Asian Journal of Chemistry Vol. 22, No. 3 (2010), 2290-2294

Kinetics and Mechanism of Pyridinium Chlorochromate Oxidation of Some N-Methyl-2,6-diphenylpiperidin-4-one Oximes

T.S. JANI BAI and S. SANTHI*
Post-Graduate and Research Department of Chemistry,
Seethalakshmi Ramaswami College (Autonomous), Tiruchirapalli-620 002, India
E-mail: santhi.muthuraman@yahoo.com

The oxidative deoximation of 1-methyl-2,6-diphenyl piperidin-4-one and its 3-alkyl substituted derivatives by pyridinium chlorochromate (PCC) in aqueous acetic acid medium exhibits a first order dependence on both the oxime and PCC. The reactions are catalyzed by hydrogen ions. The rates are accelerated by increasing the dielectric strength of the medium. The activation parameters are computed by performing the reactions at four different temperatures. On the basis of the experimental results a suitable mechanism has been proposed. The reactivity trend observed for the oximes is 1-MePPO > 1,3-diMe$_2$PPO > 1-Me-3-EtPPO > 1,3,3-Me$_3$PPO > 1-Me-3-iprPPO.

Key Words: Kinetics, Pyridinium chlorochromate, N-Methyl-2,6-diphenylpiperidin-4-one oximes.

INTRODUCTION

Metal ion oxidants are the reagents of choice for the regeneration of carbonyl compounds from the respective oximes. In general, for the preparation of ketones, oxidative hydrolysis[1] of oximes is more encouraging, since acid hydrolysis of oximes to ketones may not result in good yield. Kinetic investigation of oxidation of oximes and semicarbazones with peroxomonosulphate[2], dichromate[3], PFC[4], NBSA[5], NBS[6], QDC[7] have been carried out. A survey of literature shows the lack of work on kinetic study of oxidation of N-methyl piperidin-4-one oximes by PCC in aqueous acetic acid medium. Hence in the present investigation it is proposed to take up the study of the kinetic and mechanistic aspect of oxidation of some N-methyl-2,6-diphenyl piperidin-4-one oximes.

EXPERIMENTAL

All the chemicals used were of AR grade. Pyridinium chlorochromate (PCC) was prepared by the literature method[8]. Piperidones were prepared by the procedures given in the literature[9]. These piperidones were then converted into oximes by reacting with hydroxylamine hydrochloride in the presence of sodium acetate[10]. Acetic acid used for kinetic runs was purified by the usual procedure[11].

Kinetic measurements: The reactions were studied under pseudo-first order conditions by keeping a large excess of the oxime over PCC in 60 % (v/v) aqueous acetic acid medium in the presence of sulphuric acid and sodium sulphate. The reactions were followed by monitoring the decrease in [PCC] at 355 nm spectrophotometrically. The pseudo-first order rate constant k_{obs}, was evaluated from the linear least square plots of log [PCC] *versus* time and were found to be reproducible within 3 %. The reactions were performed at four different temperatures and the activation parameters are calculated and tabulated (Table-1).

TABLE-1
RATE DATA FOR THE OXIDATION OF
3-ETHYL-2,6-DIPHENYL PIPERIDIN-4-ONE OXIME BY PCC

[PCC] × 10^{-4} mol dm^{-3}	[3-EtPPO] × 10^{-2} mol dm^{-3}	[H_2SO_4] × 10^{-3} mol dm^{-3}	μ mol dm^{-3}	AcOH: H_2O	k_1 × 10^{-4} (s^{-1})
2.5	1.0	2.0	0.021	60:40	17.09
5.0	1.0	2.0	0.021	60:40	7.99
7.5	1.0	2.0	0.021	60:40	3.75*
10.0	1.0	2.0	0.021	60:40	2.51
7.5	0.5	2.0	0.021	60:40	2.29
7.5	0.75	2.0	0.021	60:40	2.89
7.5	1.25	2.0	0.021	60:40	4.36
7.5	1.0	1.0	0.021	60:40	2.77
7.5	1.0	3.0	0.021	60:40	4.10
7.5	1.0	4.0	0.021	60:40	4.60
7.5	1.0	2.0	0.018	60:40	3.59
7.5	1.0	2.0	0.024	60:40	4.09
7.5	1.0	2.0	0.027	60:40	4.38
7.5	1.0	2.0	0.021	40:60	6.42
7.5	1.0	2.0	0.021	50:50	4.80
7.5	1.0	2.0	0.021	70:30	2.70
2.5	1.0	2.0	0.021	60:40	17.09

*at 288K-2.19, at 298 K-6.11, at 303 K-12.51.

Stoichiometry and product analysis: The stoichiometry of the reaction was estimated by allowing a known excess of PCC to react with a known concentration of oxime in 60 % aqueous acetc acid medium and it was determined to be 1:1. The above reaction mixture was analyzed and the product was determined to be the parent ketone. This was confirmed by TLC and qualitative tests[12].

Test for free radicals: There was no polymerization of the added acrylonitrile monomer in the reaction mixture. This points out that there are no free radical intermediates in this reaction.

RESULTS AND DISCUSSION

Dependence of rate on [PCC] and [oxime]: The plots of log [PCC] *versus* time were linear indicating a first order dependence on [PCC]. However, the pseudo-first order rate constants decreased with increase in initial concentration of PCC which is common in PCC oxidations. The plot of PCC *versus* time (min) at different initial concentration of oxime but at a fixed concentration of PCC were linear and the values of k_1 s^{-1} evaluated from the slopes were found to be dependent on the initial concentration of oximes. The values of k_1 s^{-1} plotted against [oxime] gave straight lines passing through the origin exhibiting a clean first order dependence on [oxime]. Moreover from the slopes of the above plots the second order rate constants k_2 were evaluated and found to be constant confirming the first order dependence on [oxime].

Order with respect to [H^+]: The effect of variation of [H^+] on the rate of oxidation was studied at constant ionic strength. The oxidation reactions were found to be acid catalyzed. The plots of log k_1 against log [H^+] are linear and the values of the slopes indicated a fractional order.

Effect of ionic strength: The ionic strength of the medium was varied by adding required amounts of Na_2SO_4 (0.018-0.027). The rates of oxidation were not influenced by change in ionic strength of the medium. This indicates that the reaction is between an ion and a dipole[13].

Dependence on solvent polarity: The influence of solvent polarity on the reaction rates was studied and it was found that the reaction rates increased with increase in dielectric strength of the medium. This is consistent with the fact that the charge density is delocalized in the transition state.

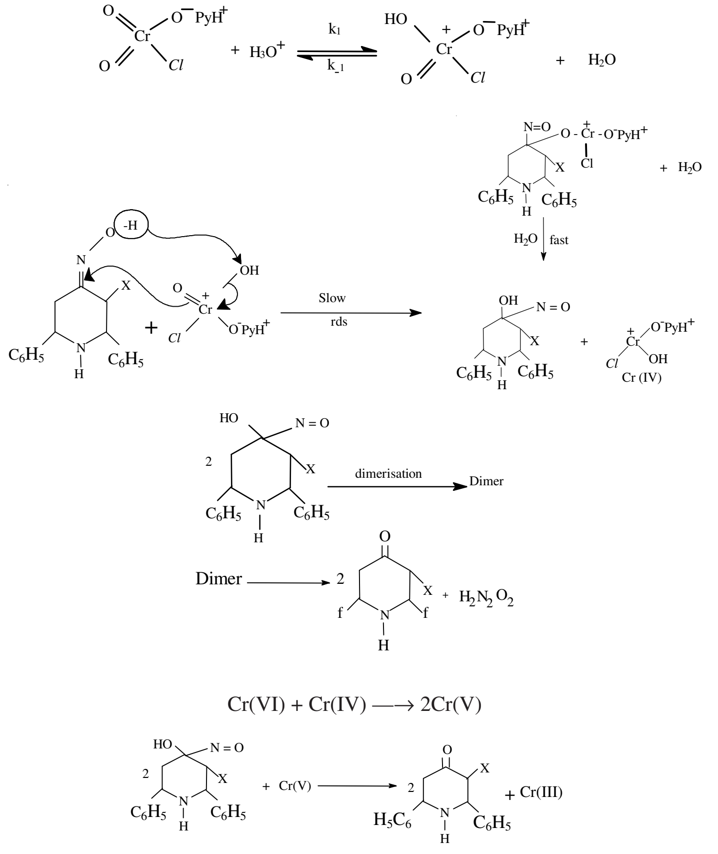
Effect of temperature and activation parameters: The second order rate constants were found to increase with increase in temperature. The plots of log k_2 *vs.* 1/T were linear in accordance with Arrhenius equation. Various activation parameters are tabulated (Table-2).

TABLE-2
RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE OXIDATION OF OXIMES

[Substrate] $=1 \times 10^{-3}$ mol dm^{-3}, [PCC] $= 7.5 \times 10^{-4}$ mol dm^{-3},
$\mu = 0.021$ mol dm^{-3}, AcOH = 60 % (v/v)

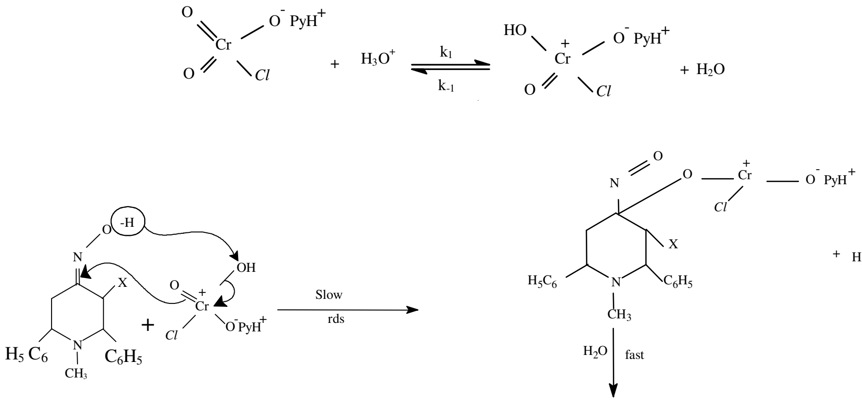
Substrate (278 K)	283 K ($k_2 \times 10^2$ 288 K)	dm^3 293 K (mol^{-1} 298 K)	s^{-1} 303 K (308 K)	Ea kJ/mol (ΔH≠ kJ/mol	ΔS≠ kJ/mol (ΔG≠ kJ/mol
1-Me-3-EtPPO	–	2.82	11.55	82.82	–2.2400
(–)	(1.880)	(4.9)	(–)	(80.38)	(81.040)
1-MePPO	17.60	41.60	–	66.17	–33.750
(10.40)	(23.80)	(–)	(–)	(63.73)	(73.620)
1,3-Me$_2$PPO	11.10	36.20	–	70.90	–19.270
(6.90)	(26.20)	(–)	(–)	(68.47)	(74.11)
1-Me-3-iprPPO	–	0.126	0.332	68.80	–72.550
(–)	(–)	(0.151)	(0.526)	(66.36)	(87.620)
1,3,3-Me$_3$PPO	–	0.770	1.390	45.83	–137.27
(–)	(0.600)	(0.880)	(–)	(43.40)	(83.620)

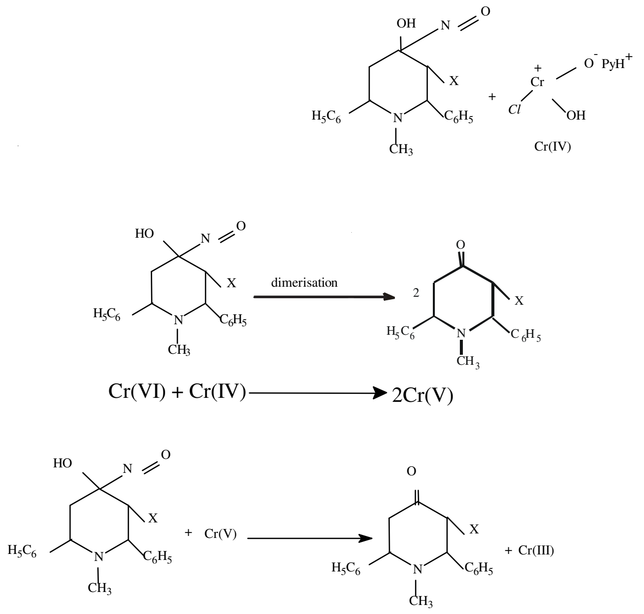
Mechanism: The oxidation reactions are catalyzed by acid. A very large increase in the oxidation rate with acidity suggests the involvement of a protonated Cr^{6+} species[14]. The participation of such species is well known in PCC oxidation. In the present study, the slow formation of a positively charged PCC ester between the oxime and protonated PCC by the removal of water molecule is proposed as reported in the chromic acid oxidation of alcohols[15], oxidation of aldehydes by PFC[16], acids by PCC[17], alicyclic ketoximes by PFC[4]. The PCC ester then undergoes hydrolysis quickly to give the corresponding ketone.



X = - H, -Me, -Et, -ipr, -3, 3 - dime

Scheme-I





X = - H, -Me, -Et, -ipr, -3,3-Me_2

Scheme-II

Influence of structure on reaction rates: The observed trend of reactivity among the various oximes is 1-MePPO > 1,3-Me_2PPO > 1-Me-3-EtPPO > 1,3,3-Me_2PPO > 1-Me-3-iprPPO. This can be attributed to the steric as well as inductive effect of the substituents.

REFERENCES

1. J.P. Freeman, *Chem. Rev.*, **73**, 283 (1973).
2. T.S. Jani Bai, Ph.D. Thesis, Bharathidasan University, Tiruchirapalli, India (1988).
3. T.S. Jani Bai, V. Usha and R. Subbalakshmi, *Asian J. Chem.*, **17**, 1611 (2005).
4. T.S. Jani Bai, R. Subbalakshmi and V. Usha, *Asian J. Chem.*, **17**, 1240 (2005).
5. T.S. Jani Bai and M. Vasuki, *J. Indian Coun. Chem.*, **21**, 60 (2004).
4. T.S. Jani Bai and R. Santhi, *J. Indian Coun. Chem.*, **21**, 55 (2004).
7. S. Shyamala, Ph.D. Thesis, Bharathidasan University (1999).
8. E.J. Corey and W.J. Suggs, *Tetrahedron Lett.*, 2647 (1975).
9. V. Baliah and C. Roller, *J. Am. Chem. Soc.*, **70**, 3853 (1948).
10. V. Baliah, K.Pandiarajan and M.A. Lakshmanan, *Indian J. Chem.*, **16B**, 72 (1978).
11. K.J.P. Ortan and A.E. Bradfield. *J. Chem. Soc.*, 983 (1927).
12. F. Feigel, Spot Tests in Organic Analysis, Elsevier Publishing Company, p. 228 (1960).
13. K.J. Laidler, Chemical Kinetics, Tata McGraw Hill Pub., New Delhi, India, p. 229 (1965).
14. M.K. Pillay and R. Kasthuri, *Indian J. Chem.*, **37B**, 544 (1998).
15. K.K. Sengupta, T. Samanta and S.N. Basu, *Tetrahedron*, **42**, 681 (1986).
16. A. Aggarwal, K. Chowdhury and K.K. Banerji, *J. Chem. Res. Synop.*, **3**, 86 (1990).
17. K.K. Banerji, *Indian J. Chem.*, **17A**, 300 (1979).

(*Received*: 30 June 2009; *Accepted*: 1 December 2009) AJC-8121