Bunton, M. J. Minch, J. Hidalgo and L. Sepulveda, J. Am. Chem. Soc., **95**, 3262 (1973).
16. C. A. Bunton, S. Diaz, L. S. Romsted and O. Valenzuela, J. Org. Chem., **41**, 3037 (1976).
17. S. Tascioglu, Tetrahedron, **52**, 11113 (1996).
18. A. Blasko, C. A. Bunton and S. Wright, J. Phys. Chem., **97**, 5435 (1993).
19. H. Yao and D. E. Richardson, J. Am. Chem. Soc., **125**, 6211 (2003).
20. Z. Li, Chemosphere, **54**, 419 (2004).
21. B. Mohammed Nawaz, K. Subramani and K. Anandaratchagan, J. Curr. Chem. Pharm. Sc., **1(1)**, 19 (2011).

22. A. Thaminum Ansari, Int. J. Chem. Tech. Res., **1(2)**, 308-313 (2009).

23. Subramanian Udhayavani, J. Chem. Bio. Phy. Sci. Sec. A, **2**(**2)**, 551-559 (2012)

24. A. Thangaraj and R. Gopalan, J. Indian Chem. Soc., **67**, 453 (1996).

25. K. Anandaratchagan, B. Mohammed Nawaz and K. Subramani, Acta Chim. Pharm. Indica, **(1)1**, 44-50 (2011).

Revised : 28.12.2012 *Accepted : 31.12.2012*