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The thesis entitled " Kinetics and Mechanism of halogenation of phenols " is being submitted to the Marathwada University, Aurangabad, for the award of the degree of Doctor of Philosophy in Chemistry.

Introduction:

Halogenophenols have been reported to possess bactericidal and fungicidal activity. Halogenobiphenyls have been used extensively for industrial purpose over the past 50 years. Polychlorinated biphenyls are used in paints, varnishes, adhesives, paper ink lubricants and in some electrical equipments. Hence the kinetics and Mechanism of bromination of some hydroxybiphenyls and some p-substituted phenols have been studied.

The thesis is divided into six chapters.

Chapter: I

This is an introductory chapter and contains the literature survey of the kinetics and mechanism of halogenation of phenols by different halogenating reagents.
Chapter: II

This chapter includes the experimental part of the work and deals with the reagents, the experimental procedure, apparatus, the kinetic data and methods of kinetic measurements.

Chapter: III

Bromination of o and p-hydroxybiphenyl by molecular bromine in acetic acid medium is studied in this chapter. The overall order in this bromination of o-hydroxybiphenyl in glacial acetic acid medium is found to depend on the concentration of the reactants, three at higher concentration and two at lower concentration region. So the rate expression is:

$$-\frac{d}{dt} \frac{[\text{ArBr}]}{} = K_3 \frac{[\text{ArH}] [\text{Br}_2]}{} + K_2 \frac{[\text{ArH}] [\text{Br}_2]^2}{}$$

In the high concentration region, the bromine molecule acts as electrophile at the rate determining step. In the overall second process, an acetic acid solvent molecule acts as an electrophile. An order in acetic acid, a solvent molecule participating in the reaction is determined and found to be one.

The overall order in p-hydroxybiphenyl is found to be two at higher and lower concentration region.
So the rate expression is:

\[
-d \frac{[\text{ArBr}]}{dt} = k_2 \frac{[\text{ArH}]}{[\text{Br}_2]}
\]

The effect of solvent and temperature on the rate have been studied. On the basis of observed results probable reaction mechanism is discussed.

Chapter: IV

Kinetics of bromination of some p-substituted phenols viz. p-cresol, p-chloro-m-cresol, p-methoxyphenol, p-hydroxybenzophenone, p-hydroxybenzaldehyde and p-hydroxybenzoic acid have been studied by molecular bromine in acetic acid medium. Overall order in p-hydroxybenzaldehyde and p-hydroxybenzoic acid is found to be three and two at higher and lower concentrations respectively. The remaining phenols studied show overall order two at lower and higher concentration region. Effect of temperature and effect of solvent on rate of bromination of phenols is investigated and probable reaction mechanism is discussed on the basis of observed results. A linear free energy correlation is attempted by casting the data into Hammett equation.
Chapter V

This chapter deals with iodine bromide catalysed bromination of o and p-hydroxybiphenyl. Overall order is three and individual order being one with respect to each reactants and catalyst. The bromination phenomenon of catalytic maximum has been investigated. On the basis of observed facts, reaction mechanism is discussed.

Chapter VI

This chapter includes the kinetics and mechanism of bromination of o and p-hydroxybiphenyl, p-hydroxybenzoic acid, p-hydroxybenzaldehyde, etc. by N-bromosuccinimide in glacial acetic acid medium. All the phenols studied show overall order two at higher and lower concentrations. Individual order is one in each reactants for phenol and as well as NBS. So the rate expression is:

\[- \frac{d}{dt} \frac{[\text{ArBr}]}{} = K_2 \frac{[\text{Phenol}]}{[\text{NBS}]} \]

Effect of solvent, sodium acetate and temperature on rate of reaction is studied. Probable reaction mechanism is proposed. A linear free energy correlation is attempted by casting the data into Hammett equation.