PAPERS PRESENTED IN CONFERENCES/SYMPOSIA
AND PAPERS PUBLISHED IN JOURNALS.


PHY-49 : Oxidation of some heterocyclic ketone thiosemicarbazones by Chloramine-T in aquo-acetic acid medium-A kinetic and mechanistic study. V. Venkateswaran* and M. Asaithambi, Department of Chemistry (Research), Erode Arts College (Autonomous), Erode-638009, India.

Kinetics of oxidation of few piperidinone thiosemicarbazones (PTSC) by chloramine-T (CAT) in 15% aqueous acetic acid medium have been investigated in the presence of perchloric acid. Oxidation of all the substrates shows first order kinetics in [CAT] and fractional order in [PTSC]. The reactions show inverse fractional order dependence on [H_3O^+]. Variation in ionic strength of the medium has negligible effect on the rate of the oxidation in all cases. The rates of reactions are found to increase with decrease in the dielectric constant of the medium. Addition of the reduced product of the oxidant, viz. p-toluene sulphonamide has no significant effect on the rates. Added acrylamide fails to polymerise eliminating the possibility of free radical pathway for the reactions. Thermodynamic parameters have been evaluated by studying the reactions at several temperatures. A negative entropy of activation reveals that the reactions have a more orderly transition state. The stoichiometry of the reaction and the product analysis have been carried out. A plausible mechanism consistent with these observations has been proposed and the rate law deduced. The relative reactivities of variously substituted PTSC have been rationalized.
REACTIVITY OF HETEROCYCLIC KETONE THIOSEMICARBAZONES TOWARDS OXIDATION BY CHLORAMINES-T: A KINETIC STUDY

V. Venkateswaran,* M. Asaithambi and M. Govindaraju

Department Of Chemistry
Erode Arts College, Erode 638 009.

Reactivity of a few piperidinone thiosemicarbazones (PTS) towards oxidation by chloramine-T (CAT), have been investigated in aqueous acetic acid. Oxidation of all the substrates showed first order kinetics in CAT and fractional order in PTS. Inverse fractional order dependence on $\text{H}_2\text{O}^+$ has been noted. Variation in ionic strength of the medium and addition of the reduced product of the oxidant viz, $p$-toluenesulphonamide had only negligible effect on the rate of oxidation. Decrease in the dielectric constant of the medium increased the rate of the reactions. Added acrylamide failed to polymerize, eliminating the possibility of free radical pathway for the reactions. Thermodynamic parameters have been evaluated by studying the reactions at several temperatures. The stoichiometry of the reaction and the product analysis have also been carried out. A plausible mechanism consistent with experimental observations, has been proposed and the relative reactivities of various substituted PTS's have been rationalized.
Dr. V. Venkateswaran
Department of Chemistry,
Ende Arts College (Mysore),
Mysore - 570003

Dear Dr. V. Venkateswaran,

I am pleased to inform you that your research on the following topics has been accepted for publication in Asian Journal of Chemistry:

1. Recovery of some hexenyllic ketone hydrocarbons from dehydrogenation and a kinetic study.
2. Kinetics of aliphatic ketone hydrocarbons in acid catalyzed dehydrogenation and mechanistic study.
3. Recovery of some halogenated ketone hydrocarbons from dehydrogenation.

These papers will appear in Volume 16 No. 3 (2005) issue of Asian Journal of Chemistry.

The papers and further communications related to this research should be addressed to the Executive Editor:

Dr. Bhagwan Agarwal
Executive Editor

Thank you for your contribution.

Sincerely yours,

Dr. K. K. Agarwal
Managing Editor