

Spectrophotometric Study of Kinetics of Oxidation of Oximes of 3,5-Dimethyl-2,6-diarylpiperidin-4-ones with Quinolinium Fluorochromate

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The rate of oxidation of 3,5-dimethyl-2,6-diarylpiperidin-4-one oximes with quinolinium fluorochromate (QFC) was followed in aqueous acetic acid medium. The influence of substrate, oxidant, H⁺ ions, ionic strength and dielectric constant on the reaction rates at varied temperature has been studied. The stoichiometry is 1:1 and the product of oxidation is the corresponding ketone. Activation parameters have been computed and a suitable mechanism has been suggested.

Key Words: Oximes, Oxidation, Kinetics.

INTRODUCTION

Oximes are highly crystalline and very useful for purification and characterization of carbonyl compounds. It is also useful as efficient protecting groups for aldehydes and ketones¹. In general, for the preparation of ketones, oxidative hydrolysis²⁻⁶ of oxime is more encouraging, since acid hydrolysis of oximes to ketones may not result in good yield. Cr(VI) has been reported as a useful reagent for the formation of carbonyl compounds from the corresponding alcohols and oximes⁷⁻⁹. A survey of literature shows that less study has been carried out on the oxidation kinetics of heterocyclic ketoximes. Hence, in the present investigation kinetics of oxidation of 3,5-dimethyl-2,6-diarylpiperidin-4-one oximes by quinolinium fluorochromate has been chosen.

EXPERIMENTAL

Quinolinium fluorochromate was prepared by the method described in the literature¹⁰. Piperidin-4-ones and the corresponding oximes (PO) were prepared by known procedure^{11,12}. The purity of the sample was confirmed with literature values which show good concordance. Acetic acid used for kinetic runs was thrice distilled by adopting the usual procedure¹³ all other chemicals used were of analytical grade.

Rate measurements were carried out in 60 % (v/v) aqueous acetic acid medium in the temperature range 283-298 °C in the presence of sulphuric acid. The reactions were carried out under pseudo-first order conditions keeping the [substrate] in

considerable excess over that of [quinolinium fluorochromate]. The progress of the reaction was followed spectrophotometrically at 355 nm upto 80 % completion of the reaction. The pseudo-first order rate constants were evaluated and found to be reproducible within ± 3 %.

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 quinolinium fluorochromate was allowed to react with a known concentration of substrate in 60 % (v/v) aqueous acetic acid medium. Estimation of the unreacted quinolinium fluorochromate 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 product 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 [QFC] in the range $2.5-10.0 \times 10^{-4}$ mol dm⁻³. From the linear plots of log [QFC] 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 quinolinium fluorochromate (Table-1). Similar observations have been reported earlier in the oxidation studies involving aromatic oximes and semicarbazones by Cr(VI)¹⁴⁻¹⁶ and in chromic acid oxidations¹⁷.

Order with respect to substrate: The reactions were investigated at varying concentration of the oxime in the range $0.50-1.50 \times 10^{-2}$ mol dm⁻³ and fixed concentrations of the other reactants. The plots of log [QFC] 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 concentration of the substrate. The plots of log k_{obs} versus log [substrate] was linear with unit slope showing a first order dependence on [oxime]. The values k_{obs} (s⁻¹) plotted against [substrate] gave straight lines passing through the origin proving a first order dependence on [oxime] as well as the absence of self decomposition of substrate. From the slopes of the above plots the second order rate constants k_2 dm³ mol⁻¹ s⁻¹ were evaluated (Fig. 1).

Effect of [H⁺]: The acidity of the medium was varied from $3-9 \times 10^{-3}$ mol dm⁻³ to study the effect of acid on the reaction rate at constant [QFC], [oxime] and ionic strength (0.3 mol dm⁻³). The oxidation reactions were found to be acid catalyzed. The plots of log k_{obs} versus log [H⁺] were linear and the slopes indicate fractional order with respect to [H⁺].

TABLE-1
RATE DATA FOR THE OXIDATION OF 3,5-DIMETHYL-2,6-bis-(2-CHLORO PHENYL)
PIPERIDIN-4-ONE OXIME BY QUINOLINIUM FLOROCHROMATE AT 293 K

[QFC] × 10 ⁴ (mol dm ⁻³)	[Substrate] × 10 ² (mol dm ⁻³)	[H ₂ SO ₄] × 10 ³ (mol dm ⁻³)	μ (mol dm ⁻³)	AcOH:H ₂ O (%) (v/v)	k ₁ × 10 ⁴ S ⁻¹ /temp. 293 K
2.50	1.00	5.00	0.030	60	6.32
5.00	1.00	5.00	0.030	60	9.14
7.50	1.00	5.00	0.030	60	12.66
10.00	1.00	5.00	0.030	60	15.96
7.50	0.50	5.00	0.030	60	6.32
7.50	0.75	5.00	0.030	60	9.14
7.50	1.25	5.00	0.030	60	15.96
7.50	1.00	1.00	0.030	60	5.86
7.50	1.00	3.00	0.030	60	9.60
7.50	1.00	7.00	0.030	60	15.28
7.50	1.00	5.00	0.015	60	12.60
7.50	1.00	5.00	0.060	60	12.48
7.50	1.00	5.00	0.075	60	12.86
7.50	1.00	5.00	0.030	70	10.74
7.50	1.00	5.00	0.030	80	9.28
7.50	1.00	5.00	0.030	90	8.42

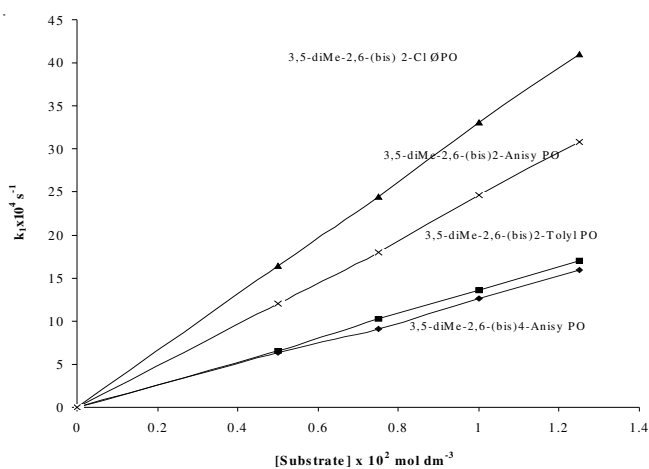


Fig. 1

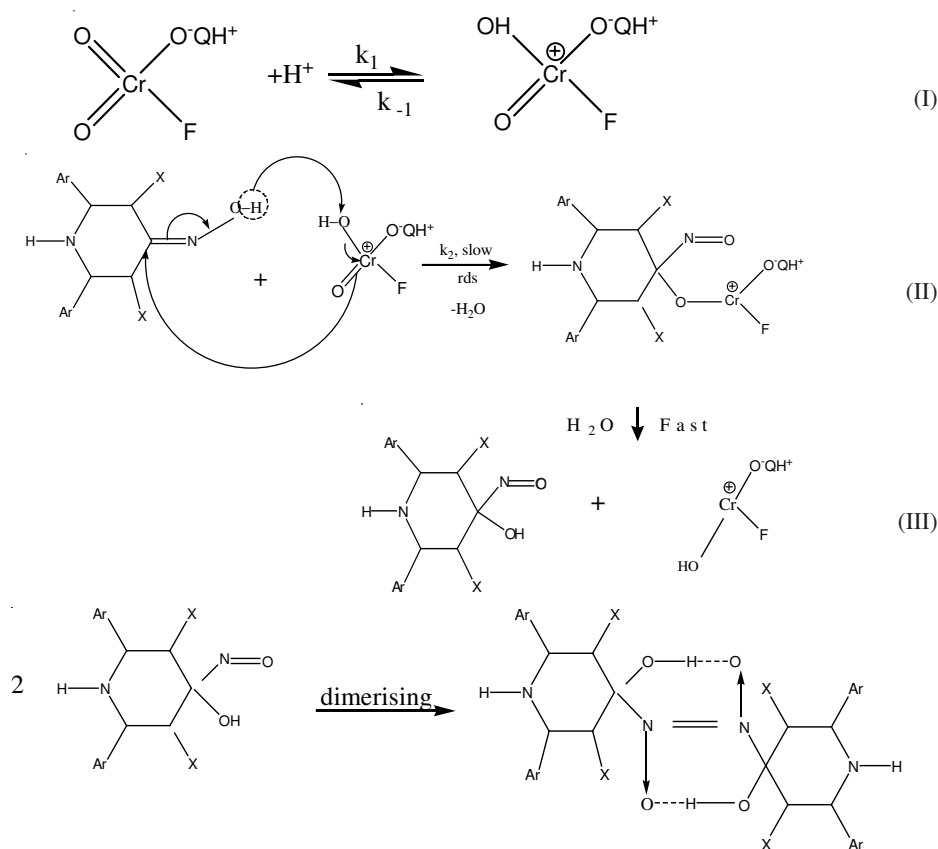
Influence of ionic strength: The rate studies were made at different ionic strengths of the medium varied by the addition of sodium sulphate maintaining constant [H⁺]. The influence of ionic strength on the rates of oxidation was negligible indicating the participation of an ion and a dipole in the rate determining step¹⁸.

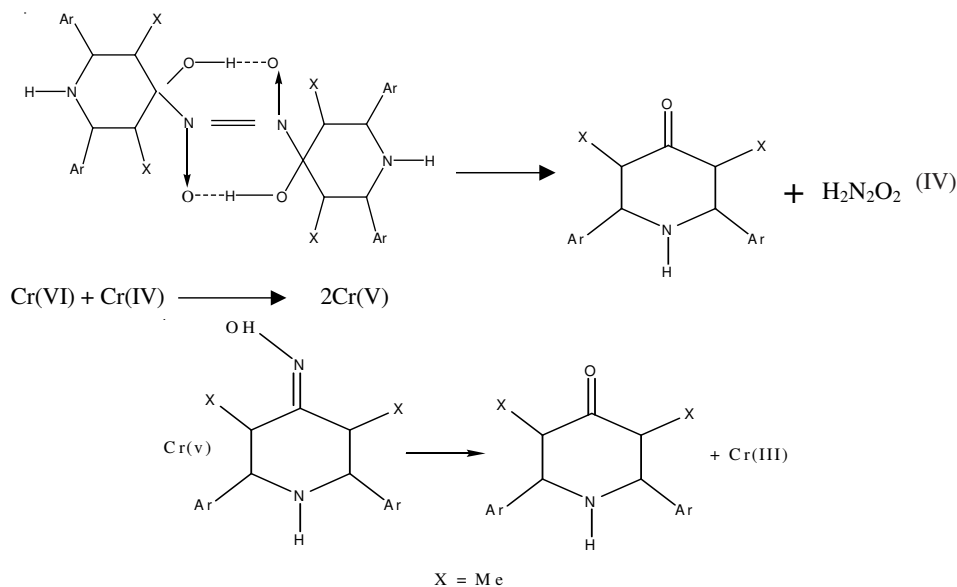
Dependence on solvent polarity: The effect of dielectric constant on the reaction rate was examined by varying the percentage of acetic acid in the range of 40-80 % (v/v). The rate constants were found to decrease on lowering the dielectric constant of the medium. This may be due to polar mechanism¹⁹.

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

Mechanism: In the light of all experimental results obtained in the present investigation and the evidences from the other investigations involving the oxidative hydrolysis of oximes, a polar mechanism may be proposed for the reaction involving quinolinium florochromate and 3,5-dimethyl-2,6-diarylpiperidin-4-ones oximes.

The mechanism involves a slow formation of a positively charged quinolinium florochromate ester between the substrate and the protonated quinolinium florochromate by the removal of water molecule as reported in the chromic acid oxidation of alcohols²⁰, oxidation of aldehydes by PFC²¹, acids by PCC²² and oximes by QFC²³. Hence in the light of these arguments a polar mechanism has been proposed for the oxidation of heterocyclic ketoximes by quinolinium florochromate, ruling out the radical mechanism involving the formation of iminoxy radicals, which is presented in **Scheme-I**.





Scheme-I

TABLE-2
RATE AND ACTIVATION PARAMETERS FOR SUBSTITUTED
3,5-DIMETHYL-2,6-DIARYL PIPERIDIN 4-ONE OXIMES

[QFC] = 7.50×10^{-4} mol dm⁻³, [substrate] = 1.00×10^{-2} mol dm⁻³,
[H₂SO₄] = 5.00×10^{-3} mol dm⁻³, μ = 0.03 mol dm⁻³, [AcOH] = 60 % (v/v)

Substitute	$k_2 \times 10^2$ (dm ³ mol ⁻¹ s ⁻¹)				E_a (KJ mol ⁻¹)	ΔH^\ddagger at 293 K (KJ mol ⁻¹)	ΔS^\ddagger at 293K (JK ⁻¹ mol ⁻¹)	ΔG^\ddagger at 293 K (KJ mol ⁻¹)
	283 K	288 K	293 K	298 K				
3,5-diMe-2,6-PPO	37.34	50.51	72.62	100.47	46.73	44.30	-96.27	72.51
3,5-diMe-2,6-bis(4-ClC ₆ H ₅)PO	23.66	36.31	48.14	76.62	53.38	50.94	-77.00	73.50
3,5-diMe-2,6-bis(4-Tolyl)PO	20.80	31.35	41.43	62.70	50.34	47.91	-88.61	73.87
3,5-diMe-2,6-bis(2-Tolyl)PO	12.20	16.70	24.10	43.80	55.46	53.02	-120.50	88.33
3,5-diMe-2,6-bis(4-Anisyl)PO	6.39	10.40	17.30	28.00	65.24	62.80	-91.50	89.61
3,5-diMe-2,6-bis(2-Anisyl)PO	2.38	4.26	10.03	18.39	85.10	82.66	-26.50	90.42
3,5-diMe-2,6-bis(2-ClC ₆ H ₅)PO	2.12	3.83	7.59	13.40	83.76	81.33	-33.70	91.20

Among diaryl substitute 3,5-dimethyl piperidin-4-one oximes the observed trend in reactivity is H > 4-Cl > 4-Me > 4-OMe > 2-Me > 2-OMe > 2-Cl the lower reactivity of *ortho*-substituted one than the *para*-substituted may be attributed by *ortho* effect.

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