# Kinetics & Mechanism of Oxidation of Diphenyl Sulphoxide by N-Chloro-3-methyl-2,6-diphenylpiperidin-4-one in Perchloric Acid Medium

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The title reaction in the presence of perchloric acid in 75% (v/v) ethanol-water mixture at 30°C is of a total second order, being first order each in [oxidant] and [substrate]. Activation parameters have been evaluated. The results are discussed in terms of a mechanism involving a rate-determining formation of an intermediate between protonated oxidant and sulphur of the sulphoxide.

The kinetics and mechanisms of oxidation of sulphoxides to sulphones by different oxidants have been investigated by several groups[1-4]. The oxidant, N-chloro-3-methyl-2,6-diphenylpiperidin-4-one (NCP) has not been used so far for such kinetic investigations and hence the present investigation. The reaction has been carried out in perchloric acid medium, since in other media oxidation of sulphoxide to sulphone is very slow[5,6] in comparison to that of sulphide.

Kinetic runs were carried out in 75% (v/v) ethanol-water mixture under pseudo-first order conditions at the desired temperature which could be maintained with an accuracy of ± 0.01°C. The rate of disappearance of oxidant was followed by the iodometric estimation of the unreacted oxidant as described by Koltholf and Carr (see ref. 6 for details).

The linearity of the rate profiles indicates that the rate of disappearance of oxidant follows first order rate law in each kinetic run. Pseudo-first order rate constants were evaluated from the gradients of the linear plots by the method of least squares using a computer IBM 1130 systems. The stoichiometry of the reaction comes out to be 1:1, i.e. 1 mol of oxidant consumed 1 mol of substrate to give diphenyl sulphone as the product which was identified by direct comparison (m.p. and m.m.p. 126°) with an authentic sample.

$$C_6H_5SOC_6H_5 + \rangle N - Cl + H_2O \rightarrow C_6H_5SO_2C_6H_5 + \rangle N - H + H^+ + Cl^-$$
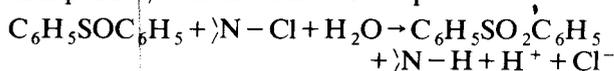
The results of the kinetic runs reveal the following characteristic features.

(i) The reaction was first order in NCP as evidenced by the linearity of log titre versus time plots and the non-invariance of the rate constants at different [NCP].

(ii) The pseudo-first order constants increased with increase in [substrate]. The plots of log $k_1$ versus log [substrate] were linear with slope of unity indicating first order in [substrate].

(iii) Increase in ionic strength of the medium from 0.1040 to 0.3885 mol dm$^{-3}$ (NaClO$_4$) increased the rate constants from $2.74 \times 10^{-4}$ s$^{-1}$ to $5.72 \times 10^{-4}$ s$^{-1}$ showing participation of charged particles in the rate-determining step.

(iv) At fixed [substrate] and [oxidant] and temperature the rate constant increased with increase in [H$^+$], the order being one as revealed by the unit slope of linear plot of log $k_1$ versus log [H$^+$].

(v) The rate constants increased with increase in water content of the reaction medium. For example in ethanol-water mixtures containing 60, 65, 70, 75 and 80% (v/v) ethanol, the rate constants were $3.86 \times 10^{-4}$, $2.88 \times 10^{-4}$, $2.26 \times 10^{-4}$, $1.75 \times 10^{-4}$ and $1.63 \times 10^{-4}$ s$^{-1}$ respectively. The increase in the rate constant with increase in the dielectric constant of the medium may probably be due to the ion-dipole interaction of the reactants.

The kinetic runs were repeated at four different temperatures 25°, 30°, 35° and 40°C under the conditions: [substrate] $= 1.012 \times 10^{-2}$ mol dm$^{-3}$, [oxidant] $= 1.055 \times 10^{-3}$ mol dm$^{-3}$, [H$^+$] $= 6.0 \times 10^{-2}$ mol dm$^{-3}$. The rate constants $(k_2)$ calculated were $1.01 \times 10^{-2}$, $1.73 \times 10^{-2}$, $2.71 \times 10^{-2}$ and $4.09 \times 10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$, respectively. The enthalpy and entropy of activation were calculated and found to be 69.59 kJ mol$^{-1}$ and $-49.40$ JK$^{-1}$ mol$^{-1}$ respectively by linear least squares method of a linear plot of log $k_2/T$ versus 1/T of the logarithmic form of Eyring's equation.

## Mechanism

In acid medium, the oxidant (NCP) is in equilibrium with its protonated form which is found to be an effective oxidising species[6-10]. The increase in the rate constant with increase in [H$^+$] also confirms the existence of such an equilibrium.

Since the reaction is first order each in [oxidant], [substrate] and [H$^+$] ion, it confirms the rate-determining electrophilic attack of the protonated NCP at the sulphur of the sulphoxide to form sulphone. The intermediate may decompose to give the sulphone by the attack of water.

The derived rate law is given below:

$$\text{Rate} = k \left[ {>}\overset{+}{N}{<}^H_{Cl} \right] \left[ \text{DPSO} \right]$$

$$\text{Where} \left[ {>}\overset{+}{N}{<}^H_{Cl} \right] = K \left[ {>}N{-}Cl \right] \left[ \overset{+}{H} \right]$$

$$\text{Rate} = kK \left[ {>}N{-}Cl \right] \left[ \overset{+}{H} \right] \left[ \text{DPSO} \right]$$

$$\frac{-d\left[\text{oxidant}\right]}{dt} = k_2(\text{obs}) \left[ {>}N{-}Cl \right] \left[ \text{DPSO} \right] \left[ \overset{+}{H} \right]$$

## References

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