

Study on the steady – state kinetics of Iodination of p – cresol

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Abstract

The kinetic study for iodination of p – cresol in aqueous solution by molecular iodine has been carried out using steady–state technique. One of the reactant, iodine has been produced at a known rate by persulfate iodine reaction and it is consumed by p–cresol. The effective concentration of iodine during the steady state is measured from its redox potential at a bright platinum foil electrode. P–cresol react rapidly with iodine and at 25–oC the specific reaction rate is $7.48 \times 10^{-2} \text{ M}^{-1} \text{ S}^{-1}$ (PH 7.13). The energy of activation and frequency factor were found to be 40 J/mole and 9.1×10^{-2} respectively.

KEYWORD: Kinetics, p–cresol, steady–state, effect of pH, energy of activation.

Introduction:

Kinetics study involves the rate determination effect of temp, concentration and pressure on rate and mechanisms of some complex reactions. Kinetic study of slow reactions are of little use for the study of rapid reaction, which are generally complete in a fraction of time. A reaction is said to be rapid if it is too fast to be followed by conventional techniques at ordinary condition of temperature, pressure and concentration with the criterion, reaction having rate constant more than 1.0 Sec^{-1} or $1.0 \text{ M}^{-1} \text{ S}^{-1}$. As the temperature decreases rate of reaction decreases, hence the rapid reaction can be slowed down by decreasing temp. Rate constant have been determined for the halogenation of various aromatic alkyl amines, Phenols and anilides by decreasing concentration of reactions.

The flow techniques employ the principle of initiating the reaction by mixing the two reactant solution in specially designed chambers in continuous flow technique, the two reactant solution are placed in two separate containers and by applying compressed air or by other means, the two solution are forced through outlet tubes from the containers into a mixing chamber. The mixed solution is then allowed to flow along the observation tube at constant flow rate, at any point of time physical properties can be evaluated and rate constant can be determined.

In steady-state technique instead of mixing two reactants, one of the reactant is produced in situ at controlled rate, either electrolytically or by chemical reaction, consequently, a steady-state is soon reached, in which the rate of formation of reactant is equal to rate of its consumption. There will be an effective concentration

of the reactant, usually very low, at the steady state and this is determined of step, rate which is determined by any suitable methods rate can be evaluated, and order of reaction can be decided.

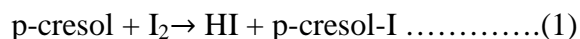
Hard et – al¹ have studied the bromination of p-cresol in presence of strong acids and reported that two addition product between p-cresol and 100% sulphuric acid could be isolated. Recently it is found that p-cresols and xylenols react with bromine to give the corresponding meta-bromo-substituted compounds in good yield,² indicating the bromination of o-protonated substrate.

The kinetic study of the bromination of the regioisomer of p – cresol in aqueous medium by molecular bromine has been carried out using the competition technique.³ These reactions are rapid and found to be second order. Teramote et-al⁴ have presented chlorination of p-cresol with gaseous chlorine using reactor composed of a bubble column and stirred with various type of gas distributors. The results were explained in terms of large liquid phase mass transfer co-efficients.

Based on kinetic study⁵ of iodination⁶ and chlorination^{7, 8} at neutral and alkaline pH, the initial bromination of phenol compounds was considered as second order reaction. The zero order dependence of rate of chlorination of p-cresol by chloramine-T on the concentration of phenol has previously been attributed to the formation of hypochlorous acid from the chlorosulphonamide as being the rate determining step.⁹ Evidence is presented to show that the reaction actually proceeds through chloramine-T and that the rate of formation of this species constitutes the rate determining step.

Kinetics of iodination of p-cresol, 2, 6-dichlorophenol imidazole and dimethylaminobenzenesulphonic acid in aqueous solution was studied using various bases as a catalyst.¹⁰ Jacquery et-al^{11, 12} have investigated the bromination of p-cresol and dimethyl phenols in antimony pentafluoride hydrogen fluoride and demonstrated the analogous reaction for chlorination of p-cresol.^{13, 14} During their study. Delamare and co-workers¹⁵ reported their observation on the bromination of p-cresol^{16, 17} in triflic acid and suggested the pathway to 3-bromo-p-cresol involving the 1, 2-bromine shift in the conjugate acid of 4-bromo-4-methylcyclohexa-2, 5-dione. Several recent studies have been concerned with the mechanism of bromination of phenol derivatives in aqueous solution.¹⁸⁻²⁵ Some of these studies deals with electrophilic bromine attack.²⁶

Use of all the halogenated compounds in organic synthesis is well known.²⁷ They are also used in the preparation of organometallic compounds^{28, 29} and coupling reactions involving transition metals.³⁰ Halogens are also used as medicinal molecular³¹⁻³³ herbicides, pesticides, fire retardants. Iodination of aromatic compounds plays an important role in synthesizing pharmaceuticals and natural product³⁴⁻³⁶ 4-nitrophenol is enhancer in chemiluminescence in liposomes.³⁷ Idourenes are used in synthesis of useful drugs.³⁸ Therefore, it is necessary to study the halogenation of aromatic compounds. In this context we have studied the kinetics of iodination of p-cresol. It is well known that p-cresol reacts quantitatively with iodine according to the equation:



The kinetics of this reaction has been studied only strongly acidic solution where the reaction is quite slow. The reaction occurs rapidly in neutral solution and surprisingly,

the kinetics of reaction has not been studied in higher pH. The usual spectrophotometric technique is of limited use in the present case because of low concentration of reactants needed for such technique and absorption due to iodine is too low for accurate measurements. Hence in present work reaction has been studied under condition where iodine is produced at controlled rate and consumed by p-cresol. The iodine is generated by slow second order reaction,



in aqueous neutral medium. From its specific rate and concentration of the reactants, rate production of iodine can be determined. The reaction between iodine and p-cresol is rapid and therefor at low concentration of p-cresol, a steady-state is established where in the rate of production of iodine:

$$\frac{d[I_2]}{dt} = k_2[S_2O_8^{--}][I^-] \text{-----(3)}$$

and its consumption

$$\frac{-d[I_2]}{dt} = k_2[I_2]^* [p\text{-cresol}] \text{ are balanced:}$$

$$k_2[S_2O_8^{--}][I^-] = [I_2]^* [p\text{-cresol}]$$

In this work iodine is present mostly as the tri-iodide, I_3^- , but for simplicity it is represented as I_2 and $[I_2]^*$ = molar concentration.

The effective concentration of iodine $[I_2]^*$ can be estimated by measurement at its redox potential. It is then possible to determine the specific reaction rate of the iodination of p-cresol.

Experimental:

All stock solutions were prepared in required pH solutions: A stock solution of $2.0 \times 10^{-2} M$ $K_2S_2O_8$ was prepared (solution-A). Another two stock solutions were prepared $4.0 \times 10^{-2} M$ KI and 2.0×10^{-3} p-cresol (solution-B and solution-C). 20 ml of solutions A and 10ml each of solution B and C were pipetted out separately into conical flask kept in thermostat at $25^\circ C$. The solution were mixed and simultaneously stop-watch was started. A bright platinum foil electrode (1cmX0.5cm) and standard calomel electrode were introduced into the solution and emf was measured at intervals of 30 seconds for about three and half minutes. The emf increased linearly during the steady state and then sharply shoots up, indicating that the p-cresol was used up. The experiment was repeated twice to check reproducibility of emf measurements. These measurements were carried out with electronic voltmeter. These emf measurements were reproducible ± 1 mv. The emf value were plotted versus time and linear curve was obtained (Fig. 1). This was extrapolated to zero time to obtain the redox potential due to the effective concentration of iodine at that instant. The extrapolation to zero time is adrontageous because the concentration of both the reactants are known most accurately. The effective concentration of iodine at zero time was evaluated from calibration curve obtained. The calibration curve was prepared by taking several iodine solution in the concentration range from $2.0 \times 10^{-3} M$ to $5.0 \times 10^{-6} M$ containing $2.0 \times 10^{-2} M$ KJ and $1.0 \times 10^{-2} M$ $K_2S_2O_8$. The solutions were kept in thermostat at desired temperature. The redox potential of these solution were measured as explained

earlier. A plot of emf versus $\log[I_3^-]$ was a straight line, from this plot and emf value of iodine during steady state, effective concentration of iodine $[I_3^-]^*$ was evaluated [fig. 2].

The above procedure for calibration was also repeated for different temperature and pH and calibration curve were prepared from these curves, effective concentration of iodine $[I_3^-]$ were evaluated. The reaction between KI and $K_2S_2O_8$ was followed conventionally. From these measurements its specific reaction rate was evaluated and hence from known initial concentration of I^- and $S_2O_8^{2-}$ the rate of production of iodine at zero time can be calculated. The reaction was studied at various temperatures in the range of 22°C to 32°C and at various pH (5.40, 7.13 and 8.18) for steady state measurements, rate of production of iodine and calibration. From the results, specific reaction rate, energy of activation and frequency factor for the reaction were evaluated.

Result and Discussion:

The specific reaction rate, k_2 at 25°C (pH=7.13) for reaction (2) was found to be $9.0 \times 10^{-1} M^{-1} S^{-1}$. Since the initial concentration of persulphate and iodine are 1.0×10^{-2} and $2.0 \times 10^{-2} M$ respectively, the rate of production of iodine at zero time was calculated by the equation;

$$\frac{d[I_2]}{dt} = 9.0 \times 10^{-1} [1.0 \times 10^{-2}] [2.0 \times 10^{-2}] = 18 \times 10^{-5} MS^{-1}.$$

Similar rate of production of iodine were determined at various temperature and pH values.

(Table.1, 2 and Fig 1).

The effective concentration of iodine $[I_3^-]$ under steady state at zero time was obtained from corresponding redox potential of iodine/iodide system. The plot of emf versus concentration of p-cresol at each instant of time was plotted. It gives straight line over a wide range of time. The value of redox potential at zero time was obtained on extrapolation to zero. The redox potential at 25°C pH(7.13) was found to be 325 mV. Similar redox potential of iodine/iodide system were determined at various temperature and pH values (Table. 3 and Fig. 2) from these values of redox potential one can evaluate the effective concentration of iodine $[I_3^-]^*$ and p-cresol at various instant of steady state, but they are less accurate than at zero time. This is because unchanging concentration of iodide and persulphate are known accurately. The effective concentration of iodine $[I_3^-]^*$ is achieved by knowing accurately emf and corresponding $\log[I_3^-]^*$ at convenient point A, on the curve and from equation

$y_2 - y_1 = m(x_2 - x_1)$ the value of x_2 gives the effective concentration of iodine $[I_3^-]^*$. The effective concentration of iodine, $[I_3^-]^*$ at 25°C (pH=7.13) was observed to be 1.208M. similar determination were made at various temperatures and pH values (Table 4 and Fig. 3).

The specific reaction rate, k for iodination of p-cresol can be evaluated from the rate of production of iodine, effective concentration of iodine and concentration of p-cresol as below

$$\text{Specific reaction rate} = \frac{\text{Rate of production of iodine}}{\text{effective conc.}^n \text{ of iodine} \times \text{conc.}^n \text{ of p - cresol}}$$

Therefore, at 25°C and pH = 7.13, the specific reaction rate, k, for iodination of p-cresol is

$$k = \frac{18 \times 10^{-2} \text{ M s}^{-1}}{1.208 \text{ M} \times 2.0 \times 10^{-3} \text{ M}} = 7.49 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$$

similar specific reaction rate, k, determination were made at various temperature and pH values (Table 5). From the values of specific reaction rate at various temperature, activation energy for iodination of p-cresol is found out by plotting the graph of logarithm of specific reaction rate versus reciprocal of time in Kelvin. The value of found out to be 40 l/mole at 25°C and pH=7.13. The frequency factor or Arrhenius constant is found out to be 9.1×10^2 . It was observed that reaction is faster in neutral medium efforts have not been made to find at the mechanism of the reaction.

Table 1: Kinetics of Iodination of p-cresol: rate of production of Iodine

Concentration of iodine: $2.0 \times 10^{-2} \text{ M}$

Concentration of persulphate: $2.0 \times 10^{-2} \text{ M}$

pH : 7.13

Temperature 25°C

Sr. No	Vol. of mixture /ml	Time t/min.	Vol. of Na ₂ S ₂ O ₃ /ml	[Persulphate] 10 ⁻⁴ /M	[Iodine] 10 ⁻⁴ /M	(a-x)/10 ⁻³	1/(a-x)
1	10	00	0.2	0.5	0.25	19.97	50.07
2	10	10	0.8	2.0	1.0	19.90	50.25
3	10	20	1.7	4.25	2.12	19.78	50.56
4	10	30	2.6	6.5	3.25	19.67	50.84
5	10	40	3.6	9.0	4.5	19.55	51.15
6	10	50	4.7	11.75	5.87	19.41	51.52
7	10	60	5.7	14.25	7.12	19.28	51.87

Specific reaction rate, $k_2 = 1/2 \times \text{Slope} = 9.1 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$

∴ Rate of production of iodine = $k_2 [\text{S}_2\text{O}_8^{2-}] [\text{I}] = 18 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$

Table 2: Kinetics of iodination of p-cresol: Rate of production of iodine at various temperature and pH

Concentration of iodine : $2.0 \times 10^{-2} \text{ M}$

Concentration of persulphate : $2.0 \times 10^{-2} \text{ M}$

Sr. No.	Temperature /		Rate of production of iodine/ 10 ⁻⁵ M ⁻¹ s ⁻¹		
	t/°C	T/K	pH=5.40	pH=7.19	pH=8.18
1	22	295	4.2	13.8	21.6
2	25	298	7.8	18.0	22.2
3	29	302	7.8	31.2	28.2
4	32	305	9.0	30.0	30.0

Table 3: Kinetics of iodination of p-cresol: Redox potential of iodine/iodide system of various temperature and pH

Concentration of p-cresol : 2.0×10^{-3} M

Sr. No.	Temperature		Redox potential of iodine/iodide system/ mV		
	t/°C	T/K	pH=5.40	pH=7.13	pH=8.18
1	22	295	247	290	324
2	25	298	333	325	313
3	29	302	364	350	342
4	32	305	374	354	312

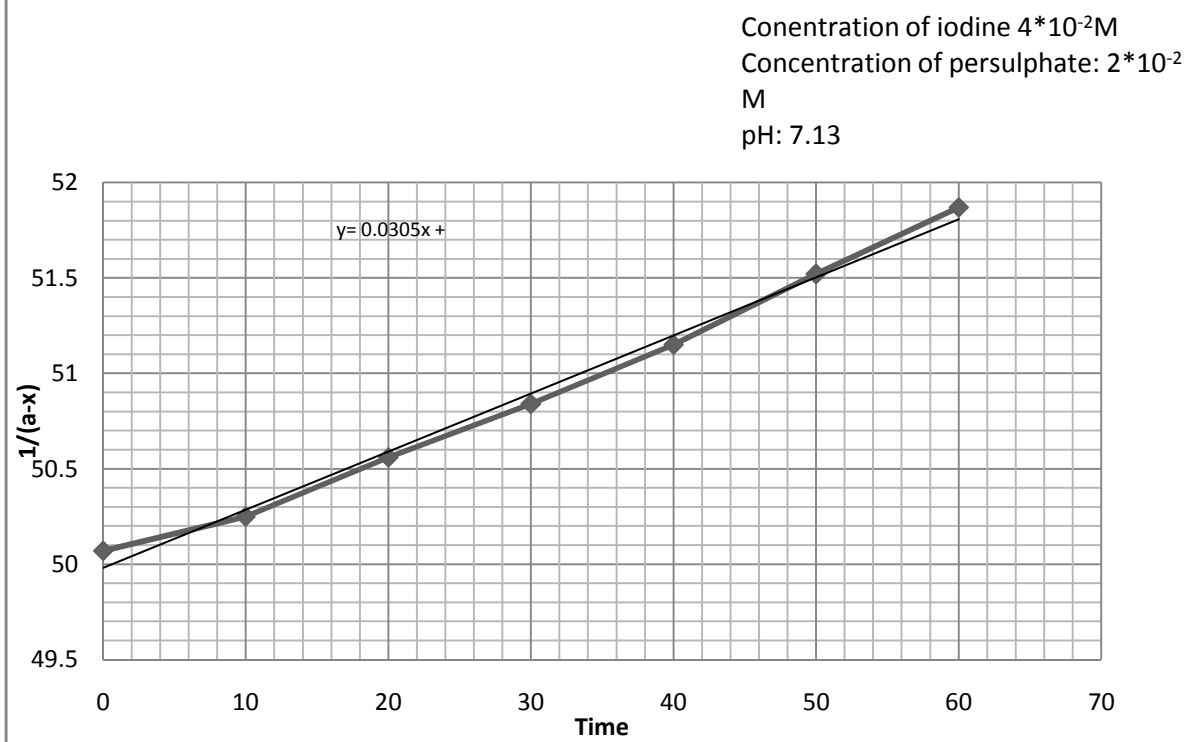
Table 4: Kinetics iodination of p-cresol: effective concentration of iodine, $[I_3^-]^*$

Sr. No.	Concentration of iodine/M	Temperature		Effective concentration of iodine, $[I_3^-]/M$		
		t/°C	T/K	pH=5.40	pH=7.13	pH=8.18
1	2.00×10^{-3}	22	295	0.929	1.214	4.215
2	3.00×10^{-4}	25	298	1.081	1.203	1.467
3	4.00×10^{-5}	29	302	0.937	1.250	0.913
4	5.00×10^{-6}	32	305	0.917	0.945	0.947

Table 5: Kinetics of iodination of p-cresol: specific reaction rate

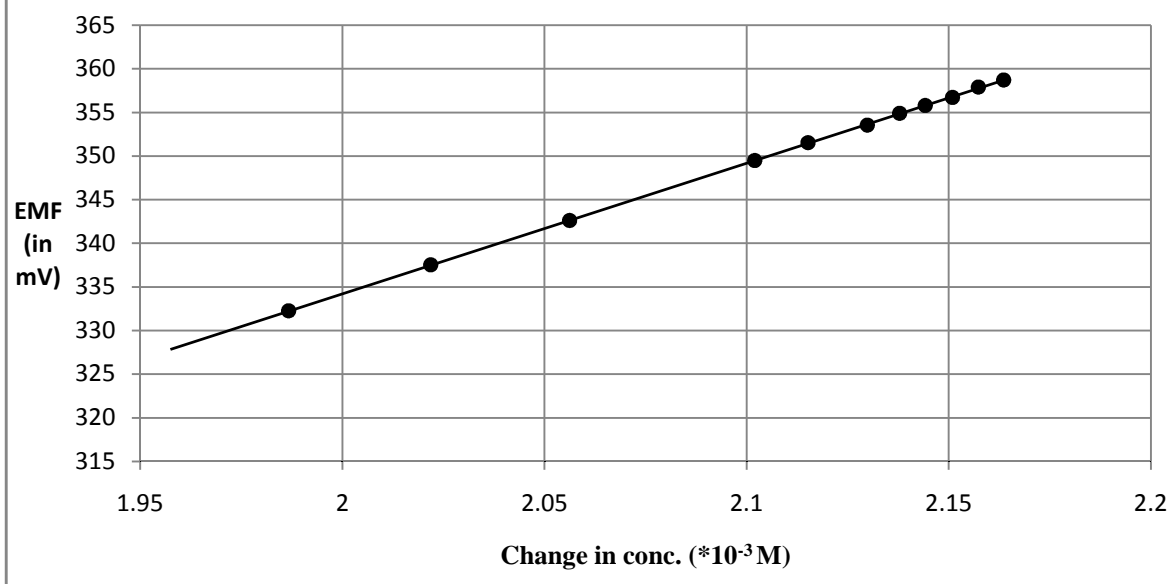
Sr. No	Temperature		Specific reaction rate, $k/10^{-2} M^{-1} S^{-1}$			Energy of activation $E_a, J/mole$		
	t/°C	T/K	pH=5.40	pH=7.13	pH=8.18	pH=5.40	pH=7.13	pH=8.18
1	22	295	2.26	5.68	3.00	30	40	50
2	25	298	3.61	7.48	9.61			
3	29	302	4.16	12.48	11.00			
4	32	305	5.51	15.87	15.80			

Fig 1: Kinetics iodination of p - cresol : measurment rate of produce

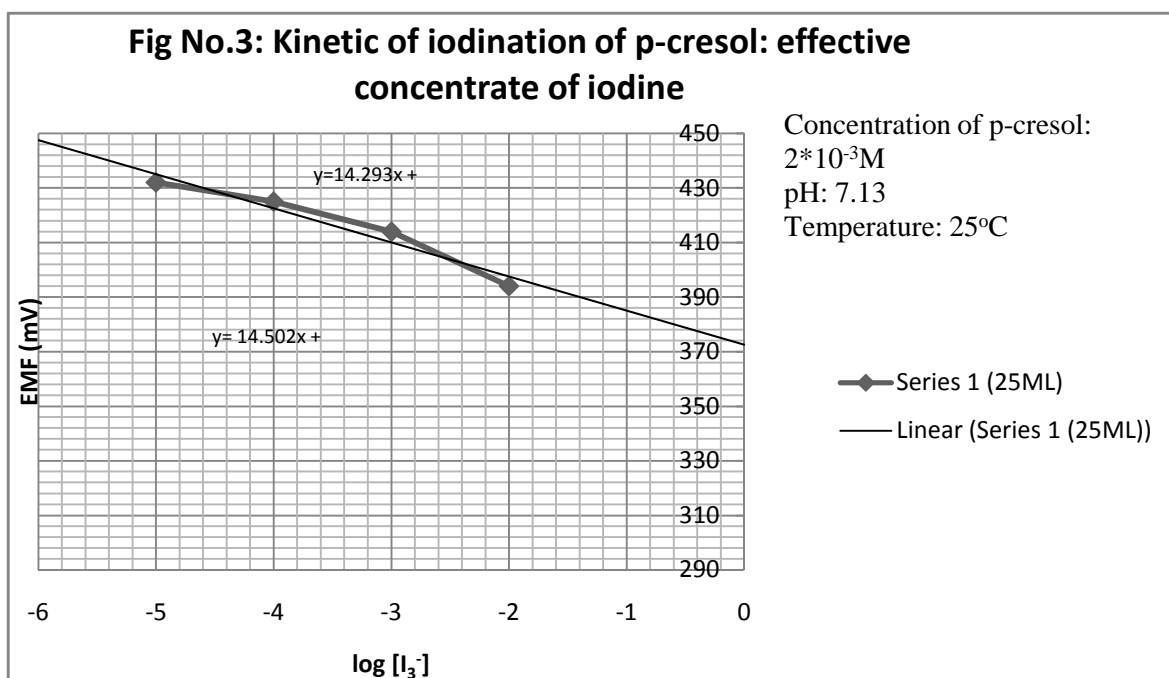


Slope=0.030

Fig 2: Kinetics of Iodination of P - cresol: Redox potatial and iodine/iodide system



Redox Potential = 325 mV



Effective concentration of iodine 1.209M

References:

1. Datin, Richard Clyde; Bromination of p-cresol in the presence of strong acids, Bachelor thesis, clifornia, Institute of technology (1972).
2. P.B.D. de la Mare, 'Electrophilic halogenation' Cambridge University Press, Cambridge (1976).
3. Bhore J. B., Dangat V. T., Bonde S. L. and Borkar V. T., Rapid kinetics of the regioisomers of cresol in aqueous medium by competition technique, *Int. Res. J. of sci. and Engg.*, 2(4), 142-144 (2014).
4. Teramote, Masaakin, M., Mgayaser Toshio, M. Mulsui Talsino, *J. Chem, Eng, Japan*, 2(2), 186-192 (1969)
5. Herve Gallard, Fabin Pellizzari, Jean Philippe Croue, B. Legube. Rate constants of reactions of Bromine with phenols in aqueous solution, 20 feb 2003
6. Bichel Y. Von-Gunten U. Formation of iodotrihalomethanes during disinfection and oxidation of iodide containing water, *Env-sci. Technol.*, 34, 2784-2791 (2000).
7. Rebenne L. M., Gonzakz A. C., Olson T. M., Aqueous chloronation kinetics and mechanism of substituted dihydroxybenzens., *Env. sci. Technol.*, 30, 2235-2242 (1996).
8. Gallard H., Von Gunten U. chlorination of phenols: Kinetics and formation of chloroform. *Env. sci. Technol.*, 36, 884-890 (2002).
9. Higuchi T., Hussain A., Mechanism of chlorination of cresol by chloromine-T. *chemical society-B, physical organic. Jan.* (1967).
10. Schutte, L. S, Havinga, E. *Tetrahedron*, 10, 2297-2304 (1970).
11. Jacquency J. C. Jouannetand, M. P. and Makani, S., *J. chem. Soc. Chem. Commun*, 110(1980).

12. Jacquicy J. C. and Jounnetand M. P., *Tetrahedron*, 37, 747 (1981).
13. Fischer, A. and Hunderson, G.N., *Can. J. chem.*, 57, 552 (1979).
14. Fischer, A. and Hunderson G. N., *J. chem. Soc. Chem. Commun.*, 1096(1979).
15. Brittain J. M., P. B. D. de la Mare and Newman, P. A., *Tetrahedron letters*, 4111 (1980).
16. Birch, A. J. Clark, J. W. Lewis and Roberson, A. V., *J. Chem. Soc.*, 3586 (1957).
17. "Halogenation of phenolic compounds," Karl Heinz Janzon, Grossauheim, Wolfgang Weigert, Germany Deutsche Goldund Silber, Germany field, June, 1 (1973), Appl. No: 365, 975.
18. Tee, O. S. , Iyengar, N. R. and Krous B., *J. org. chem.* 50, 973 (1985).
19. Tee, O. S., Iyengar N. R., *J. org. chem.*, 50, 4468(1985).
20. A) Tee, O. S. and Bennett, J. M., *J. Am. Chem. Soc.*, 110, 269, (1989).
B) Tee, O. S., Paventi, M. and Bennett, J. M., *J. Am. Org. chem.*, 111, 2233, (1989).
21. A) Tee, O. S., Iyengar N. R. and Paventi, M., *J. org. chem.*, 48, 759, (1983).
B) Tee, O. S., N. R. Iyengar, *J. Am.chem. soc.*, 107, 455, (1985).
22. Tee, O. S., N. R. Iyengar and Bennett, J. M., *J. org. chem. Soc.*, 51, 2585 (1956).
23. Tee, O. S. and Bennett, J. M., *J. Am. Chem. Soc.*, 110, 3226 (1988).
24. Tee, O. S. and Iyengar, N. R., *can J. chem.*, 65, 1714 (1987). And *Can. J. chem.*, 66, 1194, (1988).
25. Takasi, B. K. and Tee, O. S., *Can.J. chem*, 67, 193 (1989).
26. Tee, O. S. and Iyengar, N. R., " Kinetics and Mechanism of Bromination of phenol in aqueous solution Concordia University, April 5, (1990).
27. Naidu, A. B, Ganpathy, D. Sekar, G., *Synthesis*, 3509 (2010).
28. Rieke, R. D., Hanson, M. V., *Tetrahedron*, 53, 1925-1956, (1997).
29. Najera, C. Sansano, J. Yus. M., *Tetrahedron*, 59, 9255-9303 (2003).
30. Milne, J. E. Buchwalde, S. L., *J. AM. Chem. Soc.*, 126, 212 (2004).
31. Hernandas, M. Z. cavalcanti, S. M. T., Moreira, D. R. M., de Azevedo Jr. W. F., Leite, A. C. L, *current drug Forget*, 11, 3, 303-314 (2010).
32. Pinkston, K. E., Sedlak, D. L. *Environ. Sci. Technol.*, 38, 14, 4019-4023 (2004).
33. Seriven, E. F. V., Turnbull, K., *Chem. Rev.*, 88, 2, 13028-13082 (1988).
34. Larock, R. C., Lee, N. H., *J. org. chem.*, 56, 6253, (1991).
35. Joshi, S. N. Vyas, S. M., Wu Huimin, Duffel, M. W., Parkin, S., Lehmer. H. J., *Tetrahedron*, 67, 7461-7469(2011).
36. Bachi, A., Foubela, F., Yus., M. *Tetrahedron*, 50, 5139, (1994).
37. Kamidate, T. Mourya, M, Tani, H., Ishida, A. *Anal. Sci.*, 9, 1163-1166 (2009).
38. Chong, J. H. Kang, H. U. Jung, L. H., Cho, C. G., *org. let.*, 16, 2016 (2010).