

Effect of Ring Size on PFC Oxidation of Alicyclic Ketoximes—A Kinetic Study

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The oxidation of alicyclic oximes of cyclopentanone, cyclohexanone and cycloheptanone by pyridinium fluorochromate (PFC) has been studied. The reaction follows first order each in [PFC] and [Oxime]. The reactivity sequence observed is cyclohexanone oxime (CHexO) > cyclopentanone oxime (CPO) > cycloheptanone oxime (CHepO) which has been rationalized on the basis of I-strain.

Key Words: Kinetic, Oxidation, Alicyclic ketoximes.

INTRODUCTION

The chemistry of oximes is of great interest due to their wide synthetic and industrial applications and bio-activities. Oximes have been converted to the corresponding aldehydes or ketones by treatment with reagents like thallium(III)¹, manganese(III)², pyridinium chlorochromate³, 1-chlorobenzothiazole⁴ and peroxomonosulphate⁵. However, extensive work in this conversion has not been carried out with chromium containing oxidants. Hence, in the present investigation kinetics of the oxidation of alicyclic oximes by PFC has been chosen.

EXPERIMENTAL

Pyridinium fluorochromate (PFC), a complex of chromium trioxide, pyridine and hydrofluoric acid was prepared in the laboratory by the method cited in the literature⁶ and its purity was checked by iodometric method. A stock solution of PFC of strength 5×10^{-3} mol dm⁻³ was prepared in conductivity water. The alicyclic ketoximes were prepared by the standard procedures⁷. Cyclopentanone oxime and cyclohexanone oxime were recrystallized from suitable solvents and cycloheptanone oxime was purified by distillation under reduced pressure. The purity of the sample was confirmed by comparing the respective physical constants with literature values which show good concordance. Acetic acid used for kinetic runs was thrice distilled by adopting the usual procedures⁸. All other chemicals used were of analytical grade.

Rate measurements were carried out in 80% (v/v) aqueous acetic acid medium in the temperature range 288–313 K in the presence of sulphuric acid of strength 0.5 mol dm⁻³. The reactions were carried out under pseudo-first order conditions

keeping the [substrate] in considerable excess over that of [PFC]. The progress of the reaction was followed spectrophotometrically at 355 nm up to 80% completion of the reaction. The pseudo-first order rate constants were evaluated and found to be reproducible within $\pm 2\%$.

Test for free radical intermediates: The possibility of free radical formation is ruled out since there was no polymer formation when freshly distilled acrylonitrile monomer was added to the reaction mixture. This suggests a non-radical reaction pathway.

Stoichiometry and product analysis: A known excess of PFC was allowed to react with a known concentration of substrate in 60% (v/v) aqueous acetic acid medium. Estimation of the unreacted PFC from the reaction mixture after the completion of the reaction, showed that the stoichiometry of the reaction is 1 : 1. The reaction mixture was also analyzed for the products by qualitative tests. The product was detected to be the corresponding ketone which was further confirmed by TLC experiments.

RESULTS AND DISCUSSION

Order with Respect to Oxidant

The dependence of rates of reaction on oxidant concentration was studied by varying [PFC] in the range $5.5-9.5 \times 10^{-4}$ mol dm⁻³. From the linear plots of log [PFC] against time (min) the order with respect to oxidant is determined to be unity. However, the pseudo first order rate constants were found to decrease with increase in concentration of gross PFC (Table-1). Similar observations have been reported earlier in the oxidation studies involving various substrates by PFC^{9, 10} and in chromic acid oxidations¹¹.

Order with Respect to Oxime

The reactions were investigated at varying concentration of the oxime in the range $5.5-9.5 \times 10^{-3}$ mol dm⁻³ and fixed concentrations of the other reactants. The plots of log [PFC] against time (min) at different initial concentrations of oximes were linear and the values of k_{obs} (s⁻¹) evaluated from the slopes were found to be dependent on the initial concentrations of the substrates. The plot of log k_{obs} vs. log [substrate] was linear with unit slope showing a first order dependence on [oxime]. The value of k_{obs} (s⁻¹) plotted against [substrate] gave straight lines passing through the origin proving a first order dependence on the [oxime] as well as the absence of self-decomposition of PFC (Fig. 1). From the slopes of the above plots the second order rate constants k_2 dm³ mol⁻¹ s⁻¹ were evaluated.

Effect of [H⁺]: The acidity of the medium was varied from 0.1 to 0.5 mol dm⁻³ to learn the effect of acid on the reaction rate at constant [PFC], [oxime] and ionic strength (1.5 mol dm⁻³). The oxidation reactions were found to be acid catalyzed. The plots of log k_{obs} vs. log [H⁺] were linear and the slopes indicate fractional order with respect to [H⁺].

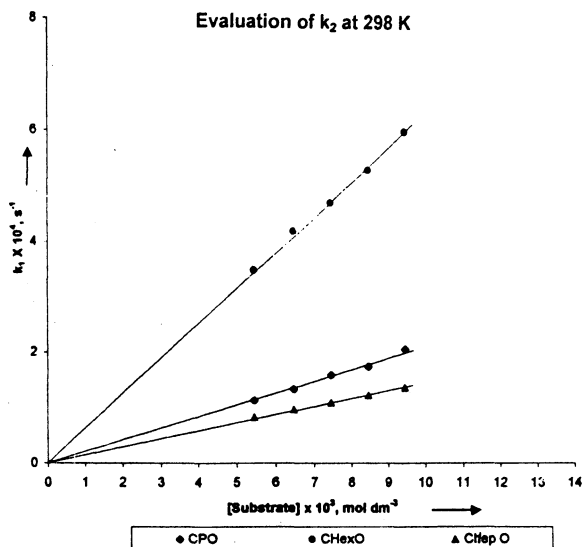


Fig. 1

TABLE-1

RATE DATA FOR THE OXIDATION OF CYCLOHEXANONE OXIME BY PFC

[PFC] $\times 10^4$ (mol dm ⁻³)	[CHexO] $\times 10^3$ (mol dm ⁻³)	[H ₂ SO ₄] (mol dm ⁻³)	μ (mol dm ⁻³)	AcOH : H ₂ O % (v/v)	$k_1 \times 10^3$ (s ⁻¹)
					Temperature 283 K
5.5	7.5	0.5	1.5	80 : 20	6.48
6.5	7.5	0.5	1.5	80 : 20	5.19
7.5	7.5	0.5	1.5	80 : 20	4.70*
8.5	7.5	0.5	1.5	80 : 20	4.11
9.5	7.5	0.5	1.5	80 : 20	3.40
7.5	5.5	0.5	1.5	80 : 20	3.49
7.5	6.5	0.5	1.5	80 : 20	4.19
7.5	8.5	0.5	1.5	80 : 20	5.19
7.5	9.5	0.5	1.5	80 : 20	5.96
7.5	7.5	0.2	1.5	80 : 20	3.19
7.5	7.5	0.3	1.5	80 : 20	3.88
7.5	7.5	0.4	1.5	80 : 20	4.45
7.5	7.5	0.5	1.6	80 : 20	4.69
7.5	7.5	0.5	1.7	80 : 20	4.72
7.5	7.5	0.5	1.8	80 : 20	4.51
7.5	7.5	0.5	1.9	80 : 20	4.56
7.5	7.5	0.5	1.5	30 : 70	21.50
7.5	7.5	0.5	1.5	40 : 60	12.00
7.5	7.5	0.5	1.5	50 : 50	8.33

* at 288 K; 2.21;

at 293 K; 3.20;

at 303 K; 7.90.

Influence of ionic strength: The rate studies were made at different ionic strengths of the medium, varied by the addition of sodium perchlorate maintaining constant $[H^+]$. The influence of ionic strength on the rates of oxidation was negligible indicating the participation of an ion and a dipole in the rate determining step¹².

Dependence on solvent polarity: The effect of dielectric constant on the reaction rate was examined by varying the percentage of acetic acid in the range 50–80% (v/v). The rate constants were found to decrease on lowering the dielectric constant of the medium. This may be due to polar mechanism.

Rate and activation parameters: From the observed kinetic data, the second order rate constants for the three alicyclic ketoximes were found to increase with increase in temperature. The plots of $\log k_2$ vs. $1/T$ were linear indicating that the Arrhenius law is being obeyed. The thermodynamic parameters E_a (kJ mol^{-1}), ΔG^\ddagger (kJ mol^{-1}), ΔH^\ddagger (kJ mol^{-1}) and ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$) have been computed and tabulated (Table-2).

TABLE-2
RATE AND ACTIVATION PARAMETERS FOR
OXIMES OF ALICYCLIC KETONES

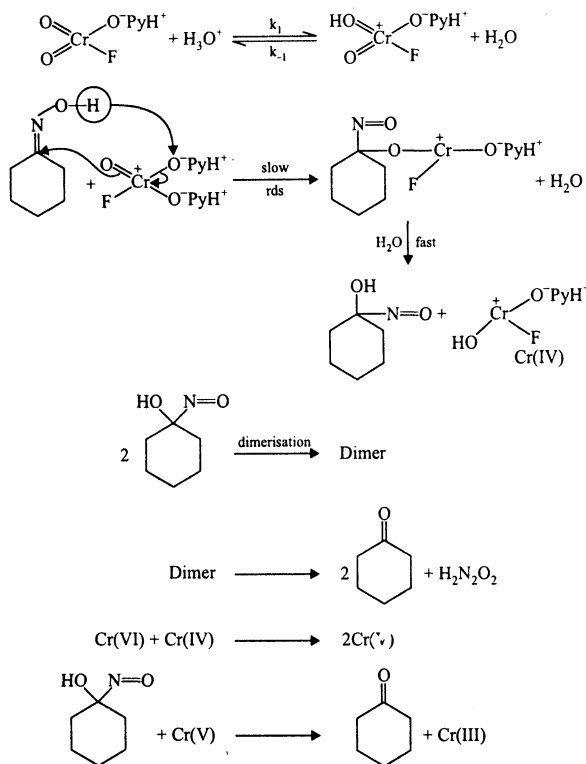
$[Substrate] = 7.5 \times 10^{-3} \text{ mol dm}^{-3}$; $[PFC] = 7.5 \times 10^{-4} \text{ mol dm}^{-3}$;
 $[H_2SO_4] = 0.5 \text{ mol dm}^{-3}$; $AcOH = 80\% (v/v)$

Sub- strate	$k_2 \times 10^2, \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} (\text{K})$						E_a (kJ mol^{-1})	$\Delta H^\ddagger_{298 \text{ K}}$ (kJ mol^{-1})	$\Delta S^\ddagger_{298 \text{ K}}$ ($\text{J K}^{-1} \text{mol}^{-1}$)	$\Delta G^\ddagger_{298 \text{ K}}$ (kJ mol^{-1})
	288	293	298	303	308	313				
CPO	—	—	2.25	3.64	5.37	11.75	82.80	80.30	-7.00	82.40
CHexo	2.79	4.10	7.04	10.23	—	—	64.50	62.00	-58.90	79.60
CHepO	—	—	1.33	2.54	4.10	5.91	77.00	74.50	-30.80	83.70

Mechanism

In the light of all the experimental results obtained in the present investigation and the evidences from the other investigations involving the oxidative hydrolysis of oximes^{3, 4}, a polar mechanism may be proposed for the reaction involving PFC and alicyclic ketoximes.

The mechanism involves a slow formation of a positively charged PFC ester between the substrate and the protonated PFC by the removal of water molecule as reported in the chromic acid oxidation of alcohols¹³, oxidation of aldehydes by PFC¹⁴, acids by PCC¹⁵ and oximes by PCC³. Hence in the light of these arguments a polar mechanism has been proposed for the oxidation of alicyclic ketoximes by PFC, ruling out the radical mechanism involving the formation of iminoxy radicals¹, which is presented in **Scheme-1**.



Scheme-1

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(Received: 31 August 2004; Accepted: 19 January 2005)

AJC-4074