Oxidative Deoximation of Heterocyclic Ketoximes by Quinolinium Fluoro Chromate-A Kinetic and Mechanistic Approach

T. Vimala* and T.S. Jani Bai

Department of Chemistry, Seethalakshmi Ramaswami College, Tiruchirappalli-620 002, India
E-mail: vimalasrc@yahoo.in

The kinetics of oxidation of 2,6-diphenyl piperidin-4-one oxime (PPO) and its 3- alkyl substituted by quinolinium fluorochromate (QFC) in aqueous acetic acid 60 % (v/v) leads to the formation of corresponding ketones. The reaction is first order each in quinolinium fluorochromate and the oximes. The acidity dependence is fractional order throughout the entire range of acidities studied. Variation in ionic strength has no perceptible change in the rate. The steric effect plays a dominant role to decide the rate of the reaction and the reactivity sequence observed is 3-H > 3-Me > 3-Et > 3,3-diMe > 3-iPr.

Key Words: Piperidin-4-one oximes, Quinolinium fluorochromate.

INTRODUCTION

Regeneration of carbonyl compounds from oxime under mild conditions is an important process in organic chemistry[1] since the liberation of parent ketone from oxime is to be achieved in maximum yield. Quinolinium fluorochromate is a mild and selective oxidizing agent which is found to react with oximes at measurable rates with quantitative conversion[2,3] we have been interested in the kinetics of oxidation of oximes by Cr(VI) and a few reports have already been emanated from our laboratory[4-6]. In continuation of our earlier work with oximes, we now report the kinetic and mechanistic study of heterocyclic ketoximes with quinolinium fluorochromate.

EXPERIMENTAL

All the chemicals used were of analar grade. Quinolinium fluorochromate was prepared by the method described in literature[7]. All the piperidones and their oximes were prepared by the reported procedures[8-10]. The purity of the oximes were checked by their melting point. Acetic acid was refluxed over chromic oxide and then fractionated[11]. The reaction was carried out in 60 % (v/v) acetic acid, under pseudo first order conditions by maintaining a large excess of substrate over quinolinium fluorochromate. The reaction mixture is homogeneous throughout the reaction course. The reaction was followed by monitoring the decrease in absorption of quinolinium fluorochromate at 355 nm. Computations of the rate constants were

made from the plot of log [QFC] against time. The pseudo first order rate constants were calculated using the relation k_1 = slope × 2.303/60. The stoichiometry was carried out in the presence of excess quinolinium fluorochromate reveal that one mole of oxidant was consumed by one mole of oxime. Oxime and quinolinium fluorochromate were allowed to react in aqueous acetic acid in the presence of H_2SO_4 at room temperature. The reaction mixture was neutralized using sodium bicarbonate and extracted with ether. The ether extract was dried over anhydrous sodium sulphate, concentrated and analyzed for the products by TLC and melting point.

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 2.5-12.5 × 10^{-4} mol dm^{-3}. From the linear plots of log [quinolinium fluorochromate] 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, Fig. 1). Similar observations have been reported earlier in the oxidation studies involving aromatic oximes and semicarbazones by PFC[12,13] QFC[14] and in chromic acid oxidations[15].

TABLE-1

RATE DATA FOR THE OXIDATION OF 3-ETHYL-2,6-DIPHENYL PIPERIDIN-4-ONE OXIME BY QUINOLINIUM FLOROCHROMATE (QFC) AT 293 K

[QFC] × 10^4 (mol dm^{-3})	[3-Et- PPO] × 10^2 (mol dm^{-3})	[H_2SO_4] x 10^3 (mol dm^{-3})	μ (mol dm^{-3})	AcOH:H_2O (%) (v/v)	k_1 × 10^4 (S^{-1}) /temp. 293 K
2.50	1.00	5.00	0.03	60	21.38
5.00	1.00	5.00	0.03	60	9.26
7.50	1.00	5.00	0.03	60	5.22
10.00	1.00	5.00	0.03	60	4.22
12.50	1.00	5.00	0.03	60	3.77
7.50	0.50	5.00	0.03	60	2.64
7.50	0.75	5.00	0.03	60	3.98
7.50	1.25	5.00	0.03	60	6.37
7.50	1.50	5.00	0.03	60	7.78
7.50	1.00	1.00	0.03	60	3.84
7.50	1.00	3.00	0.03	60	4.55
7.50	1.00	7.00	0.03	60	5.85
7.50	1.00	9.00	0.03	60	6.55
7.50	1.00	5.00	0.015	60	4.94
7.50	1.00	5.00	0.060	60	5.03
7.50	1.00	5.00	0.075	60	5.20
7.50	1.00	5.00	0.03	40	8.61
7.50	1.00	5.00	0.03	50	5.90
7.50	1.00	5.00	0.03	70	4.53
7.50	1.00	7.50	0.03	80	3.35

Order with respect to substrate: The reactions were investigated at varying concentration of the oxime in the range 0.50-1.50 × 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 substrates. The plot 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 dm^3 mol^{-1} s^{-1} were evaluated (Fig. 2).

Fig. 1

Fig. 2
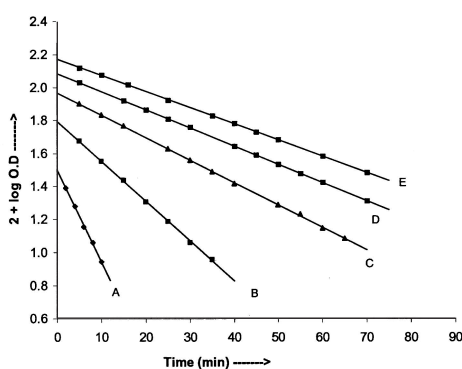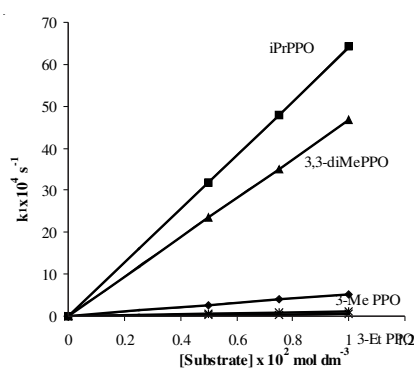
Effect of [H$^+$]: The acidity of the medium was varied from 3.0-9.0 × 10^{-3} mol dm^{-3} to learn the effect of acid on the reaction rate at constant [QFC], [oxime] and ionic strength (0.03 mol dm^{-3}). The oxidation reactions were found to be acid catalyzed. The plots of log k_{obs} *versus* log [H$^+$] were linear and the slopes indicate fractional order with respect to [H$^+$].

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 step[16].

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 mechanism.

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}), $\Delta G^{\#}$ (KJ mol^{-1}), $\Delta H^{\#}$ (KJ mol^{-1}) and $\Delta S^{\#}$ (J K^{-1} mol^{-1}) have been computed and tabulated (Table-2).

X = -H, -Me, -Et, -3,3-diMe, -3,5-diMe; R = -Me
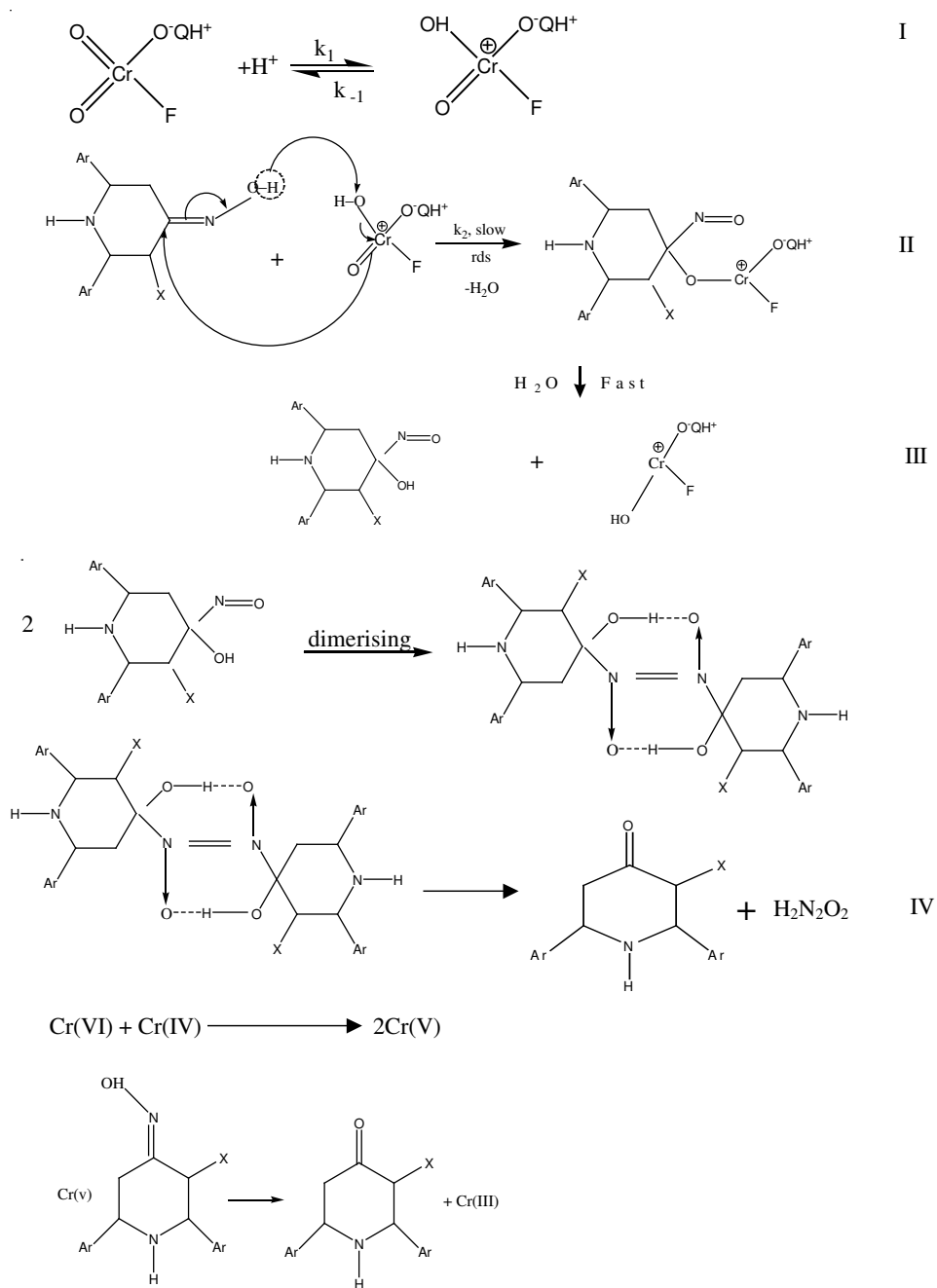
Scheme-I

TABLE 2
RATE AND ACTIVATION PARAMETERS FOR 3-SUBSTITUTED-
2,6-DIPHENYL PIPERIDIN-4-ONE OXIME

[QFC] = 7.5×10^{-4} mol dm^{-3} [substrate] = 1×10^{-2} mol dm^{-3} [H$_2$SO$_4$] = 5.00×10^{-3} mol dm^{-3}
μ = 0.03 mol dm^{-3} [AcOH] = 60 % (v/v) [AcOH] = 60 % (v/v)

Substitute	$k_2 \times 10^2$ (dm^{-3} mol^{-1} s^{-1})							E_a KJ mol^{-1}	$\Delta H^\#$ at 293 K KJ mol^{-1}	$\Delta S^\#$ at 293 K (JK^{-1} mol^{-1})	$\Delta G^\#$ 293 K (KJ mol^{-1})
	283 K	288 K	293 K	298 K	303 K	313 K	323 K				
PPO	14.47	38.55	63.89	92.67	–	–	–	84.98	82.54	-19.31	81.08
3-Me PPO	12.21	22.66	46.42	60.60	–	–	–	68.58	66.15	-45.52	79.50
3-Et PPO	–	3.39	5.08	7.63	9.75	–	–	52.01	49.58	-100.38	78.99
3,3-diMe PPO	–	–	1.10	–	2.61	5.48	12.21	62.65	60.22	-76.77	82.72
3-iPr PPO	–	–	0.46	–	0.86	1.36	3.01	47.84	45.40	-134.59	87.28

Mechanism: In the light of the experimental results obtained in the present investigation and the evidences from the other involving the oxidative hydrolysis of oximes, a polar mechanism has been proposed and is presented in **Scheme-I**. The mechanism involves a slow formation of a positively charged quinolinium fluorochromate ester between the substrate and protonated quinolinium fluorochromate by the removal of water molecule as reported in the chromic acid oxidation of alcohols[17], oxidation of aldehydes by PFC[18], acids by PCC[19] and oximes by PCC[20]. Hence in the light of these arguments a polar mechanism has been proposed for the oxidation of heterocyclic ketoximes by quinolinium fluorochromate, ruling out the radical mechanism involving the formation of iminoxy radicals[21], which is presented in **Scheme-I**.

From the magnitude of the rate constants the reactivity trend observed for oximes of different-3-alkyl substituted-2,6-diphenyl piperidin-4-one is 3-H > 3-me > 3-et > 3,3-di-me > 3-i-Pr. It is observed that the reactivity decreases as the size of the alkyl substituent increases. This indicates that there should be more steric crowding in the transition state than in the ground state. This trend can be attributed to the change of the central carbon atom from a trigonal to a tetragonal state[22-25]. It is evident that the increase in the steric crowding is proportional to the bulkiness of the substituent in the third position.

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