Kinetics of Oxidation of Acetophenone Oxime by Pyridinium Fluorochromate

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Kinetics of the oxidation of acetophenone-oxime and its *p*-substituted derivatives by pyridinium fluorochromate has been studied at 30°C. 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, Acetophenone oxime, Pyridinium fluorochromate.

INTRODUCTION

Oxidative hydrolysis[1] of oximes is generally utilized for the preparation of ketones since acid hydrolysis of oximes to ketones does not proceed in high yield. Pyridinium fluorochromate (PFC) is a versatile oxidizing 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 ketoxime by PFC has not been reported so far and hence in the present work pyridinium fluorochromate oxidation of acetophenone oxime and some *para*-substituted acetophenone oximes in acid medium is 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 ratio 1 : 1.5 : 1. The bright orange crystalline reagent was isolated by filtration[7]. It was then recrystallised from water (m.p. 106–109°C). The substrates were purified by recrystallization. All other chemicals used were of AR grade. Acetophenone oxime or its *para*-substituted derivatives were prepared from the corresponding ketones by standard procedure[8].

Kinetic Measurements: The aromatic ketoxime and PFC solution in acetic acid (5 mL each) in test tubes and glass stoppered bottles, respectively, were placed in a thermostat at the required temperature. After the solutions reached the bath temperature, aromatic ketoxime solution was added quickly into the 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 standard sodium thiosulphate solution. The kinetic studies were made by determining the concentration of PFC reacted iodometrically 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 acetophenone oxime, p-methylacetophenone oxime, p-methoxyacetophenone oxime, p-chloroacetophenone oxime by PFC in glacial acetic acid solvent has been investigated. The overall order determined by fractional life method is found to be two at low and high concentrations (Table-1). It is also proved by calculating second order rate constants (K_2) for the oxidation of aromatic ketoxime by PFC in acetic acid at 30°C by graph of $1/(a - x)$ vs. time (t) to show the overall order as two (Table-1).

TABLE-1
DETERMINATION OF OVERALL ORDER IN OXIDATION OF
AROMATIC KETOXIMES BY 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
Acetophenone oxime	20	Δ0.020 *0.002	0.040 0.004	72	140	2.0
	30	Δ0.010 *0.001	0.020 0.002	192	384	2.0
p-Methoxyacetophenone oxime	20	Δ0.010 *0.001	0.020 0.002	42	84	2.0
	20	Δ0.0050 *0.0005	0.010 0.001	84	166	1.96
p-Methylacetophenone oxime	20	Δ0.010 *0.001	0.020 0.002	48	95	1.96
	25	Δ0.0050 *0.0005	0.010 0.001	120	242	2.0
p-Chloroacetophenone oxime	15	Δ0.040 *0.004	0.080 0.008	48	96	2.0
	20	Δ0.020 *0.002	0.040 0.004	140	280	2.0

C_1 and C_2 (Δ = [oxime] and * = [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 is found to be one (Table-2). It is also proved by calculating first order rate constants (K_1) for the oxidation of aromatic ketoxime by PFC in acetic acid at 30°C by a graph of log (a − x) *vs.* time (t) to show individual order as one (Table-2).

TABLE-2

DETERMINATION OF INDIVIDUAL ORDER IN OXIDATION OF
AROMATIC KETOXIME BY 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
Acetophenoneoxime:						
(a) Order in PFC						
[oxime] = 0.05 M	20	0.00125	0.0025	60	120	1.0
[PFC] = varied	25	0.00250	0.0050	148	282	0.9
(b) Order in oxime						
[PFC] = 0.004 M	20	0.02	0.04	96	192	1.0
(oxime) = varied	25	0.01	0.02	240	484	1.0
p-Methoxyacetophenone oxime:						
(a) Order in PFC						
[oxime] = 0.04 M	20	0.001	0.002	48	96	1.0
[PFC] = varied	25	0.002	0.004	120	260	1.0
(b) Order in oxime						
[PFC] = 0.002 M	20	0.010	0.02	60	120	1.0
(oxime) = varied	25	0.005	0.01	180	410	1.1
p-Methyl acetophenone oxime:						
(a) Order in PFC						
[oxime] = 0.05 M	20	0.010	0.002	48	96	1.0
[PFC] = varied	25	0.002	0.004	120	240	1.0
(b) Order in oxime						
[PFC] = 0.002 M	20	0.010	0.02	60	120	1.0
(oxime) = varied	25	0.005	0.01	144	310	1.1
p-Chloroacetophenone oxime:						
(a) Order in PFC						
[oxime] = 0.1 M	20	0.0025	0.005	72	146	1.0
[PFC] = varied	25	0.0050	0.010	194	388	1.0
(b) Order in oxime						
[PFC] = 0.008 M	20	0.04	0.08	96	190	0.96
(oxime) = varied	25	0.02	0.04	240	476	0.86

The effect of solvent on the second order rate constant of substrate and PFC reaction is studied (Table-3). The results show that the dielectric constant and rate of reaction are directly proportional to each other. The rate of reaction is faster in aqueous acetic acid than in 100% acetic acid. The effect of temperature on the

reaction is studied by keeping the concentration of 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°C (Table-4). The energy of activation values are calculated from the graph relating to the rate constants at different temperatures, against 1/T. The other thermodynamic parameters are also calculated. The comparatively small value of energy of activation may be attributed to the rapid oxidation and the high value of energy of activation may be due to slow rate of reaction in acetic acid medium. The effect of varying concentration of perchloric acid and sodium perchlorate on the rate of oxidation of acetophenone oxime and substituted acetophenone oxime is studied. The plots of $1/(a - x)$ vs. time and log K vs. log C are drawn.

TABLE-3
SOLVENT EFFECT

Temperature = 303 K, [Aromatic ketoxime] = 0.05 M, [PFC] = 0.005 M

Solvent % AcOH: water	Dielectric constant (D)	$K_2 \times 10^4$ (mol L^{-1} s^{-1})			
		Substrate			
		Acetophenone oxime	p-Methoxy-acetophenone oxime	p-Methyl-acetophenone oxime	p-Chloro-acetophenone oxime
100 : 0	6.15	0.87	7.45	1.90	0.79
95 : 5	8.75	1.69	8.10	2.80	1.56
90 : 10	10.77	2.25	8.50	3.60	1.98
85 : 15	12.66	2.92	8.92	4.20	2.45
80 : 20	15.22	3.22	9.30	5.40	2.76

TABLE-4
SECOND ORDER RATE CONSTANTS OF OXIDATION OF AROMATIC KETOXIME
BY PFC IN ACETIC ACID AT DIFFERENT TEMPERATURES

[aromatic ketoxime] = 0.05 M, [PFC] = 0.005 M

Substrate	$K_2 \times 10^4$ (mol L^{-1} s^{-1})					$\Delta E^{\#}$	$\Delta H^{\#}$	$-\Delta S^{\#}$	$\Delta G^{\#}$	log A
	Temperature (K)						(kJ mol^{-1})			
	298	303	308	313	318					
Acetophenone oxime	3.72	4.50	7.60	12.70	23.70	86.63	83.49	30.78	86.77	11.61
p-Methoxy acetophenone oxime	6.92	8.38	14.15	23.65	43.57	77.01	74.44	57.19	2.04	10.22
p-Methyl acetophenone oxime	5.50	6.65	11.24	18.79	34.61	78.93	76.36	52.82	9.98	10.45
p-Chloro acetophenone oxime	2.19	2.65	4.47	7.85	13.77	90.48	87.78	22.61	61.82	12.04

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

TABLE-5

EFFECT OF PERCHLORIC ACID ON RATE OF OXIDATION OF
AROMATIC KETOXIME BY PFC

[Aromatic ketoxime] = 0.05 M, [PFC] = 0.005 M, [NaCl] = 0.002 M, [NaClO$_4$] = 0.002 M,
Solvent = AcOH (100%), Temperature = 303 K

[HClO$_4$] × 10^3 M	$K_2 \times 10^4$ (mol L^{-1} s^{-1})			
	Substrate			
	Acetophenone oxime	p-Methoxy-acetophenone oxime	p-Methyl-acetophenone oxime	p-Chloro-acetophenone oxime
5	5.52	9.28	7.78	9.40
10	6.25	12.06	8.28	9.00
20	7.08	16.12	8.85	7.89
25	9.21	18.60	9.98	6.65

TABLE-6

EFFECT OF SODIUM PERCHLORATE ON RATE OF OXIDATION OF AROMATIC
KETOXIME BY PFC

[Aromatic ketoxime] = 0.05 M, [PFC] = 0.005 M, [NaCl] = 0.002 M, [HClO$_4$] = 0.002 M,
Solvent = AcOH (100%), Temperature = 303 K

[NaClO$_4$] × 10^3 M	$K_2 \times 10^4$ (mol L^{-1} s^{-1})			
	Substrate			
	Acetophenone oxime	p-Methoxy-acetophenone oxime	p-Methyl-acetophenone oxime	p-Chloro-acetophenone oxime
2	4.25	7.12	3.33	4.10
5	3.38	5.24	2.98	3.90
10	2.26	3.18	2.22	3.48
20	1.98	1.54	1.66	3.10

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