The kinetics of oxidation of (arylthio)acetic acids with the N-halo oxidants, N-bromophthalimide and N-Chlorosaccharin and of diaryl sulphides with N-chlorosaccharin have been investigated with a view to elucidate the mechanisms. The results obtained and the conclusions arrived at in the three systems are summarized below:

**N-Bromophthalimide – (Arylthio)acetic Acid System**

The kinetics of oxidation of (arylthio)acetic acids with N-bromophthalimide have been studied potentiometrically in 80:20 (v/v) acetonitrile-water medium at 298 K. The reaction is first-order each with respect to thioacid and NBP and shows a negative dependence on [H⁺]. NBP itself is shown to be the active oxidizing species. The reaction rate is not significantly affected by the change in ionic strength of the medium, indicating the involvement of a neutral species in the rate determining step. It has been found that added phthalimide has no influence on the rate of oxidation and this excludes the reversible nature of the reaction step, which involves saccharin as one of the products. The operation of a one-electron oxidation giving rise to free radicals is excluded, as the rate of oxidation is unaffected in the presence of acrylonitrile. Added KBr does not affect the rate of oxidation, thus excluding the presence of bromide or bromonium ion as reactive species. It has also been found that the rate of oxidation increases remarkably with increase in the water content of the acetonitrile-water solvent mixture, which supports the formation of a polar intermediate. Based on the kinetic results, a
suitable mechanism and a rate law consistent with the experimental results have been proposed.

The effect of substituents on the reaction rate has been studied by employing several p-substituted (phenylthio)acetic acids. The electron-releasing substituent in the phenyl ring of the thioacid accelerates the reaction rate while the electron-withdrawing substituent retards the rate. The Hammett plot is excellently linear ($r = 0.996$) and the value of reaction constant ($\rho$) is -3.22. The negative $\rho$ value indicates the accumulation of positive charge in the transition state.

The effect of temperature on the reaction rate has been studied by carrying out the oxidation at four different temperatures and it has been found that the $\rho$ value decreases with increase in temperature. The activation parameters have been evaluated from Arrhenius and Eyring plots. It has been shown that there exits a good correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values and the iso-kinetic temperature comes out to be 523 K. The existence of iso-kinetic relationship in the present study establishes that the mechanism of oxidation of all the (arylthio)acetic acids with NBP is one and the same.

**N-Chlorosaccharin – (Arylthio)acetic Acid System**

The kinetics of oxidation of (arylthio)acetic acids with N-chlorosaccharin have been studied potentiometrically in 80:20 (v/v) acetonitrile-water medium at 298 K. The reaction is first-order each with respect to thioacid and NCSA and shows a negative dependence on [H$^+$].
NCSA itself is shown to be the active oxidizing species. The reaction rate is not significantly affected by the change in ionic strength of the medium, indicating the involvement of a neutral species in the rate determining step. It has been found that added saccharin has no influence on the rate of oxidation and this excludes the reversible nature of the reaction step, which involves saccharin as one of the products. The operation of a one-electron oxidation giving rise to free radicals is excluded, as the rate of oxidation is unaffected in the presence of acrylonitrile. Added NaCl does not affect the rate of oxidation, thus excluding the presence of chloride or chloronium ion as reactive species. It has also been found that the rate of oxidation increases remarkably with increase in the water content of the acetonitrile-water solvent mixture, which supports the formation of a polar intermediate. Based on the kinetic results, a suitable mechanism and a rate law consistent with the experimental results have been proposed.

The effect of substituents on the reaction rate has been studied by employing several $p$-substituted (phenylthio)acetic acids. The electron-releasing substituent in the phenyl ring of the thioacid accelerates the reaction rate while the electron-withdrawing substituent retards the rate. The Hammett plot is excellently linear ($r = 0.999$) and the value of reaction constant ($\rho$) is -3.12. The negative $\rho$ value indicates the accumulation of positive charge in the transition state.

The effect of temperature on the reaction rate has been studied by carrying out the oxidation at four different temperatures and it has
been found that the ρ value decreases with increase in temperature. The activation parameters have been evaluated from Arrhenius and Eyring plots. It has been shown that there exits a good correlation between $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values and the iso-kinetic temperature comes out to be 555 K. The existence of iso-kinetic relationship in the present study establishes that the mechanism of oxidation of all the (arylthio)acetic acids with NCSA is one and the same.

**N-Chlorosaccharin – Diaryl Sulphides System**

The kinetics of oxidation of diphenyl sulphide with N-chlorosaccharin have been studied potentiometrically in 70:30 (v/v) acetonitrile-water medium at 298 K. The reaction is first-order each with respect to DPS and NCSA and fractional-order with respect to $H^\ddagger$. Protonated NCSA and NCSA are proposed to be the active oxidizing species. The reaction rate is unaffected by the change in ionic strength of the medium. It has been found that added saccharin has no influence on the rate of oxidation and this excludes the reversible nature of the reaction step, which involves saccharin as one of the products. The operation of a one-electron oxidation giving rise to free radicals is excluded, as the rate of oxidation is unaffected in the presence of acrylonitrile. Added NaCl does not affect the rate of oxidation, thus excluding the presence of chloride or chloronium ion as reactive species. It has also been found that the rate of oxidation increases remarkably with increase in the water content of the acetonitrile-water solvent mixture, which supports the formation of a polar intermediate. Based on
the kinetic results, a suitable mechanism and a rate law consistent with the experimental results have been proposed.

The effect of substituents on the reaction rate has been studied by employing several \( p \)-substituted diphenyl sulphides. The electron-releasing substituent in the phenyl ring of the sulphide accelerates the reaction rate while the electron-withdrawing substituent retards the rate. The Hammett plot is excellently linear \((r = 0.998)\) and the value of reaction constant \((\rho)\) is -3.28. The negative \( \rho \) value indicates the accumulation of positive charge in the transition state.

The effect of temperature on the reaction rate has been studied by carrying out the oxidation at four different temperatures and it has been found that the \( \rho \) value decreases with increase in temperature. The activation parameters have been evaluated from Arrhenius and Eyring plots. It has been shown that there exits a good correlation between \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \) values and the iso-kinetic temperature comes out to be 574 K. The existence of iso-kinetic relationship in the present study establishes that the mechanism of oxidation of all the diaryl sulphides with NCSA is one and the same.