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Research Article

OXIDATIVE DECOMPOSITION KINETICS OF BENZANILIDE BY IMIDAZOLIUM FLUOROCHROMATE

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ABSTRACT

The kinetics of oxidation of benzanilide by imidazolium fluorochromate (IFC) has been studied in 65% water - 35% acetic acid medium. The reaction is first order with each in imidazolium fluorochromate and hydrogen ion concentration. The reaction is second order with respect to benzanilide.The rate of the reaction increases with decrease in dielectric constant of solvent suggests ion-dipole interaction. Increase in ionic strength by the addition of sodium perchlorate has no effect on the rate of the reaction. There is no polymerization with acrylonitrile and absence of free radical mechanism was proved. Azobenzene has been identified as a main product of oxidation. The rate of the reaction has been conducted at five different temperatures and thermodynamic parameters have been calculated. Based on the kinetic results plausible mechanism has been proposed.

Keywords: Imidazolium fluorochromate, Benzanilide, Kinetics, oxidation, Mechanism

1. INTRODUCTION

Cr(VI) reagents have been proved to be versatile reagents capable of oxidizing chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds [1]. Halochromates have been used as mild and selective oxidizing reagents in synthetic organic chemistry [2]. Imidazolium fluorochromate (IFC) is an important reagent [3] and has the following advantages over already reported Cr (VI) reagents: (i) quite stable at room temperature (ii) not photosensitive (iii) less hygroscopic and hence a suitable reagent for the oxidation of acid sensitive and ring strained alcohols. IFC is readily soluble in acetic acid. A survey of literature shows that reports on the oxidation of anilides by oxidants like Mn(VII) and Cr(VI) are scanty [4-8]. Similarly, kinetics of oxidation of benzanilide by chromic acid has been already studied [9]. However, the kinetics of oxidation of benzanilide by imidazolium fluorochromate has not yet been reported. Hence, in the present investigation, the oxidation of benzanilide by Imidazolium fluorochromate in aqueous acetic acid medium and the corresponding mechanism are reported.

2. EXPERIMENTAL

2.1. Materials

Imidazolium fluorochromate was prepared by reported method [3]. AnalaR grade benzanilide was recrystalized from water-methanol mixture and dried in vacuum desiccator. Acetic acid was purified by standard method [10] and the fraction distillate at 118 °C was collected and its purity was checked by an iodometric method. All other chemicals used were of AnalaR grade. All the solutions were prepared in double distilled water.

2.2. Kinetic measurements

The kinetic studies were carried out under pseudo-first order conditions in 65% - 35%*(v/v)* aqueous acetic acid medium with the concentration of the benzanilide in large excess compared to the oxidant. All reactant solutions were placed in a thermostat water bath for one hour to attain a temperature of 30°C. Appropriate quantities of the reagent solutions were mixed in a 250 cm^3 conical flask already placed in the thermostat bath. The reaction rate was followed by measuring the decrease in absorbance at 430nm for up to 80% completion of the reaction by using systronics UV-vis spectrophotometer. The reactions were followed determining the concentration of the unreacted IFC, at known intervals of time. The pseudo-first order rate constants k_1 computed from the linear plots of log absorbance *versus* time by the least square method were reproducible within ±3%.

2.3. Stoichiometry and product analysis

Reaction mixture containing an excess of oxidant over benzanilide was kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unreacted oxidant showed that two mole of substrate consumed one mole of the oxidant. The reaction mixture was allowed to go for completion by keeping it in a thermostat at 303 K for 24 h to ensure the completion of the reaction. The product obtained had melting point 68°C. TLC analysis was done with azobenzene as references. The product was also confirmed by IR, GC-MS spectra.

3. RESULTS AND DISCUSSION

Oxidation of benzanilide by imidazolium fluorochromate has been conducted in 65% water and 35% acetic acid *(v/v)* medium at 303K under pseudo-first order conditions and the observed results were as discussed below.

3.1. Effect of oxidant

The order of the reaction with respect to imidazolium fluorochromate was found to be unity as shown by the linearity of log absorbance *versus* time plot(Figure.1).At constant concentrations of substrate and perchloric acid, increasing the concentration of imidazolium fluorochromate did not affect the rate of reaction (Table-1).The linear constancy in the value of k_1 irrespective of the concentration of the imidazolium fluorochromate confirms the first order dependence on imidazolium fluorochromate.

Table 1: Rate constant for the varying concentration of oxidant

[IFC] $x10^3$ *mol dm^{-3}*	$k_1 10^4 s^{-1}$
2.0	8.16
2.5	8.28
3.0	8.49
3.5	8.77
4.0	8.90

[BA]=2.5x10^{-2} mol dm^{-3}, Solvent=35% AcOH-65% H_2O (v/v)
[$HClO_4$]=2.5 x10^{-1} mol dm^{-3}, Temperature =303K

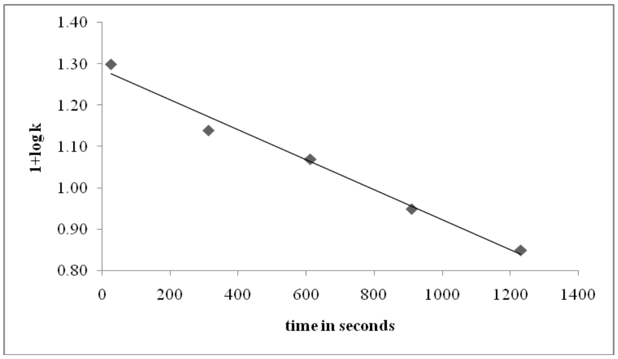


Fig.1: Plot of log absorbance versus time

3.2. Effect of substrate

Varying the concentration of benzanilide and keeping all other reactants concentration as constant, the rates were measured (Table-2). The rate of oxidation has increased progressively on increasing the concentration of benzanilide. The plot of log k_1*versus* log[Benzanilide] (Figure.2) gave the slope of 1.9(r= 0.99), shows that the oxidation reaction was second order with respect to benzanilide.

Table 2: Rate constant for the varying concentration of substrate

[BA] $x10^2$*mol dm^{-3}*	$k_1 10^4 s^{-1}$
1.0	1.23
1.5	2.82
2.0	5.01
2.5	8.16
3.0	9.01

[IFC]=2.0x10^{-3} mol dm^{-3}, Solvent=35% AcOH-65% H_2O (v/v) [$HClO_4$]=2.5 x10^{-1} mol dm^{-3} , Temperature =303K

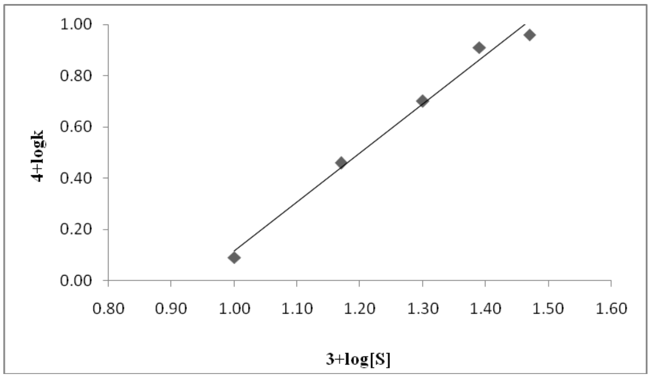


Fig. 2: Plot of logk versus log[substrate]

3.3. Effect of ionic strength

The change in ionic strength by the addition of sodium perchlorate has no effect on the rate constant (Table-3) indicating the involvement of an ion and neutral molecule in the rate determining step [11].

Table 3: Rate constant for the varying concentration of ionic strength

[$NaClO_4$] 10^2 *mol dm^{-3}*	k_1 10^4 s^{-1}
0.0	8.16
0.5	8.14
1.0	8.12
1.5	8.13
2.0	8.11

[IFC]=2.0x10^{-3}moldm^{-3}, Solvent=35%AcOH-65%H_2O(v/v), [BA]=2.5 x10^{-2}mol dm^{-3}, [$HClO_4$] =2.5 x10^{-1} mol dm^{-3}. Temperature =303 K

3.4. Effect of hydrogen ion concentration

The reaction was followed with different concentrations of perchloric acid and keeping all other concentrations of other reactants as constant and rate was measured (Table-4). The rate of the reaction increases with the increasing $[H^+]$. A plot of logk_1 *versus* log $[H^+]$ (Figure 3) gave a straight line with a slope of 0.9 (r= 0.99),it indicates first order with respect to hydrogen ion concentration.

Table 4: Rate constant for varying the hydrogen ion concentration

$[HClO_4]\ 10^1$ *mol dm*$^{-3}$	$K_1\ 10^4 s^{-1}$
2.5	8.16
3.0	9.85
3.5	11.04
4.0	12.97
4.5	14.66

[IFC] =2.0x10^{-3} mol dm^{-3}, Solvent=35% AcOH-65% H_2O (v/v) [BA] =2.5 x10^{-2}mol dm^{-3}, Temperature =303K

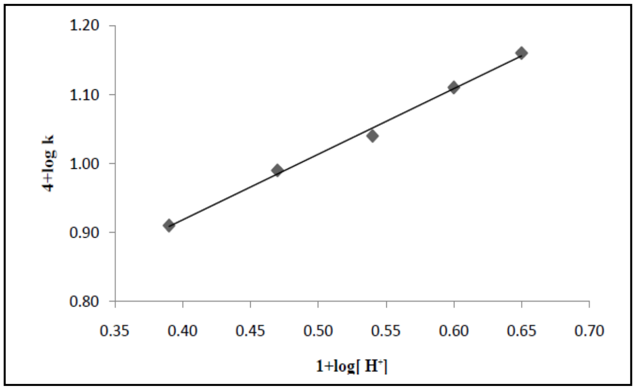


Fig. 3: Plot of log k *versus* log $[H^+]$

Table 5: Rate constant for the varying concentration of solvent composition

$AcOH-H_2O$ %*(v/v)*	D	$k_1\ 10^4 s^{-1}$
35-65	54.15	8.16
40-60	50.46	8.76
45-55	46.76	9.41
50-50	43.07	10.23
55-45	39.38	11.41

[IFC] =2.0x10^{-3}mol dm^{-3},[HClO$_4$] =2.5 x10^{-1}mol dm^{-3}, [BA] =2.5 x10^{-2} mol dm^{-3},Temperature =303K

3.5. Effect of solvent composition

The effect of solvent composition on the reaction rate was studied by varying the concentration of acetic acid 35%-65% *(v/v)*. The reaction rate increases with increase in the proportion of acetic acid in the medium (Table-5). The plot of log k_1*versus* 1/D (Figure.4) gave a straight line with a positive slope, it suggesting ion-dipole interaction [12].

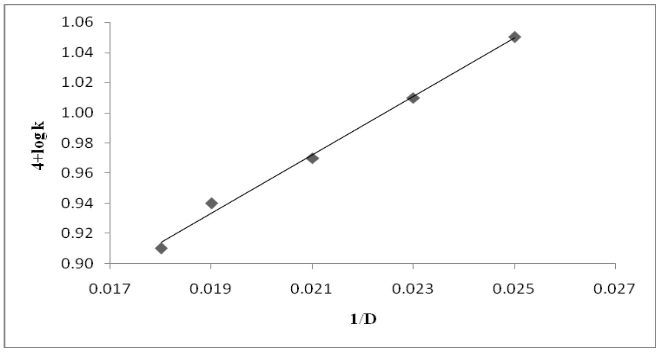


Fig. 4: Plot of log k versus 1/D

3.6. Effect of acrylonitrile

In the clear mixture containing benzanilide and imidazolium fluorochromate when allowed to stand with a drop of acrylonitrile [13] no turbity was formed suggesting the noninvolvement of free radicals in this reaction.

3.7. Effect of $AlCl_3$

The reaction was carried out with the varying of the concentration of Al^{3+} ion and keeping all other factors as constant. The added Al^{3+}decreases the rate of the reaction. It indicates the involvement of three electron processes in the reaction.

Table 6: Rate constant for the varying concentration of AlCl3

$[AlCl_3]\ 10^2$ *mol dm*$^{-3}$	$k_1\ 10^4 s^{-1}$
0.0	8.16
0.5	7.24
1.0	6.01
1.5	4.98
2.0	3.17

[IFC]=2.0x10^{-3}moldm^{-3}, Solvent=35% AcOH-65% H_2O(v/v), [BA]=2.5 x10^{-2}mol dm^{-3},[HClO$_4$] =2.5 x10^{-1} mol dm^{-3},Temperature =303 K

3.8. Effect of temperature

The rate constants were measured at five different temperatures and the activation parameters were calculated from a plot of lnk_2/T *versus* 1/T (Figure.5)(r=0.99) of the Eyring's equation [14] and it was found to be linear [15]. This negative value of entropy of activation ($\Delta S^{\#}$) indicates a polar transition state with extensive charge separation which promotes high degree of solvation of the transition state compared to the reactants. The rate constant and thermodynamic parameters are tabulated in (Table-7)

Table 7: Rate constant and activation parameters for the oxidation of Benzanilide by IFC

Temperature K	k_1 $10^4 s^{-1}$	Thermodynamic parameters
303	8.16	$\Delta H^{\#} = 11.94 kJmol^{-1}$ $\Delta S^{\#} = 151.10 JK^{-1} mol^{-1}$ $\Delta G^{\#} = 58.48 kJmol^{-1}$ at 303 K Ea $= 14.46$ $kJmol^{-1}$ at 303 K
308	8.70	
313	9.47	
318	10.88	
323	11.85	

[IFC]=2.0x10⁻³moldm⁻³,solvent=35%AcOH 65% H₂O (v/v), [BA]=2.5 x10⁻²mol dm⁻³,[HClO₄] =2.5 x10⁻¹ mol dm⁻³

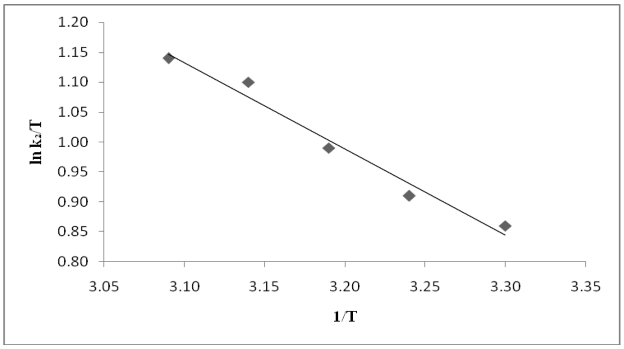
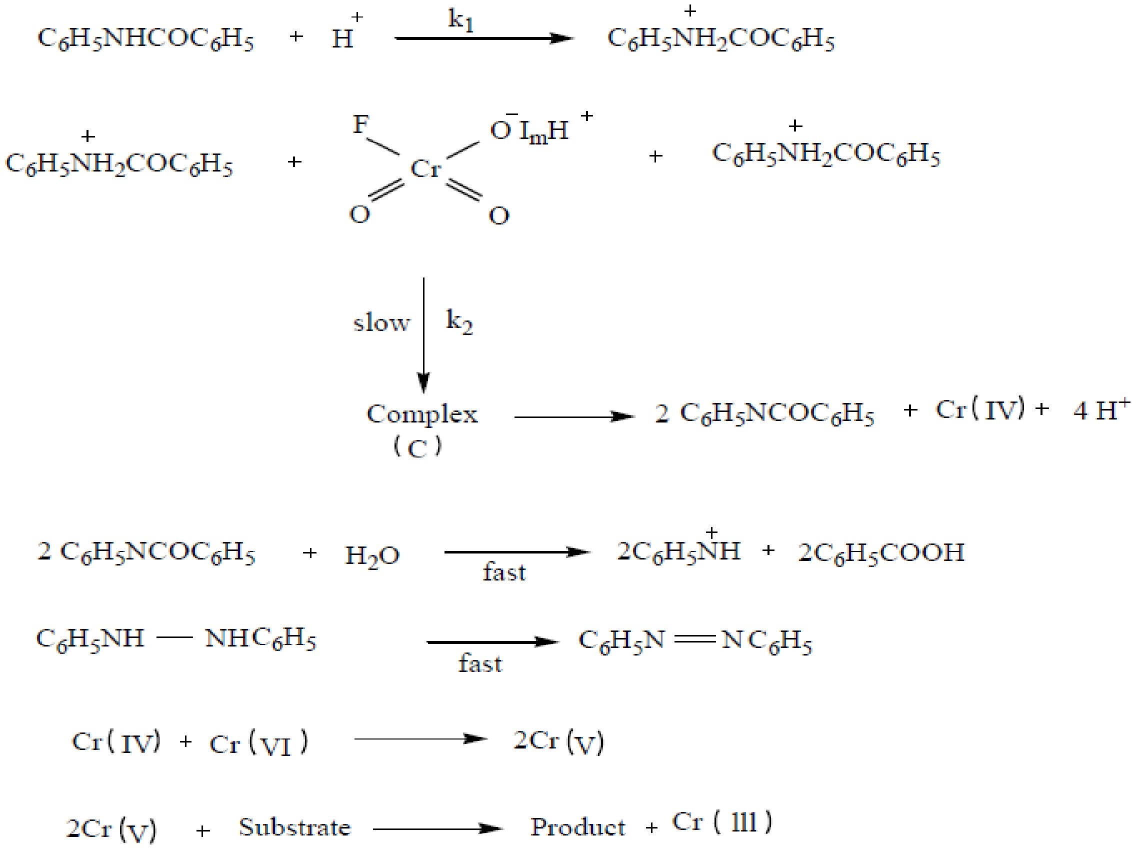


Fig.5: Plot of ln k_2/T *versus* 1/T

3.9. Mechanism

The order with respect to both Imidazolium fluorochromate, H^+ was one and second order with respect to benzanilide. The observed stoichiometry of the reaction was 2:1. The main oxidation product is azobenzene. Based on the present experimental observation, a probable mechanism and rate law for the oxidation of benzanilide by Imidazolium fluorochromate is given below. The large increases in the rate with acidity suggest the involvement of protonated substrate species in this reaction. Positive slope of log k_1 *Vs* 1/D plot indicates that the reaction involves a ion-dipole type of interactions in the rate determining step.

The reaction is initially two electron transfer process with the formation of chromium (IV) has been formulated. Nitrogen which is more basic in character and it can take only proton from the water molecule which is the hydrolysis agent. The mechanism for this study involvs the formation of $C_6H_5NCOC_6H_5$ as a slow step which later decomposes a series of step to give benzoic acid and azobenzene as a main product.



Scheme – I Mechanism of oxidation of benzanilide by IFC in the presence of perchloric acid

Rate law$= \frac{-d[IFC]}{dt} = k_1k_2[IFC]\,[BA]^2\,[H^+]$

4. CONCLUSION

The kinetics of oxidation of benzanilide has been investigated in aqueous acetic acid medium by spectrophotometrically. The first order with respect to [oxidant], $[H^+]$ and second order with respect to [benzanilide]. The lowering dielectric constant of reaction medium increases the reaction rate significantly. The reaction does not the polymerization which indicates the absence of free radical intermediate in the oxidation. Azobenzene is a main product of oxidation. It is mainly used as a reagent of antibacterial activity and azodye preparation.

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6. REFERENCES

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