ISSN: 2321-3132

Research Article

International Journal of Chemistry and Pharmaceutical Sciences

www.pharmaresearchlibrary.com/ijcps

Kinetics and Mechanism of Oxidation of Phenol by Imidazolium Fluorochromate in Aqueous Acetic Acid

S. N. Hallale[1], S.B. Patwari[2], Suresh D. Dhage[3], S. G. Patil[1]
[1]Dept. of Chemistry, Maharashtra Udayagiri Mahavidyalaya, Udgir- 413517 Dist. Latur (M.S.)
[2]Dept. of Chemistry, LBS College, Dharmabad. Dist. Nanded (M.S.) India
[3]Dept. of Chemistry, SSJES, Arts, Commerce and Science College, Gangakhed-431514, Parbhani (M.S.) India

Abstract

The Kinetics of Oxidation of phenol, m-methoxy phenol and m-Chloro phenol by Imidazolium Flurochromate in the presence of 50%. Acetic acid has been studied. The reaction rate shows first order kinetics with respect to phenol and IFC. The reaction rate increases with increase in [H^+]. Effect of ionic strength on the rate was found negligible. Decrease in dielectric constant increases the rate of reaction. From the Hamett Plot it was found that rate of reaction increases for electron donating substituent while decreases for electron withdrawing substituents. The effect of temperature on the rate has been studied and activation parameters were evaluated. On the basis of observed data, a suitable mechanism is proposed.

Keywords: Phenol, Oxidation, Imidazolium Flurochromate, Kinetics.

Contents

Received 15 December 2013
Accepted 18 January 2014
Available Online 27 January 2014

***Corresponding author**
S. N. Hallale
E-mail: snhallale@yahoo.com
Manuscript ID: PRL2014-IJCPS1963

PAPER-QR CODE

1. Introduction

A variety of halochromates such as pyridinium chlorochromate[1], pyridinium Flurochromate[2], quinolinium Flurochromate[3], quinolinium bromichromate[4], imidazolium flurochromate[5], etc. have been used for the study of oxidation of various organic substrates IFC is highly selective, mild and stable oxidizing agent. Kinetics of oxidation of Thioacids. Methyl Phenyl Sulphides, Benzaldehyde, Methionine, Diols, Oximes, Anilines by IFC was reported.[5-13] But literature survey reveals that, kinetics of oxidation of phenols by IFC has not yet reported. Therefore, in this article we report the kinetics of oxidation of phenol and some meta substituted phenols by IFC.

2. Materials and Methods

Experimental

All the chemicals used were of AR grade and Acetic Acid was purified by the method of Orton and Bradfield. All the stock solutions were prepared by dissolving known amount of samples in doubly distilled water. Imidazolium Flurochromate was prepared by the reported method[5] and purity was checked by iodometric method. The source of H^+ ions was perchloric acid (60% Merck). All the kinetic measurements were carried out at 303K. First of all, the reaction vessels were kept in thermostatic bath to attain the equilibrium. The reaction was carried out under pseudo first order conditions by keeping large excess of Phenol over IFC. The known volume of IFC was rapidly added to the reaction mixture containing phenol, perchloric acid and water. The progress of the reaction was followed potentiometrically by setting up a cell made up of reaction mixture in which the platinum electrode and reference electrode (SCE) were dipped[14]. The emf of the cell was measured after regular intervals of time by using equiptronics digital potentiometer. From the plots of log $(\text{emf})_{\text{time}}$ versus time, the pseudo first order rate constant were evaluated.

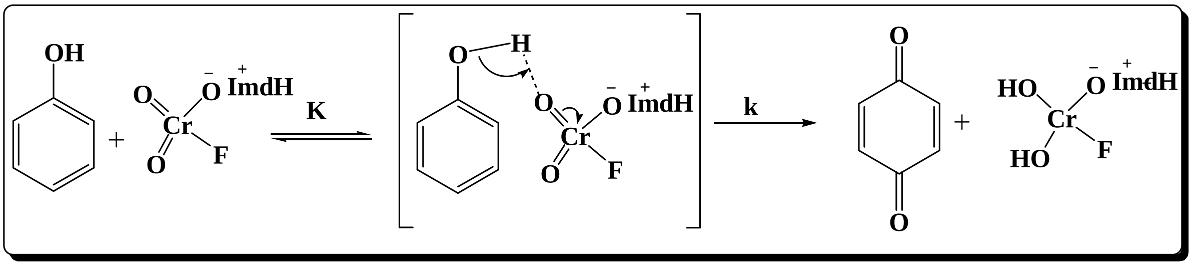
Stoichimometry and product analysis:

The stoichiometry of the reaction was determined by keeping known excess of IFC over substrates in 50% acetic acid and perchloric acid was added. The reaction mixture was kept for 48 hours to ensure the completion of the reaction. Estimation of the unconsumed IFC showed that one mole of phenol consumes one mole of IFC. The product analysis was made by monitoring TLC. The product was confirmed by noting the melting point of corresponding quinine (M P-112^{0}C -114^{0}C) and compared with the authentic sample. Then the product obtained was mixed with the authentic sample and no change in the melting point was observed.

Mechanism

The reaction involves a direct transfer of hydride ion from O-H group to give an intermediate and decomposition of the intermediate in the second slow step. On the basis of experimental observations, the probable mechanism for the oxidation of phenol by IFC is suggested.

Possible mechanism



On the basis of the above mechanism, the rate law is Rate = Kk[Phenol][IFC][H^+]

Table 1: Effect of variation of [substrate], [IFC] and [$HClO_4$]

Acetic acid: H_2O (50:50), T = 303K

10^2[substrate] mol dm^{-3}	10^3[IFC] mol dm^{-3}	[$HClO_4$] mol dm^{-3}	10^4 k_{obs} s^{-1}		
			Phenol	m-OCH_3	m-Cl
2	2	1	2.72	3.19	2.42
4	2	1	4.89	4.97	4.23
6	2	1	7.00	7.21	6.18
8	2	1	9.94	10.31	8.84
10	2	1	14.44	14.96	12.90
10	2	0.75	9.67	10.24	8.89
10	2	0.50	6.53	6.92	6.01
10	2	0.25	4.35	4.70	4.00
2	4	1	2.82	3.12	2.40
2	6	1	2.79	3.16	2.43
2	8	1	2.80	3.14	2.42
2	10	1	2.75	3.20	2.45
10	02	1	14.50[a]	14.92[a]	12.94[a]
10	02	1	12.23[b]	12.62[b]	10.04[b]

a- Contain 0.001 mol dm^{-3} Acrylonitrile
b- Contain 0.0005 mol dm^{-3} $MnSO_4$

3. Results and Discussions

The kinetics of oxidation of phenol by IFC were studied at different initial concentrations of the substrate, IFC and $HClO_4$ by keeping all other concentrations constant.

Effect of [Substrate] :

The concentration of the substrate was varied in the range 2 x 10^{-2} to 10 x 10^{-2} mol dm^{-3}. It was found that increase in [Substrate] increases the rate of reaction. (Table 1). The plot of log k_{obs} versus log [substrate] was linear with slope = 0.933 (R^2= 0.9820) indicates the order of reaction with respect to substrate is one (Fig.1).

Effect of [Oxidant]:

The concentration of IFC was varied in the range 2 x 10^{-3} to 10 x 10^{-3} mol dm^{-3}. The plot of log E_t versus time was linear indicates the order in IFC is one. The pseudo first order rate constant computed by varying [IFC] were found constant (Table.1).

Effect of [$HClO_4$]:

At constant [substrate], [IFC], ionic strength, the effect of [H^+] was studied. Table 1 shows that the rate of reaction increases with increase in perchloric acid concentration. The plot of log k_{obs} versus log [H^+] was linear with slope equal to unity indicates the reaction is first order with respect to [H^+].

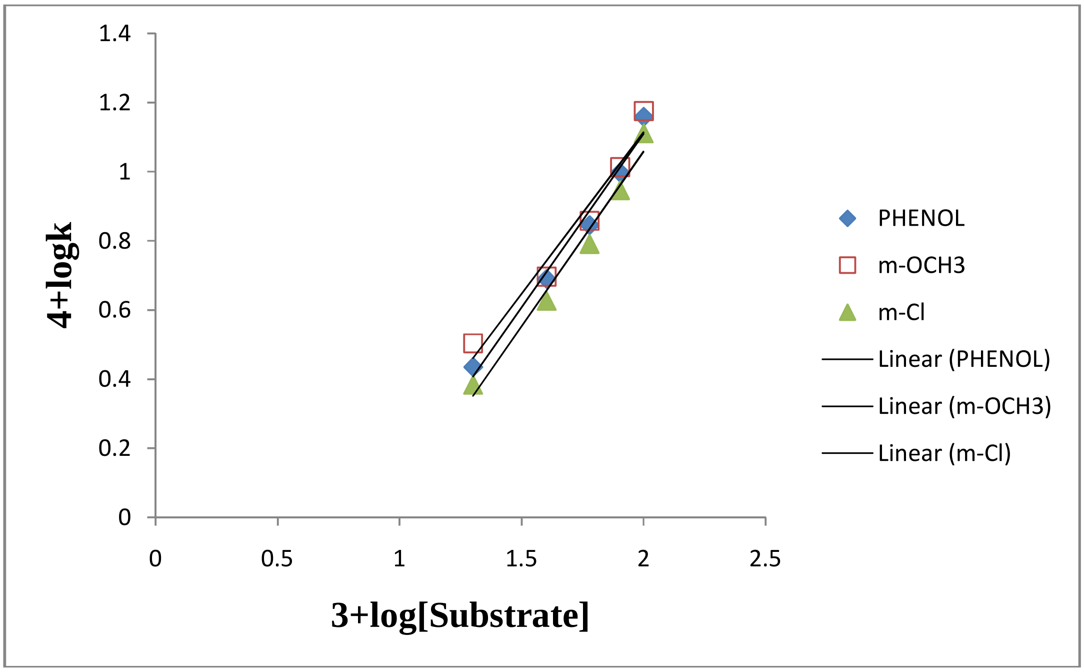


Figure.1

Effect of Salt:

The effect of salt was studied by varying [NaCl] sodium Chloride. The effect of increase in concentration of sodium Chloride on the rate of reaction was negligible

Effect of Solvent:

The reaction rate were determined at different % compositions of Acetic acid. Decrease in dielectric constant of the reaction medium increases the rate of reaction. (Table 2)

Table 2: Effect of solvent

10^2 [substrate] = 2 mol dm^{-3},
[$HClO_4$] = 1 mol dm^{-3}**,**
10^3 [IFC] = 2 mol dm^{-3}, T = 303K

% Acetic acid : Water	10^3 1/D	10^4 k_{obs} S^{-1}		
		Phenol	m-OCH_3	m-Cl
50 : 50	26.66	2.72	3.19	2.42
55 : 45	28.77	3.12	3.61	2.78
60 : 40	31.74	3.57	4.25	3.09
65 : 35	35.04	3.99	4.89	3.52
70 : 30	37.03	4.59	5.62	3.87

Effect of Temperature:

The effect of temperature on the rate of reaction were studied in the temperature range 303K to 318K by keeping the concentration of all reactants constant. The various activation parameters were evaluated from the plot of log k_2 versus 1/T K^{-1} (Fig.2)

The second order rate constants were obtained as $k_2 = k_{obs}$ / [Phenol] (Table. 3)

Table 3: Effect of temperature and activation parameters at 303 K

10^2 [substrate] = 10 mol dm^{-3} [HClO4] = 1, mol dm^{-}3, 103 [IFC] = 2 mol dm^{-3}

Temperature K	10^2 k_2 dm^3 mol^{-1}s^{-1}		
	Phenol	m-OCH_3	m-Cl
303	1.44	1.49	1.29
308	2.16	2.25	2.06
313	3.28	2.87	3.34
318	4.99	3.60	5.45
E_a KJ mol^{-1}	67.24	47.05	77.95
$\Delta H^{\neq}$ KJ mol^{-1}	64.70	45.77	75.41
$-\Delta S^{\neq}$ J mol^{-1}	67.74	136.68	3.87
$\Delta G^{\neq}$ KJ mol-1	27.16	87.79	84.76
A	5.6×10^9	1.9×10^6	1.41×10^{12}

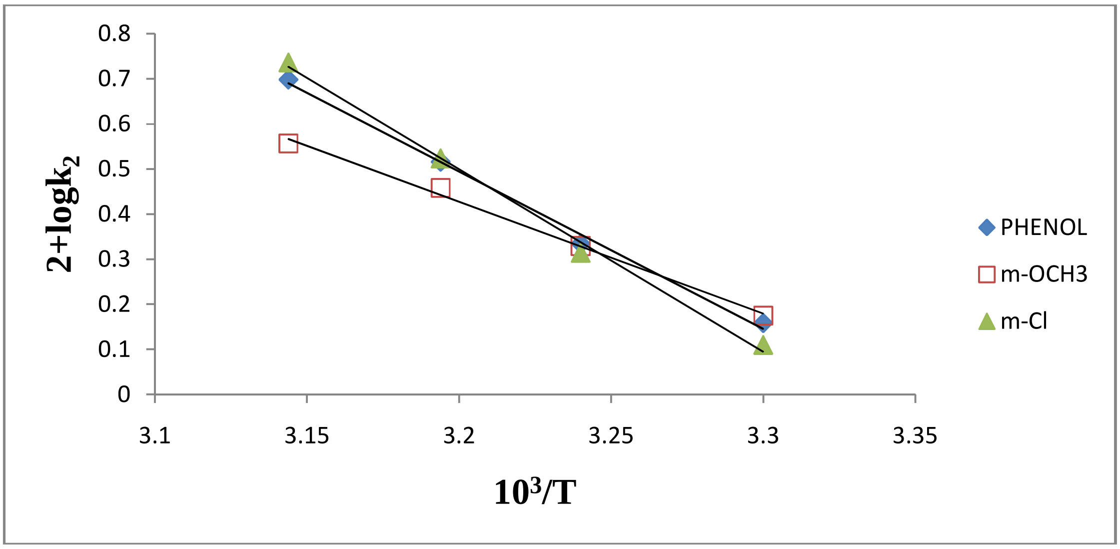


Figure.2

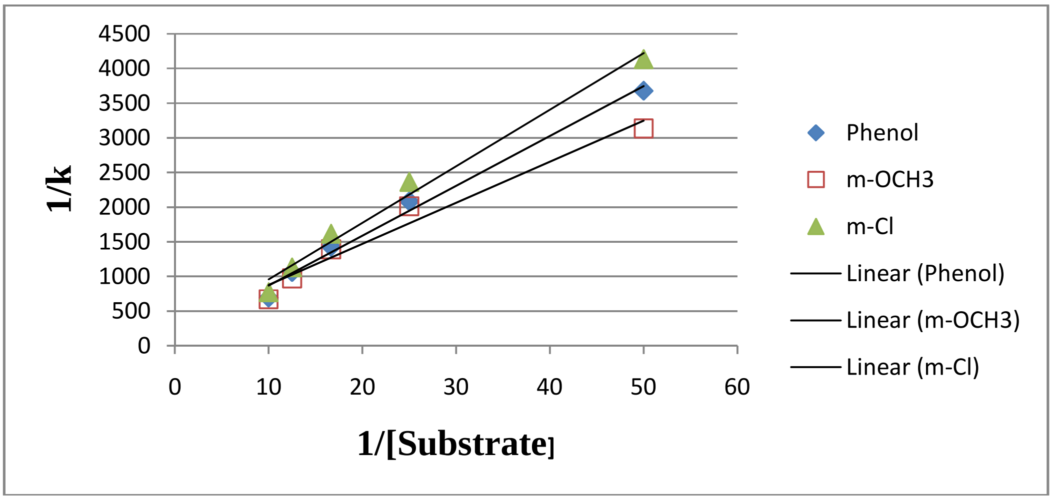


Figure.3

Discussion:

From the observed data it concludes that the reaction follows first order Kinetics with respect to IFC, Phenol and Acid. The plot of $1/k_{obs}$ versus 1// [substrate] was a straight line with positive intercept(**Fig:3**) suggest that the reaction proceeds with the formation of the complex between oxidant and substrate and follows the Michaelis-Menten mechanism. Increase in rate of reaction with decrease in dielectric constant suggests that the reaction is of ion-dipole type[15]. The effect of ionic strength was negligible and indicates the involvement of neutral molecule in the rate determining step.[16] The rate of reaction increases with increase in an acid strength suggested the involvement of protonated Cr (V1) in the rate determining step.[17]

From the activation parameters, the high negative values of the entropy suggests that the transition state is more ordered than the reactants due to increase in solvation. The high values of free energy of activation and enthalpy of activation suggests that highly solvated transition state is existed. The Exner plot of log k_2(308K) versus logk_2(303K) was linear ($R^2=0.944$) and the isokinetic temperature evaluated was 315.52K.[18] This suggests that the decomposition of Michaelis- Menten complex follows the similar mechanism for all phenols. The Hamett plot of logk versus σ is linear with a slope as reaction constant $\rho = -0.142$ indicates that the electron releasing substituent enhances the rate while electron withdrawing substituent retards the rate.[19] The order of reactivity is m-O CH_3 > H > m – Cl. The rate of reaction remains unaffected by the addition of acrylonitrile and suggests the absence of free radical mechanism. The rate of reaction was retarded by the addition of Mn (II) which suggests two electron transfer in the reaction. Further similar values of free energy of activation suggests that the similar mechanism is operative for all phenols.

4. Conclusion

The reaction between IFC and phenol follows the first order dependence on IFC, phenol and H^+. Increase in the percentage of acetic acid increases the rate of reaction. The reaction is acid catalyzed and has stoichiometry 1:1. The reaction yields corresponding quinones. The rate of reaction increases for electron releasing substituent whereas retards for electron withdrawing substituents. The negative $\Delta S^{\neq}$ gave support to the formation of highly ordered transition state. Almost similar $\Delta G^{\neq}$ values suggests that similar mechanism is operative for all phenols.

5. References

1. Corey E. J. and Boger D.L., Tetrahedron Lett. 28, 1978, 2461
2. Bhattacharjee M N Choudhari M K Dasgupta H S Rou N & Khating D T, synthesis, 1982, 588.
3. Pandurangan A, Murugesan V oxidation communi 1997, 20, 93.
4. Dhariwal V, Yajurvedi D and Sharma P K Indian J chem., 2006, 45 A 1158.
5. A Panduranga, G.A. Rajkumar, B Arabindaoo, V Murugesan, Indian J Chem, 38 B (1999) 99.
6. Bincy John, M. Pandeeswaran, D S Bhuvaneshwari and K P Elango J serb Chem Soc 71 (1) 2006, 19.
7. D S Bhuvaneshwari and K P Elango J ind chem. Soc 86, 2009, 242.
8. D Sharma, P Panchariya, Shweta Vyas, Int J of Chem 2012 1(1) 29-37.
9. Deepika Baghmar, Pryanka Purohit, Shweta Vyas and Vinita Sharma, Int J Current Chem 2(1) 2011 9-18.
10. Monica Gehilot, Mamta Gilla, PTSRK Prasad Rao and Vinita Sharma,- Int. J. Chem. Sci. 8(3) 2010. 1943-52.
11. NMI Alhaji, A Shajahan and G K Ayyadurai- Chem. Sci. Trans. 2(2) 2013, 429-434.
12. Basim Asgar, S Sheik Mansoor, V Saleem Malik- Euro. Chem. Bull 2(8), 2013,538-544.
13. D Baghmar, P Purohit, S Vyas and Vinita Sharma J, Ind. Coun. Chem. 27(2), 2010, 134-139
14. N Mathiyalagan, V. Priya and John Bosco, J Ind. Chem. Soci. 86, 2009, 453-457.

15. E S Amis “solvent effect on reaction rates and mechanism” Academic press New York 1967, 42.
16. Palaniappan A N, Sekar K G and Ravishankar M, Oxidation Communication, 18, 52-57.
17. Banerjee K K, J Chem. Soc. Perkin Trans. 2, 1978, 639
18. O Exner, Collect Chem. Czech Commun. 31, 1966, 3222.
19. J Rajaram, J C Kuriacose, “Kinetics and Mechanism of Chemical Transformations” Macmillan India 1993, 393.
20. Ahmed Al , Ajlouni, Andreja Bakac and James H Espenson- Inorg. Chem. American Chemical Society 32, 1993, 5792-5796.
21. Reddy T S, Jagannadham V, Proce. Natl. Acad. Sci. India -56(A),1986, 129.
22. Banerjee K K, Bull. Chem. Soc. Japan 51, 1978, 2732
23. D S Bhuvaneshari and K P Ealango, J. Ind. Chem. Soc. 86, 2009, 24.