



Kinetics and Mechanism of Oxidation of Thiosemicarbazide by Waugh-type 9-Molybdomanganate(IV) in Aqueous Perchloric Acid

S. S. More¹, V. M. Gurame² and G. S. Gokavi^{1*}

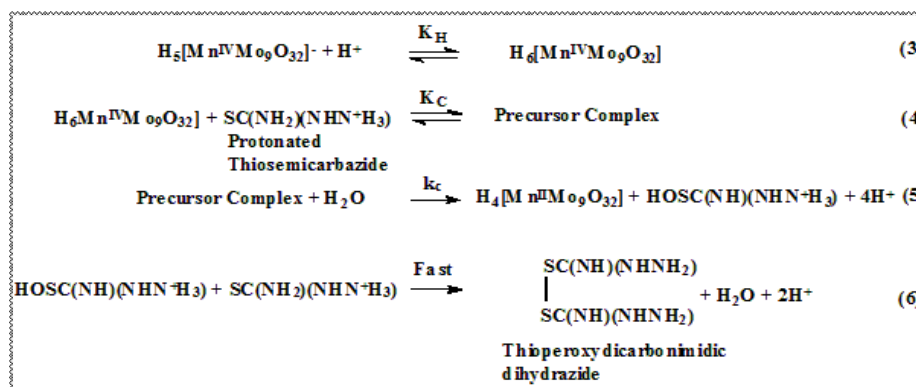
1. Department of Chemistry, Shivaji University, Kolhapur 416004, **INDIA**
2. Department of Chemistry, Shri Shivaji Mahavidyalaya, Barshi 413411, **INDIA**
Email: gsgokavi52@gmail.com

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ABSTRACT

Kinetics and mechanism of oxidation of thiosemicarbazide by Waugh-type polyoxometalate, 9-molybdomanganate (IV), was investigated under pseudo-first-order condition in aqueous perchloric acid. The stoichiometry was found to be 1 mole of $[Mn^{IV}Mo_9O_{32}]^{6-}$ per two moles of thiosemicarbazide indicating thioperoxy dicarbonimidic dihydrazide as the product. The rate of reaction increases with increase in hydrogen ion, 9-molybdomanganate (IV) and thiosemicarbazide concentrations. The protonated forms of both the oxidant and thiosemicarbazide are active species. The thiosemicarbazide is in its protonated form and converted into a tautomeric form, with a negative charge on the sulfur atom and interact with the active form of the oxidant at the oxygen atoms of type-2 forming a precursor complex. The precursor complex formed decomposes with the formation of sulfenic acid as an intermediate. The results of effects of ionic strength, solvent polarity and the temperature also support the proposed mechanism.

Graphical Abstract



Scheme 3

Keywords: Polyoxometalate oxidation, Reaction mechanism, 9-molybdomanganate, Thiosemicarbazide.