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Kinetics of Oxidation of Aromatic Aldoximes by Pyridinium Fluorochromate

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Kinetics of the oxidation of benzaldoxime and its *para*-substituted derivatives such as *p*-hydroxy benzaldoxime, *p*-chloro benzaldoxime, *p*-nitro benzaldoxime by pyridinium fluorochromate have been studied at 30 ºC. The product analysis indicates that the reaction is oxidative hydrolysis. The rate increases with the increase in concentration of hydrogen ions. The first order rate dependence on the substrates. The effect of temperature, solvent, perchloric acid and sodium perchlorate has been studied. The activation energy and other thermodynamic parameters are determined.

Key Words: Kinetics, Oxidation, Aromatic aldoxime, Pyridinium fluorochromate.

INTRODUCTION

Oxidative hydrolysis[1] of oximes is generally utilized for the preparation of aldehydes since acid hydrolysis of oximes to aldehydes does not proceed in high yield. Pyridinium fluorochromale (PFC) is a very versatile oxidising agent for the oxidation of aromatic compounds. It is a neutral and mild oxidizing agent and also a more convenient reagent for selective oxidation. Kinetics and oxidation of some organic substrates[1-5] by pyridinium dichromate have already been reported. However, the kinetics of oxidation of aromatic aldoxime by pyridinium fluorochromate has not been reported. In the present work, the oxidation of bezaldoxime and some *p*-substituted bezaldoxime in acid medium by pyridinium fluorochromate are reported.

EXPERIMENTAL

Acetic acid (BDH) laboratory reagent (99.5 % assay) was dried and distilled according to the method of orton and bradfield[6].

Pyridinium fluorochromate (PFC) was prepared from pyridine aqueous 40 % hydrofluoric acid, chromium(IV) oxide in the molar ration (1:1.5:1). The bright orange crystalline reagent was isolated by fillration[7]. It was then recrystallized from water (m.p. 106-109 ºC). All other chemicals used were of A.R. grade. bezaldoxime or its *para*-substituted derivatives were prepared from the corresponding aldehydes by standard procedure[8].

Kinetic measurements: Aromatic aldoxime and pyridinium fluorochromate solution in acetic acid (5 mL each) in test tubes and glass stoppered bottles, respectively, were placed in a thermostat at required temperature. After the solutions

reached the bath temperature, aromatic aldoxime solution was added quickly to PFC solution and the mixture was allowed to cool for a definite time after which potassium iodide (10 %, 5 mL) solution was added to stop the reaction immediately, after 1 min, the liberated iodine was titrated against standared sodium thiosulphate solution. The kinetic studies were made by determining the concentration of PFC treated iodo-metrically and expressing it as a function of time. The overall orders were evaluated by the fractional life method, graphical method and individual orders from the initial rates as well as by Oswald's isolation method.

RESULTS AND DISCUSSION

The kinetics of oxidation of benzaldoxime, *p*-hydroxy benzaldoxime, *p*-chloro benzaldoxime, *p*-nitro benzaldoxime by PFC in glacial acetic acid solvent the over all order determined by fractional life method was found to be two at low and high concentrations (Table-1). It also proved by calculating second order rate constants (k_2) for the oxidation of aromatic aldoxime by PFC in acetic acid at 30 ºC by graph of 1/(a-x) *vs.* time (t) to show overall order as two (Table-1).

TABLE-1
DETERMINATION OF OVERALL ORDER FOR OXIDATION OF AROMATIC ALDOXIMES BY PYRIDINIUM FLUOROCHROMATE (PFC) IN ACETIC ACID (100 %) BY FRACTIONAL LIFE METHOD AT 303 K

Substrate	PFC reacted (%)	C_1 (mol L^{-1})	C_2 (mol L^{-1})	t_1 (s)	t_2 (s)	Order
Benzaldoxme	20	0.0200[a] 0.0020[b]	0.040 0.004	2.0	4.0	2.00
	30	0.0100[a] 0.0010[b]	0.020 0.002	6.0	12.0	2.00
p-Hydroxy benzaldoxime	20	0.0100[a] 0.0010[b]	0.020 0.002	1.5	3.0	2.00
	30	0.0050[a] 0.0005[b]	0.010 0.001	4.0	8.5	2.06
p-Chloro benzaldoxime	20	0.0300[a] 0.0030[b]	0.060 0.006	3.0	6.0	2.00
	30	0.0150[a] 0.0015[b]	0.030 0.003	9.0	19.0	2.06
p-Nitro benzaldoxime	20	0.0400[a] 0.0040[b]	0.080 0.008	5.0	10.0	2.00
	30	0.0200[a] 0.0020[b]	0.040 0.004	14.0	27.0	1.90

C_1 and C_2 ([a]oxime and [b]PFC initial concentrations; t_1 and t_2 = time required for constant percentage of reaction.

The individual order for substrate and PFC determined by isolation method was found to be one (Table-2). It is also proved by calculating first order rate constants (k_1) for the oxidation of aromatic aldoxime by PFC in acetic acid at 30 ºC by a graph of log (a-x) *vs.* time (t) to show individual order as one (Table-2).

TABLE-2
DETERMINATION OF INDIVIDUAL ORDER FOR OXIDATION OF AROMATIC ALDOXIME BY PYRIDINIUM FLUOROCHROMATE (PFC) IN ACETIC ACID (100 %) BY FRACTIONAL LIFE METHOD AT 303 K

Substrate	PFC reacted (%)	C_1 (mol L^{-1})	C_2 (mol L^{-1})	t_1 (s)	t_2 (s)	Order
Benzaldoxime						
(a) Order in PFC						
Oxime = 0.05 M	20	0.00125	0.0025	1.5	3	1.00
PFC = varied	30	0.00250	0.0050	5.0	11	1.10
(b) Order in oxime						
PFC = 0.004 M	20	0.02000	0.0400	2.0	4	1.00
Oxime = varied	30	0.01000	0.0200	6.0	13	1.00
p-Hydroxy benzaldoxime						
(a) Order in PFC						
Oxime = 0.04 M	20	0.00100	0.0020	2	4	1.00
PFC = varied	30	0.00200	0.0040	6	14	1.20
(b) Order in oxime						
PFC = 0.002 M	20	0.01000	0.0200	3	6	1.00
Oxime = varied	30	0.05000	0.0100	8	16	1.00
p-Chloro benzaldoxime						
(a) Order in PFC						
Oxime = 0.01 M	20	0.00250	0.0050	2.0	4	1.00
PFC = varied	25	0.00500	0.0100	5.0	10	1.00
(b) Order in oxime						
PFC = 0.008 M	20	0.04000	0.0800	2.5	5	1.00
Oxime = varied	25	0.02000	0.0400	6.0	11	0.86
p-Nitro benzaldoxime						
(a) Order in PFC						
Oxime = 0.2 M	20	0.05000	0.0100	5	10	1.00
PFC = varied	25	0.10000	0.0200	12	24	1.00
(b) Order in oxime						
PFC = 0.01 M	20	0.05000	0.1000	2	12	1.00
Oxime = varied	25	0.02500	0.0500	14	26	0.87

The effect of solvent on the second order rate constant of substrate and PFC reaction was studied (Table-3). The results show that the dielectric constant and rate of reaction are directly proportional to each other. The rate of reaction was faster in aqueous acetic acid than in 100 % acetic acid. The effect of temperature on the reaction was studied by keeping the concentration of the substrate = 0.05 M and PFC = 0.005 M in 100 % acetic acid. The second order rate constants are determined in the temperature range 25-45 ºC (Table-4). The energy of activation values calculated from the graph relating to the rate constants at different temperatures, against 1/T. The other thermodynamic parameters also calculated. The comparatively small value of energy of activation attributed to the rapid oxidation and the high value of energy of activation due to slow rate of reaction in acetic acid

TABLE-3
SOLVENT EFFECT
Temperature = 303 K, Aromatic aldoxime = 0.05 M, [PFC] 0.005 M

Solvent (%) AcOH:H_2O	Dielectric constant (D)	$k_2 \times 10^4$ (mol L^{-1} s^{-1})			
		Substrate			
		Benzaldoxime	*p*-Hydroxy benzaldoxime	*p*-Chloro benzaldoxime	*p*-Nitro benzaldoxime
100:0	6.15	3.49	8.1	2.0	0.58
95:5	8.75	4.2	8.6	2.7	1.1
90:10	10.77	4.9	9.3	3.4	2.3
85:15	12.66	5.5	9.8	4.6	2.9
80:20	15.22	6.3	10.0	5.7	3.8

TABLE-4
SECOND ORDER RATE CONSTANTS OF OXIDATION OF AROMATIC ALDOXIME BY PFC IN ACETIC ACID AT DIFFERENT TEMPERATURES
[Aromatic aldoxime] = 0.05 M, [PFC] = 0.005 M

Substrate	$k_2 \times 10^4$ (mol L^{-1} s^{-1})				
	Temperature (K)				
	298	303	308	313	318
Benzaldoxime	1.50	3.50	5.60	7.50	14.00
p-Hydroxy benzaldoxime	3.50	8.20	13.00	17.7	32.80
p-Chloro benzaldoxime	0.89	2.00	3.30	4.50	8.20
p-Nitro benzaldoxime	0.25	0.57	0.92	1.26	2.32
	ΔE (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})	log A
Benzaldoxime	80.86	78.29	13.74	60.65	11.96
p-Hydroxy benzaldoxime	77.01	74.44	19.34	49.45	12.21
p-Chloro benzaldoxime	90.48	87.19	13.37	71.01	13.93
p-Nitro benzaldoxime	100.00	97.56	34.76	11.74	15.05

TABLE-5
EFFECT OF PERCHLORIC ACID ON RATE OF OXIDATION OF AROMATIC ALDOXIME BY PFC
Aromatic aldoxime = 0.05 M, PFC = 0.005 M, NaCl = 0.002 M
$NaClO_4$ = 0.002 M, Solvent = AcOH (100 %), Temperature = 303 K

$HClO_4 \times 10^3$ M	$k_2 \times 10^3$ (mol L^{-1} s^{-1})			
	Substrate			
	Benzaldoxime	*p*-Hydroxy benzaldoxime	*p*-Chloro benzaldoxime	*p*-Nitro benzaldoxime
2	1.50	2.84	2.0	0.67
4	1.69	3.91	2.3	0.89
6	3.20	4.65	2.6	1.20
10	3.70	5.58	3.2	2.30

medium. The effect of varying concentration of perchloric acid and sodium perchlorate on the rate of oxidation of benzaldoxime, *p*-hydroxy benzaldoxime, *p*-chloro benzaldoxime, *p*-nitro benzaldoxime is studied. The plots of 1/(a-x) *vs.* time and log K *vs.* log C are drawn.

It was observed that with increase in the concentration of perchloric acid rate of the reaction increases (Table-5) and with increase in the concentration of sodium perchlorate, rate of the reaction decreases (Table-5).

TABLE-6
EFFECT OF SODIUM PERCHLORATE ON RATE OF OXIDATION OF AROMATIC ALDOXIME BY PFC
Aromatic aldoxime = 0.05 M, PFC = 0.005 M, NaCl = 0.002 M, $HClO_4$ = 0.002 M, Solvent = AcOH (100 %), Temperature = 303 K

$NaClO_4 \times 10^3$ M	$k_2 \times 10^3$ (mol L^{-1} s^{-1})			
	Substrate			
	Benzaldoxime	*p*-Hydroxy benzaldoxime	*p*-Chloro benzaldoxime	*p*-Nitro benzaldoxime
2	3.00	3.71	1.90	0.89
4	2.50	3.20	1.67	0.79
6	1.98	2.42	1.25	0.67
10	1.30	1.80	0.97	0.36
25	1.95	0.61	0.50	0.27

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