Oxidation of Naphthol by Imidazolium Fluorochromate in Aqueous Acetic Acid: A Kinetic Study

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ABSTRACT

The Kinetic study of Oxidation of 1-Naphthol and 2-Naphthol by Imidazolium Fluorochromate in 50% Acetic acid has been made. The reaction shows first order dependence on IFC and order of reaction with respect to phenol was found to be one. The rate of reaction rate was found to be increased with an increase in concentration of perchloric acid and the order of reaction with respect to [HClO₄] was found to be nearly one. The reaction rate was not affected by the addition of sodium chloride. Decrease in the polarity of the medium increases the rate of reaction. The effect of temperature on the rate has been studied at four different temperatures and activation parameters were evaluated.

Keywords: Naphthol, Oxidation, Imidazolium, Fluorochromate, Kinetics.

1. INTRODUCTION

Synthesis of halochromate compounds for selective oxidation of organic substrates is one of the main thrust area of research in chromium (VI) chemistry [1-7]. Imidazolium chlorochromate[8] and Imidazolium flurochromate[9] are developed as new reagents for the oxidation alcohols. IFC is more efficient 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 at room temperature. Kinetics of oxidation of Thioacids, Methyl Phenyl Sulphides, Benzaldehyde, Methionine, Diols, Oximes, Anilines by IFC was reported [10-16].

In the present study, we report the kinetics of oxidation of 1-naphthol and 2-naphthol by IFC in aqueous acetic acid medium.

2. 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 perchloric acid (60% Merck) was used to study the effect of acid strength on the rate of reaction.

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 naphthol over IFC. The known volume of IFC was rapidly added to the reaction mixture containing naphthol, 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 [17]. The emf of the cell was measured after regular intervals of time by using equiptronics digital potentiometer., the pseudo first order rate constant were evaluated from the plot of log (emf)time versus time.

2.1. Stoichimometry and product analysis

The product analysis of the naphthol IFC reaction is made. Phenol (0.01M) was dissolved in acetic acid (10 ml), IFC in acetic acid (0.01Ml) 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-124^{0}C and 142^{0}C).

The oxidation of naphthol by IFC yields naphthoquinone. Isolation of the product is carried out under kinetic conditions also by keeping large excess of naphthol over IFC.

In a typical experiment, naphthol (0.05 mol) and IFC (0.01 mol) were made upto 50 ml in acetic acid and kept in dark for 15 hours 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 over night 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 naphthoquinone.The stoichiometry of the reaction was determined by taking large excess of [IFC] over [phenol]. A mixture of naphthol (0.02 mol), IFC (0.04 mol), $HClO_4$ (0.1 mol) was made upto 50 ml with water – acetic acid mixture 50 %. After the completion of the reaction, the excess of IFC was determined iodometrically and gives 1 mol of naphthol reacts with 1 mol of IFC (1 : 1). FT-IR (KBr) : 3364, 2631, 1627, 1585, 1230, 1157, 922 cm^{-1}

3. RESULT AND DISCUSSION

The data of the kinetics of oxidation of 1-naphthol and 2-naphthol by IFC at different initial concentrations of the substrate, IFC and $HClO_4$ by keeping all other concentrations constant are discussed below.

3.1. Effect of [Naphthol]

The effect of concentration of the Naphthol on the rate of reaction was studied by varying the concentration of Naphthol 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 [Naphthol] increases the rate of reaction. (Table 1). The plot of log k_{obs} versus log [Naphthol] was linear with slope = 0.9834 (R^2= 0.9700) indicates the order of reaction with respect to naphthol is nearly one (Figure 1). The second order rate constants are constant supports the first order dependence on [Naphthol].

3.2. Effect of [IFC]

At fixed [H$^+$] and by keeping substrate in excess, the effect of change of IFC concentration on the rate of reaction were studied by varying the concentration of IFC in the range 2×10^{-3} to 10×10^{-3} 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 IFC. The pseudo first order rate constant evaluated were found constant. (Table 1).

3.3. Effect of [HClO$_4$]

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 [HClO$_4$] suggests that the highly reactive protonated IFC in the reaction. The plot of log k_{obs} versus log [H$^+$] was linear with slope around one i.e.0.74 indicates that the reaction is first order with respect to [H$^+$] figure 2.

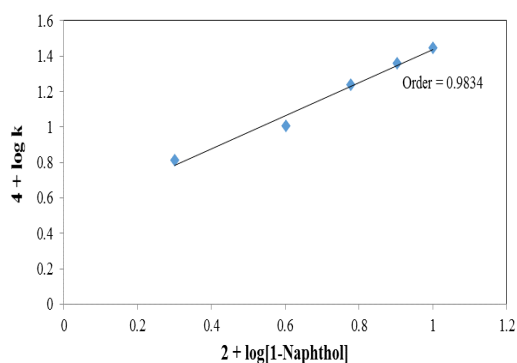| Table - 1: Effect of variation of [Naphthol], [IFC] and [HClO$_4$]				
10^2[substrate] mol dm^{-3}	10^3[IFC] mol dm^{-3}	10^2[HClO$_4$] mol dm^{-3}	10^4 k$_{obs}$ s^{-1}	
			1-Naphthol	2-Naphthol
2	2	2	6.52	4.14
4	2	2	10.20	8.55
6	2	2	17.38	10.40
8	2	2	22.91	14.31
10	2	2	27.98	16.96
2	2	0.5	2.42	1.42
2	2	1	4.22	2.61
2	2	1.5	5.75	3.07
2	4	2	6.98	3.64
2	6	2	7.29	3.53
2	8	2	6.67	3.72
2	10	2	6.52	3.87
Acetic acid: H$_2$O (50:50) T = 303K.				

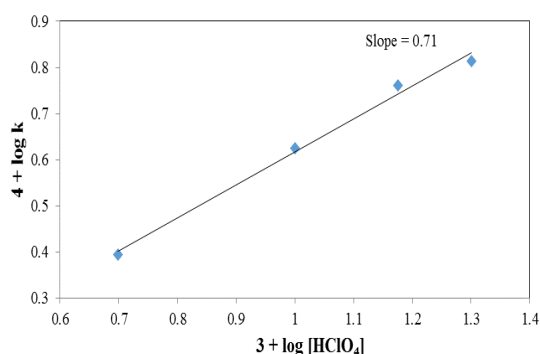**Figure -1: Effect of [Naphthol].**

Figure -2: Effect of [HClO$_4$].

3.4. 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 step.

Table - 2: Effect of Dielectric constant of the medium on the rate of reaction.

% Acetic acid : Water	10^3 1/D	10^4 k_{obs} S^{-1}	
		1-Naphthol	2-Naphthol
50 : 50	26.66	6.52	4.14
55 : 45	28.77	9.48	4.26
60 : 40	31.74	10.05	4.45
65 : 35	35.04	11.20	5.52
70 : 30	37.03	12.28	6.67

[substrate] = 0.02 mol dm^{-3} [HClO$_4$] = 0.02 mol dm^{-3}, [IFC] = 0.002 mol dm^{-3}, Temperature = 303K

3.5. Effect of Solvent Composition

The effect of variation in the solvent composition on the pseudo first order rate constant was studied at fixed [Naphthol], [IFC] ,[HClO$_4$] and 303K temperature. The rate of reaction was determined at different percentage composition of Acetic acid. It was found that the

rate of reaction increases significantly with increase in the percentage of Acetic acid. This suggests that decrease in polarity of the reaction medium increases the rate of reaction. (Table 2) A plot of log k against 1/D was linear with positive slope indicates that there is involvement of reaction between ion and molecule figure 3.
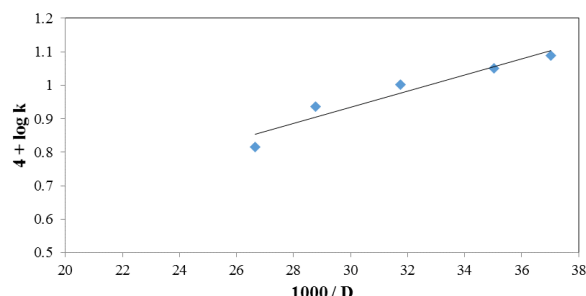

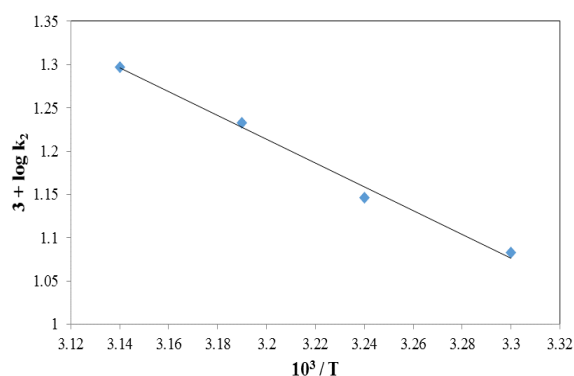**Figure - 3: Effect of dielectric constant.**

Figure - 4: Effect of Temperature.

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

Temperature K	10^2 k_2 dm^3 mol^{-1}s^{-1}	
	1-Naphthol	2-Naphthol
303	1.20	0.71
308	1.40	0.86
313	1.70	1.15
318	1.95	1.53
E$_a$ KJ mol^{-1}	26.26	41.68
ΔH$^{\neq}$ KJ mol^{-1}	23.75	39.16
-ΔS$^{\neq}$ J mol^{-1}	200.05	153.55
ΔG$^{\neq}$ KJ mol-1	84.36	85.69
Log A	2.61	5.04

10^2 [substrate] = 2 mol dm^{-3}, 10^3 [HClO4] = 5 mol dm^{-3}, 10^3 [IFC] = 2 mol dm^{-3}

3.6. 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 k_2 versus $1/T$ K^{-1} (Figure 4).

The second order rate constants were obtained as

$$k_2 = k_{obs} / [Phenol] \text{ (Table 3)}$$

From the observed kinetic data, The activation parameters were calculated from the plot of log k_2 versus $1/T$. It is observed that the decomposition of Michaelis-Menten complex is neither iso-enthalpic nor iso-entropic but due to the compensation effect, gives an isokinetic relationship. The entropy of activation is an indication of the ease of the formation of the activated complex. 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 $\Delta S^{\#}$. Similar values of $\Delta G^{\#}$ suggests that the similar mechanism is operative in both cases.

As the reactions are of ion-dipolar type, it is expected that the entropy of the activated complex for both naphthol should be of the same order of magnitude but due to difference in the polarity of different naphthol, there is a difference in the extent of solvation and hence the values of entropy of activation may be different for different naphthols. Further, the results suggested that the entropy of activation depends upon the nature of the substrate and solvent. This may be due to the fact that the solvation depends upon various factors like cavity produced by the dissolved molecules in the solvent, the orientation of molecules and intermolecular forces. Therefore the magnitude of $\Delta S^{\#}$ may be due to the combination of one or more factors.

In the present study, the large negative values of entropy of activation suggests that the solvent molecules are strongly oriented or frozen around the ions thereby resulting in the loss of entropy [18].

As the rate of reaction increases with decrease in dielectric constant of the medium was seen, indicates that there is a reaction between an ion and dipole or molecule. The activated complex will have the same charge as that of the ion. And rate of reaction is more since the dipole is correctly oriented.

Negative value of entropy of activation further indicated that a greater degree of ordering in the transition state than in the initial state, as due to increase in solvation during the activation

process. In less polar solvent mixture, which have a small or no dipole moment, the solvent molecules will be relatively un-oriented and so have largest k values. Consequently can have higher values of entropy. This confirms that the decrease in polarity of the medium results in increase in entropy value and the number of unbound molecules in the solution increases [19].

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 plays a significant role in addition to the solute. Solvent interactions in governing the rate of reaction [20].

An increase in the percentage of acetic acid in acetic acid water mixture suggests that the transition state is less cationic (less polar) in nature when compared to the reactants and such a transition state is stabilized by a medium of lesser basicity. A plot of log k against reciprocal of dielectric constant of the medium is straight line with a positive slope indicates that the reaction between ion and dipole [21]. As the rate of reaction increases with decrease in dielectric constant of the medium was seen, indicates that there is a reaction between an ion and dipole or molecule. The activated complex will have the same charge as that of the ion. And rate of reaction is more since the dipole is correctly oriented.

4. CONCLUSION

The reaction between IFC and naphthol follows the first order dependence of the rate on IFC, phenol and perchloric acid. Decrease in polarity (dielectric constant) of the medium increases the rate of reaction. The reaction is acid catalyzed and has stoichiometry 1:1. The oxidation of naphthol yields corresponding naphthoquinones. The negative $\Delta S^{\neq}$ gave support to the formation of highly ordered transition state. An almost similar $\Delta G^{\neq}$ values suggest the operation of similar mechanism is for all phenols [22-24].

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

$$Rate = Kk[Naphthol][IFC][H^+]$$

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