ABSTRACT
The Thesis entitled "Kinetics and Mechanism of Oxidation of Organic Compounds" deals with oxidative degradation of few selected drugs i.e. Paracetamol and Diclofenac sodium by potassium permanganate and potassium dichromate as an oxidant under pseudo-first order conditions with an aim to determine various kinetic parameters i.e. Specific rate constant, order of reaction with respect to each reactants, over all order of the reaction, rate expression and activation parameters of the reactions. An attempt has also been made to suggest the possible structure of the different products formed during the course of oxidation reactions process through UV-visible spectral analysis technique in order to have a better understanding of the mechanism involved in these processes. This thesis is divided into four chapters.

The **Chapter 1** deals with "Introduction-An Overview on the Characteristics, Environmental Relevance and Degradation of Paracetamol and Diclofenac sodium". This chapter completely describes an introduction giving an overview on (i) The characteristics of these drugs, (ii) Their environmental relevance, (iii) Results published in literature on their degradation and (iv) Research work carried on these drugs by various research groups.

The **Chapter 2** deals with "Oxidative Degradation of Paracetamol by Permanganate in neutral medium-A Kinetic and Mechanistic Pathway" to study the kinetic parameters under pseudo-first order conditions to obtain reaction order with respect to each reactant using first-order integrated rate equation.

\[
\log ([A]_o / [A]) = kt/2.303
\]

The spectrophotometric kinetic studies were performed on the basis of the absorbance (optical density) noted at \(\lambda_{max}\) (wavelength) as a function of time. These reading were conveniently made with a Genesis 20 spectrophotometer for relatively slow reactions. The sample was withdrawn from the thermostated reaction mixture for measurement. The progress of the oxidative degradation was also followed by UV-visible spectroscopy. The reaction rate increases with [Paracetamol] in the range of \(1.81 \times 10^{-3}\) to \(4.28 \times 10^{-3}\) min\(^{-1}\). The structural characterization was studied by UV-visible spectroscopy. The spectral change (characteristic peaks) in the course of reaction was observed in the region 400 nm to 525 nm and there was a gradual decrease in
absorption intensity at its \( \lambda_{\text{max}} \) (525 nm). The kinetic data for the oxidation of paracetamol indicates the order with respect to each reactant, i.e.; both [Paracetamol] and [MnO_4^-] is one. The slope of \( \log k \) versus \( 1/T \) also confirms the first order dependence on the reactant. The activation parameters such as \( E_a, \Delta H^\circ, \Delta S^\circ \) and \( \Delta G^\circ \) were also evaluated for the reaction and found to be 23.9 kJ.mol\(^{-1}\), 21.4 kJ.mol\(^{-1}\), -225 J.K\(^{-1}\) mol\(^{-1}\) and 88.4 kJ.mol\(^{-1}\), respectively. Probable mechanism with the observed kinetic results has been suggested.

**Chapter 3** “Kinetics and Mechanism of Oxidative Degradation of Paracetamol by Potassium dichromate in Acidic Medium”. The study deals with the kinetics of oxidative degradation of paracetamol by dichromate in acidic medium was studied spectrophotometrically, in order to evaluate the kinetic parameters under pseudo-first order conditions. The reaction-order with respect to each reactant using first-order integrated rate equation is given in chapter 2. The degradation process was slow with pseudo-first order rate constant \( 26.3 \times 10^3 \) min\(^{-1}\) to \( 08.4 \times 10^3 \) min\(^{-1}\) at various concentration of dichromate. The rate increased with an increase in the concentration of both of the reactants. The kinetic data for the oxidation of paracetamol indicates the order with respect to each reactant, i.e.; both [Paracetamol] and [Dichromate] is one. The course of degradation was studied by UV-visible spectroscopy. The spectral change in the course of reaction, the absorption intensity in the region 345-350 nm decreased gradually as the reaction proceeded. Increasing reaction temperature and oxidant concentration can accelerate the paracetamol degradation rates. The activation energy with respect to slow step of the mechanism is calculated and discussed \( (E_a = 14.1 \text{ kJ.mol}^{-1}) \).

Thermodynamic quantities \( \Delta H^\circ, \Delta S^\circ, \) and \( \Delta G^\circ \) are computed by using Eyring equation and found to be 11.5 kJ.mol\(^{-1}\), -242 JK\(^{-1}\).mol\(^{-1}\) and 85.9 kJ.mol\(^{-1}\), respectively. A probable mechanism for the reaction has been suggested.

**Chapter 4** “Oxidative Degradation of Diclofenac sodium by Permanganate in neutral medium-A Kinetic and Mechanistic Pathway” deals with the kinetics of oxidation of Diclofenac sodium with potassium permanganate in neutral medium under pseudo-first order conditions to obtain the different kinetic parameters of the reaction. The reaction follows truly first-order kinetics with respect to each reactant.
The course of degradation was studied by UV-visible spectroscopy. The spectral change in the course of reaction was studied in the range 450-750 nm. As expected, the absorption intensity in the region 510-600 nm (characteristic peak complex for permanganate) decreased gradually as the reaction proceeded. Increasing reaction temperature and oxidant concentration can accelerate the Diclofenac sodium degradation rates. The effect of temperature on reaction rate is discuss with the help of Arrhenius equation i.e. \( k = z e^{-\frac{E_a}{RT}} \). This equation also helps to calculate the activation energy of the reaction and it was found to be 21.1 kJ.mol\(^{-1}\).

The plot of log \( k \) versus \( 1/T \) of the reaction give straight line with negative slope that confirm that reaction follows first-order kinetics with respect to each of the reactant. Thermodynamic quantities \( \Delta H^\circ, \Delta S^\circ, \text{ and } \Delta G^\circ \) are computed by using Eyring equation and found to be 18.5 kJ.mol\(^{-1}\), \(-236 \text{ JK}^{-1}\text{.mol}^{-1}\) and 88.9 kJ.mol\(^{-1}\), respectively. Thus, finally the rate expression is deduced for the reaction under study.

Other oxidants like potassium dichromate, ammonium molybdate were also used with Diclofenac sodium in acidic as well as in neutral medium but they did not show degradation behavior.