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N-Methyl-2,6-diphenylpiperidin-4-one oxime Oxidized by Quinaldinium Fluorochromate in Aqueous Acetic Acid Medium

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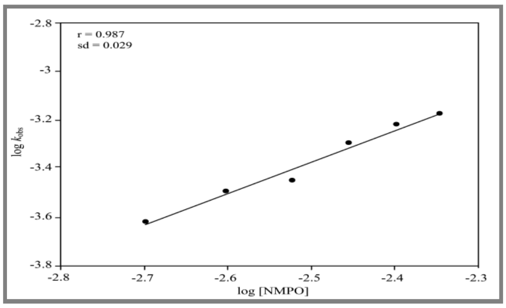
ABSTRACT

Kinetics of oxidation of [NMPO] by [QNFC] in protic solvent system has been studied at 308 K. The product has been identified as corresponding ketonic group. A first order dependence of the reaction with respect to [QNFC] and [NMPO] has been observed. The reaction has been found to be catalyzed by H^+ *ions. The rate constant increased with increase in the concentration of perchloric acid. Increasing the percentage of the acetic acid medium increases the rate. Addition of sodium perchlorate decreases the rate of reaction appreciably. No polymerization with acrylonitrile. The reaction has been conducted at four different temperature and the activation parameters were calculated. From the observed kinetic results a suitable mechanism was proposed.*

Graphical Abstract



Plot of log k_{obs} *versus* log [NMPO].

Keywords: NMPO, QNFC, Oxime, Acetic acid.

INTRODUCTION

Oxidation reaction has been a subject of major importance to many chemists and elucidation of the mechanism is undoubtedly one of the most fascinating problems in the mind of chemists. The investigation of reaction kinetics in chemical reactions is the most important in deciding the reaction mechanisms. The kinetics deal with the study of change in concentrations of the components of the reaction system with the passage of time and the results are summarized in the form of rate expressions.

Quinaldinium fluorochromate (VI) as an oxidant: Chromium compounds have been widely used in aqueous and non-aqueous media for the oxidation of a variety of organic compounds [1-7]. Chromium compounds have been proved to be a versatile reagent for the oxidation of almost all the organic functional groups [8-12]. Generally Cr(VI) oxidation reactions have been performed in aqueous acidic conditions, the source of Cr(VI) being chromium trioxide, sodium dichromate, potassium dichromate, chromyl chloride, chromyl acetate and t-butyl chromate or co-oxidation complexes chromic acid exhibits the following equilibria in an aqueous solution in the absence of other ions [13].

Oxidation of N-methyl-2,6-diphenylpiperidin-4-one oxime [NMPO]: The oxidation reaction is the most important role of kinetic reaction, like oxime oxidations [14-23].

MATERIALS AND METHODS

Preparation of [NMPO]: The corresponding oxime was prepared as described by Krishnasamy *et al.* [24].

Other chemicals: [QNFC] was prepared by the method described in the literature [25]. All other chemicals were used as supplied without further purification used in this experiment are all of AR grade samples.

Product analysis and stoichiometry oxidation of [NMPO] by [QNFC]: The required quantity of [NMPO] (0.1 mol), [QNFC] (0.1 mol) were mixed together with perchloric acid (2.0 M) in 50% (v/v) in aqueous acetic acid (total volume 100 mL). The reaction mixture was set aside for about 24 h to ensure the completion of the reaction. It was then evaporated and extracted with ether. The ether layer was separated and dried. The residue was confirmed as corresponding ketone (m.p.199°C; lit. 200°C) and 2,4-dinitrophenylhydrazine derivative test.

Purification of water: Deionized water was distilled twice in a corning vessel. The second distillation was over potassium permanganate. All solutions were prepared from double distilled water. The following solutions of required concentrations were prepared and used for the kinetic studies: i) QNFC, perchloric acid, sodium perchlorate and manganous sulfate in water, ii) NMPO in acetic acid.

Kinetics and oxidation of [NMPO] by [QNFC]: All the kinetic reactions were carried out under pseudo-first order conditions, keeping [substrate] >> [QNFC] in a solvent system of 50% (v/v) acetic acid-water medium at 308 K unless otherwise mentioned and the course of the reaction were followed by iodometrically.

RESULTS AND DISCUSSION

Effect of varying [QNFC]: The reactions were investigated with varying concentration of [QNFC] and keeping all other reactant concentrations constant and the rate constants were calculated (Table 1). First order dependence on [QNFC] was evidenced from the linear plot of log titre *versus* time (s) (r = 0.999, B = 1.52).

Effect of varying [NMPO]: The reaction was investigated with varying concentration of [NMPO] and keeping all other reactant concentrations constant and the observed rate constant values were given in table 2. A plot of log k_{obs} *versus* log [NMPO] (Figure 1) is linear with a slope (r = 0.987, B = 1.20). This shows that this oxidation reaction is first order dependence with respect to [NMPO].

Table 1. Effect of varying the [QNFC]

10^3 [QNFC] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})
1.00	3.43
1.50	3.46
2.00	3.51
3.00	3.56
4.00	3.60
5.00	3.65

[NMPO] = 3.00×10^{-2} mol dm^{-3}, [H$^+$] = 1.50×10^{-2} mol dm^{-3}, solvent = 50-50 (% v/v) AcOH-H_2O, temperature = 308 K

Table 2. Effect of varying the [NMPO]

10^2 [NMPO] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})
2.00	3.00
2.50	3.22
3.00	3.51
3.50	5.00
4.00	5.96
4.50	7.11

[QNFC] = 2.00×10^{-3} mol dm^{-3}, [H$^+$] = 1.50×10^{-2} mol dm^{-3}, solvent = 50-50 (% v/v) AcOH-H_2O, temperature = 308 K

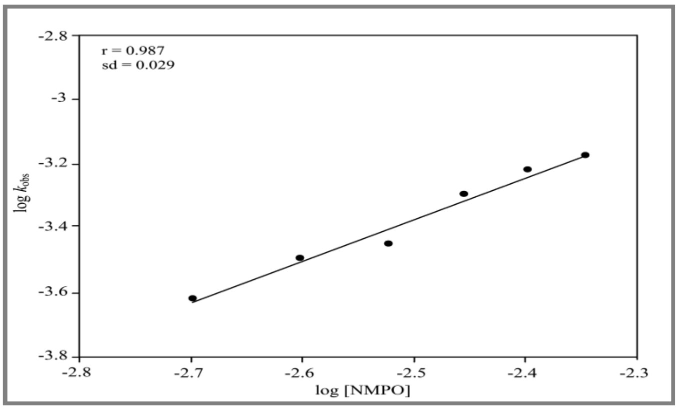


Figure 1. Plot of log k_{obs} *versus* log [NMPO].

Effect of varying [H$^+$]: The reaction was carried out with varying concentration of perchloric acid and keeping all other reactant concentrations constant and measured the rate constant values. The rate constant increased with increase in the concentration of [perchloric acid] were given in table 3. The plot of log k_{obs} *versus* log [H$^+$] gives a straight line with a slope (r = 0.992, B = 0.48) shows that this reaction is fractional order dependence with respect to [H$^+$].

Table 3. Effect of varying the [H$^+$] concentration

10^2 [H$^+$] (mol dm^{-3})	$10^4 k_{obs}$ (s^{-1})
0.50	1.89
1.00	2.61
1.50	3.51
2.00	4.70
2.25	5.00
2.50	6.06

[NMPO] = 3.00×10^{-2} mol dm^{-3}, [QNFC] = 2.00×10^{-3} mol dm^{-3}, solvent = 50-50 (% v/v) AcOH-H_2O, temperature = 308 K

Effect of varying solvent composition: The reaction was carried out with different solvent composition of acetic acid-water mixtures and keeping all other reactant concentrations constant and the corresponding rate constant values were given in table 4. The kinetic results show that increase in the percentage of acetic acid in the reaction mixture, the rate constant increased. This suggests that an ion-dipole interaction may be involved in the mechanistic pathway.

Table 4. Effect of varying the solvent composition

AcOH-H_2O (% v/v)	$10^4\ k_{obs}$ (s^{-1})
45:55	2.98
50:50	3.51
55:45	5.00
60:40	5.63

[NMPO] = 3.00 × 10^{-2} mol dm^{-3}, [QNFC] = 2.00 × 10^{-3} mol dm^{-3},
[H^+] = 1.50 × 10^{-2} mol dm^{-3}, temperature = 308 K

Effect of varying [$NaClO_4$], [acrylonitrile] and [$MnSO_4$]: The rate data were measured with different concentration of $NaClO_4$ and keeping all other reactant concentrations constant. The rate constant decreases with increasing the concentration of $NaClO_4$ suggest that the reaction may be between an ion and neutral molecule. Added acrylonitrile rules out the possibility of radical pathway mechanism. Added Mn^{2+} slightly increases the reaction rate [26] (Table 5).

Table 5. Effect of varying the [$NaClO_4$], [acrylonitrile] and [$MnSO_4$]

10^4 [$NaClO_4$] (mol dm^{-3})	$10^4\ k_{obs}$ (s^{-1})
0.00	3.51
2.50	3.01
10.00	2.90
12.50	1.99
10^4 [Acrylonitrile] (mol dm^{-3})	**$10^4\ k_{obs}$ (s^{-1})**
2.50	3.50
10.00	3.60
12.50	3.55
10^4 [$MnSO_4$] (mol dm^{-3})	**$10^4\ k_{obs}$ (s^{-1})**
2.50	3.52
5.00	3.60
12.50	3.79

[NMPO] = 3.00 × 10^{-2} mol dm^{-3}, [QNFC] = 2.00 × 10^{-3} mol dm^{-3}, [H^+] = 1.50 × 10^{-2} mol dm^{-3},
solvent = 50-50 (% v/v) AcOH-H_2O,temperature = 308 K

Effect of different oxidizing agents: The reactions were carried out in the presence of different oxidizing agents *viz.*, NDC, QNFC, BIFC, PFC and keeping the concentration of all other reactant concentrations as constant and the measured rate constant values were given in table 6. The observed

Table 6. Rate constants for the oxidation of various chromium(VI) reagents

Oxidants	10^3 [Oxidant] (mol dm^{-3})	$10^4\ k_{obs}$ (s^{-1})
NDC	2.00	3.13
NDC*	2.00	4.16
QNFC	2.00	3.51
QNFC*	2.00	5.05
BIFC	2.00	5.90
BIFC*	2.00	7.42
PFC	2.00	6.73
PFC*	2.00	8.98

[NMPO] = 3.00 × 10^{-2} mol dm^{-3}, [H^+] = 1.50 × 10^{-2} mol dm^{-3}, solvent = 50-50 (% v/v) AcOH-H_2O, temperature = 308 K ,*In the presence of [4,5-Diazophen] = 15.00 × 10^{-3} mol dm^{-3}

results show that both catalytic and uncatalytic system of the all fluorochromium compounds is higher oxidizing capability than NDC.

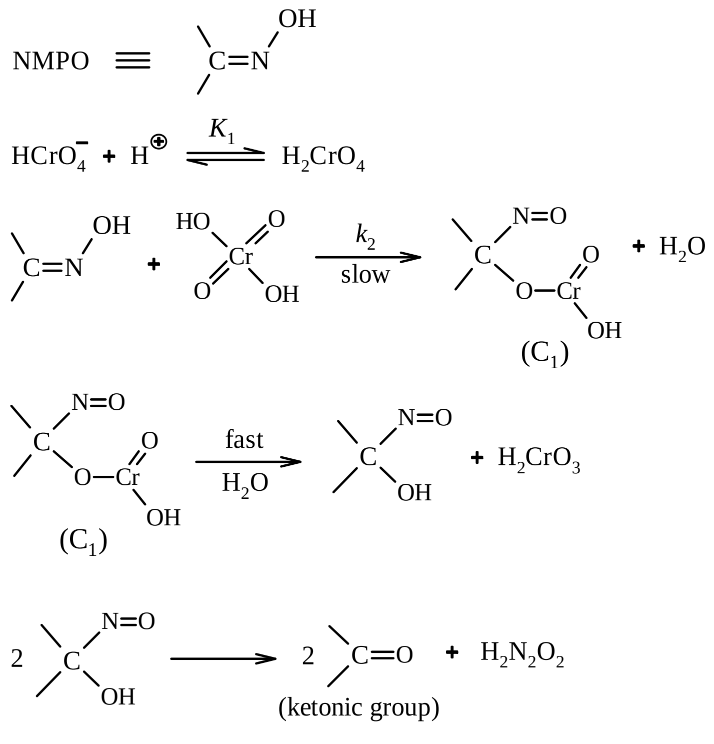
Effect of temperature: The reactions were carried out at four different temperatures *viz.*, 298, 303, 308 and 313K and keeping all other reactant concentrations constant and the rate constants were calculated (Table 7). The thermodynamic parameters were calculated from the Eyring's plot of ln k_{obs}/T *versus* 1/T are given below $\Delta H^{\#}$ = 26.32 kJ mol^{-1}, $\Delta S^{\#}$ = -186.35 J $K^{-1}mol^{-1}$.

Table 7. Effect of temperature various reaction rates

Temperature (K)	$10^4 k_{obs}$ (s^{-1})
298	2.88
303	3.41
308	3.51
313	6.95

[NMPO] = 3.00×10^{-2} mol dm^{-3}, [QNFC] = 2.00×10^{-3} mol dm^{-3}, $[H^+] = 1.50 \times 10^{-2}$ mol dm^{-3}, solvent = 50-50 (% v/v) AcOH-H_2O

Mechanism and rate law: The $HCrO_2^-$ first protonates to give H_2CrO_4 in an equilibrium step. $HCrO_4^-$ reacts with NMPO to give a complex (C_1) in the slow step. Then this complex (C_1) dissociates to give products as follows:



The proposed mechanism has been characterized with the following rate law:

$$\text{Rate law} = \frac{-\,d[\text{Cr(VI)}]}{dt} = \frac{K_1 k_2 [\text{NMPO}][\text{Cr(VI)}][H^+]}{\{1 + K_1 [H^+]\}}$$

The proposed mechanism explains the first order dependence on [NMPO] [QNFC] and also the fractional order dependence on $[H^+]$.

APPLICATION

Oxidation reaction has been a subject of major importance to many chemists and elucidation of the mechanism is undoubtedly one of the most fascinating problems in the mind of chemists.

CONCLUSION

The reaction is carried out in aqueous acetic acid medium at 308 K and the following results were obtained. Unit order dependence with respect to [QNFC] and [NMPO] and the fractional order [H^+] has been observed. Increase in the percentage of acetic acid increases the rate of the reaction. Added acrylonitrile has no effect on the reaction rate, ruling out the possibility of free radical pathway mechanism. The reaction is characterized by low enthalpy of activation and negative entropy of activation.

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