



A Comparative study of Kinetics of Oxidation of Phenol by Imidazolium Fluorochromate and 1-Methyl Imidazolium Fluorochromate in Aqueous Acetic acid

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Abstract

The Kinetic study of oxidation of phenol by imidazolium fluorochromate (IFC) and 1- methyl imidazolium fuorochromate (MFC) in 50 % acetic acid has been made. The reaction shows first order dependence on the both IFC and MFC. The rate of reaction rate was found to be higher in the presence of MFC than IFC. The reaction rate was not affected by the addition of sodium chloride. The effect of temperature on the rate has been studied at four different temperatures and activation parameters were evaluated.

Keywords: Phenol, Oxidation, IFC, MFC.

Introduction :

Halochromate compounds were used for the selective oxidation of different organic substrates and is one of the thrust area of research in chromium (VI) chemistry¹⁻⁷. Imidazolium Chlorochromate⁸ and Imidazolium Fluorochromate⁹ are developed as new reagents for the oxidation alcohols. IFC is an efficient oxidizing agent than ICC and can be used to minimize the existing difficulties encountered in the oxidation of organic compounds by chromium (VI) based oxidants. IFC is soluble in water, acetone, DMF, DMSO, acetic acid and acetonitrile. IFC is less hygroscopic mild and quite stable oxidizing agent as compared to our newly reported 1- methyl Imidazolium fluorochromate at room temperature. Kinetics of oxidation of thioacids, methyl phenyl sulphides, benzaldehyde, methionine, diols, oximes, anilines by IFC was reported¹⁰⁻¹⁶.

In the present study, we report the comparative study of kinetics of oxidation of phenol by Imidazolium fluorochromate and 1-Methyl Imidazolium Fluorochromate in aqueous acetic acid medium.

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 Fluorochromate was prepared by the reported method⁵ and by using the 1-methyl imidazole, we have synthesized 1-methyl imidazolium fluorochromate and purity was checked by iodometric method.

The kinetic measurements were carried out at 303K. Initially 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 the oxidant. The known volume of oxidant was rapidly added to the reaction mixture containing phenol, perchloric acid and water. The progress of the reaction was monitored potentiometrically by setting up a cell made up of reaction mixture in which the platinum electrode and reference electrode (SCE) were dipped¹⁷. The emf of the cell was measured after regular time intervals by using equipronics digital potentiometer. The pseudo first order rate constant were evaluated from the plot of $\log(\text{emf})_{\text{time}}$ versus time.

Stoichiometry and product analysis:

The product analysis of the Phenol - IFC reaction is made. Phenol (0.01 mol) was dissolved in acetic acid (10 ml), IFC in acetic acid (0.01 mol) was added and the reaction mixture was refluxed for 2 hours. After evaporation of the solvent, mixture was extracted with ether. The obtained product was confirmed by TLC, melting point and spectral analysis. The structures of the compound were confirmed by taking melting point and mixed melting point with authentic sample prepared by known methods (M P 114-116 ° C).

The oxidation of phenol by IFC yields 1,4 - benzoquinone. Isolation of the product is carried out under kinetic conditions also by keeping large excess of phenol over IFC.

In a vessel, phenol (0.05 mol) and oxidant (0.01 mol) were made upto 50 ml in acetic acid and kept in dark for 15 h to ensure completion of the reaction. The solution was then treated with an excess of (150 ml) a saturated solution of 2, 4 - dinitrophenyl hydrazine in 2 M hydrochloric acid and kept overnight in a refrigerator. The precipitated 2, 4 - dinitrophenyl hydrazone (DNP) was filtered off, dried, weighed and re-crystallized from ethanol and weighed again. The yields of the DNP before and after re-crystallization were 86 % and 73 % respectively. The DNP was found to be identical (M P and mixed M P) with DNP of benzoquinone. The stoichiometry of the reaction was determined by taking large excess of [oxidant] over [phenol]. A mixture of phenol (0.02 mol), oxidant (0.04 mol), HClO₄ (0.1 mol) was made upto 50 ml with water - acetic acid mixture 50 %. After the completion of the reaction, the excess of oxidant was determined iodometrically and gives 1 mol of phenol reacts with 1 mol of oxidant (1 : 1).

Result and Discussion:

The data of the kinetics of oxidation of phenol by IFC and MFC at different initial concentrations of the substrate in the presence of HClO₄ by keeping all other concentrations constant are discussed below.

Effect of [phenol]:

The effect of concentration of the phenol on the rate of reaction was studied by varying the concentration of phenol in the range 2×10^{-2} to 10×10^{-2} mol dm⁻³ at fixed [IFC], [H⁺] and constant temperature.

It was found that an increase in [phenol] increases the rate of reaction (Table 1). The plot of $\log k_{\text{obs}}$ versus \log [phenol] was linear with slope = 0.978 **fig 1**(IFC) and slope = 0.8625 **fig 2**(MFC) shows first order dependence with respect to phenol.

Effect of [oxidant]:

At fixed $[H^+]$ and by keeping substrate in excess, the effect of change of oxidant concentration on the rate of reaction were studied by varying the concentration of oxidant in the range 0.002 to 0.01 mol dm⁻³. The plot of $\log E_t$ versus time was found to be linear suggests that the reaction shows first order dependence on oxidant. The pseudo first order rate constant evaluated were found constant.

Effect of [HClO₄]:

The effect of added perchloric acid on the pseudo first order rate constant was studied at fixed [substrate], [IFC], ionic strength. Table 1 shows that there is an increases rate of reaction with increase in [HClO₄] suggests that the highly reactive protonated IFC in the reaction¹⁸.

Table 1: Effect of variation of [phenol] on the rate of oxidation

Acetic acid: H₂O (50:50)

[Oxidant] = 0.002 mol dm⁻³

[HClO₄] = 0.02 mol dm⁻³

T = 303K

10 ² [substrate] mol dm ⁻³	10 ⁴ k _{obs} s ⁻¹	
	IFC	MFC
2	2.68	3.45
4	4.98	6.14
6	7.67	8.06
8	9.97	10.74
10	13.05	14.58

Fig:1 Plot of log k v/s log [phenol] for IFC oxidation of phenol

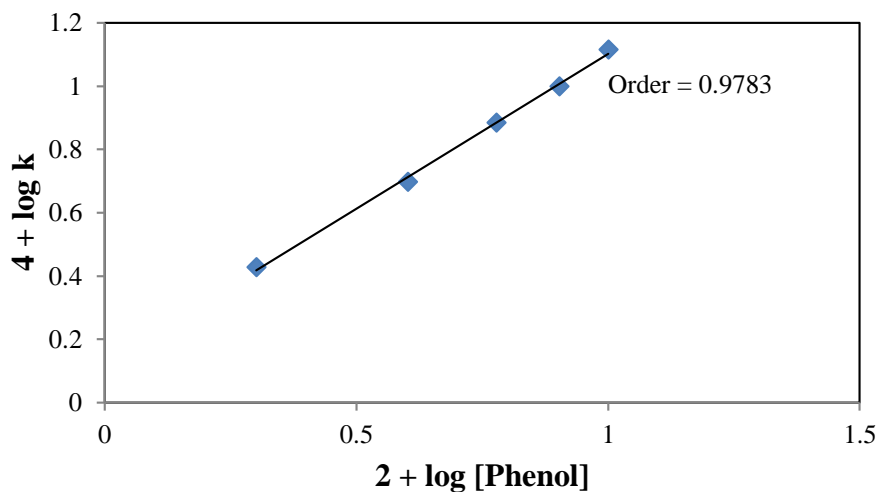
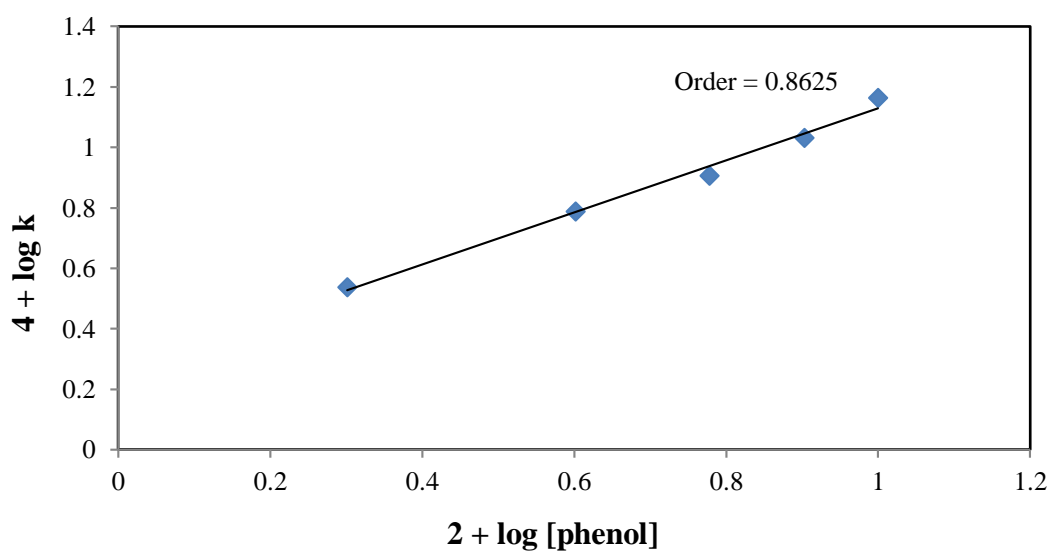


Fig 2 : Plot of log k v/s log [phenol] for MFC oxidation of phenol



Effect of ionic strength:

The effect of ionic strength of the medium was studied by varying [NaCl]. An increase in concentration of NaCl does not affect the rate of reaction. This is an indication of the involvement of neutral molecule in the rate determining step¹⁸.

Table 2:

Effect of temperature on the rate of reaction

[substrate] = 0.02 mol dm⁻³

[HClO₄] = 0.02 mol dm⁻³

[oxidant] = 0.002 mol dm⁻³

% Acetic acid : Water = 50 : 50

Temperature	10 ⁴ k _{obs} s ⁻¹	
	IFC	MFC
303	0.9595	3.45
308	1.573	5.37
313	2.379	7.29
318	3.416	9.59

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 rate of reaction was found to be increases with an increase in temperature. The activation parameters were calculated from the plot of log k₂ versus 1/T K⁻¹. **Fig: 3 and 4**

The second order rate constants were obtained as

k₂ = k_{obs} / [Phenol] (Table 3)

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

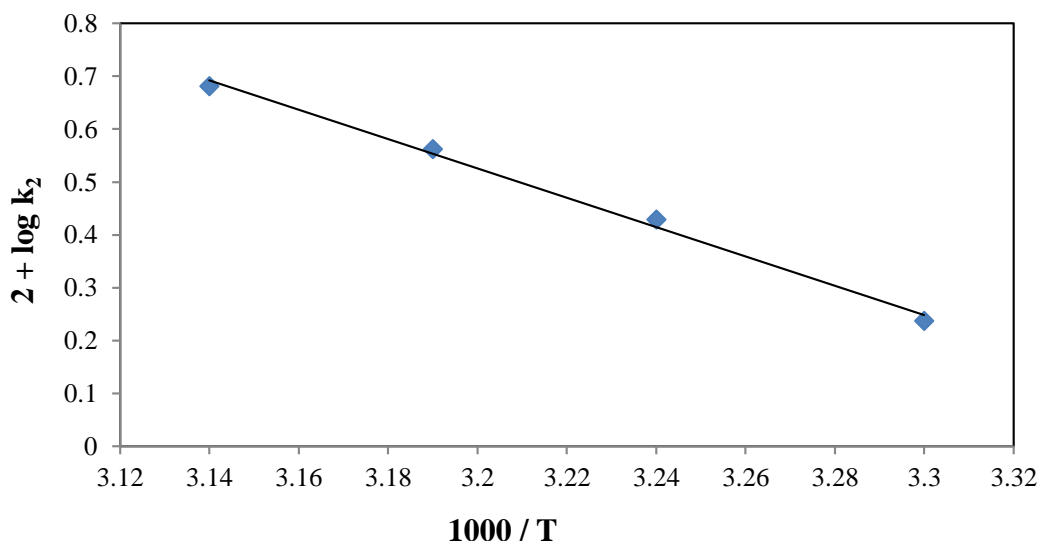
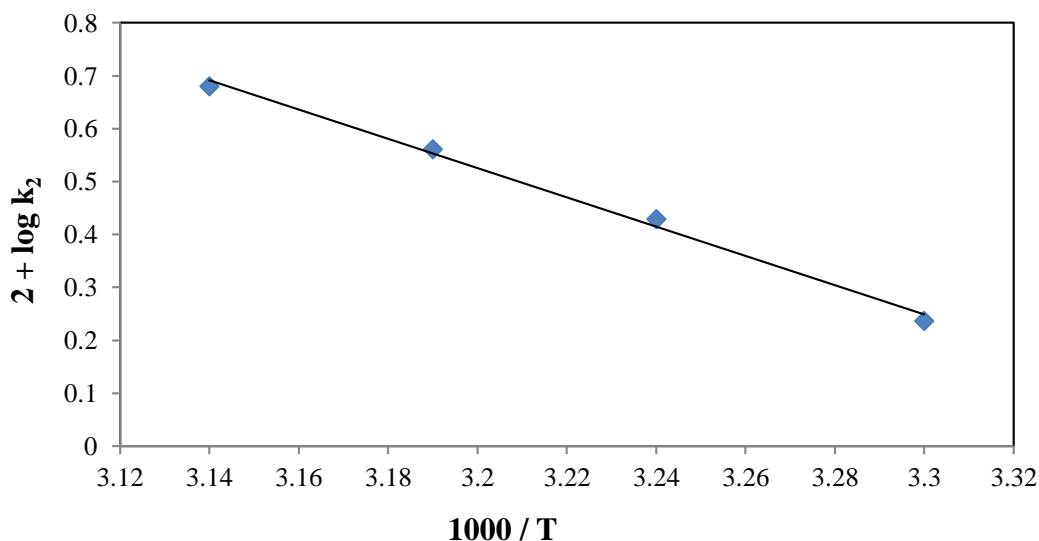
[substrate] = 0.02 mol dm⁻³

[HClO₄] = 0.02 mol dm⁻³

[oxidant] = 0.002 mol dm⁻³

Acetic acid : Water = 50 : 50

Temperature K	10 ² k ₂ dm ³ mol ⁻¹ s ⁻¹	
	IFC	MFC
303	0.479	1.72
308	0.786	2.68
313	1.189	3.64
318	1.708	4.29
E _a KJ mol ⁻¹	58.03	52.54
ΔH [‡] KJ mol ⁻¹	55.78	50
-ΔS [‡] J mol ⁻¹	103.62	110.35
ΔG [‡] KJ mol ⁻¹	87.18	83.44
Log A	7.73	7.27

Fig 3: Plot of $\log k_2$ v/s $1/T$ for the effect of temperature on rate constant of Phenol by IFC**Figure 4: Plot of $\log k_2$ v/s $1/T$ for the effect of temperature rate constant of Phenol by MFC****Discussion:**

The activation parameters were calculated from the plot of $\log k_2$ versus $1/T$. It is observed that the higher energy of activation in the presence of IFC than in the presence of MFC indicates the reaction proceeds with higher rate in the presence of MFC. The entropy of activation is an indication of the ease of the formation of the activated complex and proceeds in more ordered manner in the presence of MFC. The factors like relative orientation of the atoms in the transition state, bulk of the transition state and solvation of the transition state

compared to the reactants influences the entropy of activation. As charge density on the surface in the transition state will be more results into an increase in solvation leading to negative ΔS^\ddagger . The reaction is little faster in the presence of MFC may be due to more electron density at the reaction centre in the later case.

Further, the results suggested that the entropy of activation depends upon the nature of the substrate and solvent. The results shows that the value of ΔS^\ddagger depends upon the nature of the substrate and solvent and the reason may be due to the fact that the dependence of solvation upon various factors like cavity produced by the dissolved molecules in the solvent, the orientation of molecules and intermolecular forces. So, the magnitude of ΔS^\ddagger may be due to the combination of one or more factors.

The negative values of ΔS^\ddagger suggests that the solvent molecules are strongly oriented or frozen around the ions¹⁹ and indicated a greater degree of ordering in the transition state than in the initial state, as due to increase in solvation during the activation process²⁰. This also give the reason for the decrease in the rate coefficient values with increase in the polarity of the medium. Hence, in the present study, solvent interactions play a significant role in addition to the solute-solvent interactions in governing the rate of reaction.²¹

Conclusion

The reaction between oxidant and phenol follows the first order dependence of the rate on oxidant and phenol. The rate of reaction increases in the presence of MFC than IFC. The reaction is acid catalyzed and has stoichiometry 1:1. The oxidation of phenol yields 1,4- benzoquinone. The negative ΔS^\ddagger gave support to the formation of highly ordered transition state. ΔG^\ddagger values were found nearly same suggests the operation of similar mechanism²².

On the basis of the above data, the rate law is

$$\text{Rate} = Kk[\text{phenol}][\text{oxidant}][\text{H}^+]$$

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