ABSTRACT

Oxidation of amino acids is one of the most prevalent forms of chemical reactions and is susceptible to modification by a wide array of oxidants. Uncharacteristic oxidation reactions are of particular concern in biotechnology and medicine. Therefore, it is important to understand the amino acid metabolism with a model system towards oxidants. In textile industry and tanneries the waste sent out to nearby area contain some simple amino acids which rise up the nutrients on that particular place. This may not be suitable for living plants and affects their growth and population. Therefore, before discharge, they may be treated completely and converted into ecofriendly products.

Peroxomonosulphate (PMS) is a highly effective oxidant for various oxidation reactions of both inorganic and organic substrates. It is a versatile oxidant and widely used in waste water treatment as well. Metal ion-catalyzed oxidation of amino acids was performed by researchers to mimic the oxidative decarboxylation of bioactive molecules. With these objectives in mind, the model system of kinetics of metal ions (VO$^{2+}$ and Cu$^{2+}$) catalyzed oxidation of amino acid was constructed to mimic the enzymatic oxidative decarboxylation in to non enzymatic mode by using effective oxidant such as PMS.

Kinetic studies were carried out at 308K in perchloric acid medium under pseudo first order conditions with a large excess of [amino acids]$\rightarrow$ [PMS]. The reaction rate was measured by monitoring the concentration of unreacted [PMS]$\rightarrow$ at various time intervals by iodometry. The kinetics and mechanism of VO$^{2+}$ catalyzed oxidation of five structurally different amino acids such as glycine, alanine, valine, N-methyl glycine and 2-amino isobutyric acid by PMS in perchloric acid medium was studied. The reaction did not proceed at all in the absence of VO$^{2+}$ ions. The VO$^{2+}$ ion was not oxidized by PMS under this condition. The reaction rate increases with increase in [AA], [VO$^{2+}$] and decreases with [H$^+$]. The reaction rate was also measured at different temperatures to calculate the thermodynamic parameters like free energy of activation ($\Delta G^\circ$), enthalpy of
activation \((\Delta H^\#)\) and entropy of activation \((\Delta S^\#)\). The activation enthalpies and entropies of the various amino acids were linearly interrelated, revealing that all the amino acids were oxidized by the same mechanism. The reaction proceeded by a non radical pathway as confirmed by EPR studies. Cyclic voltammetric and UV-Vis spectral studies confirmed the formation of \(\text{VO}^{2+} - \text{amino acid} - \text{PMS}\) complex. The proposed mechanism involved the abstraction of hydrogen from amine group of amino acid by \(\text{HSO}_5^-\) followed by the elimination of \(\text{CO}_2\) to give the vanadyl imine intermediate which on hydrolysis gave the corresponding carbonyl compound as a product, which was confirmed by Gas Chromatography (GC).

Kinetic of N-Phenyl Glycine (NPG) was very fast at 308K and unable to follow the reaction rate by iodometric method. Hence the kinetic studies of this reaction were carried out at 278K and the oxidation of NPG by PMS was studied both in the absence and presence of \(\text{Cu}^{2+}\) and \(\text{VO}^{2+}\) ions. The reaction rate increases with increase in [NPG], [\(\text{VO}^{2+}\)], [\(\text{Cu}^{2+}\)] and decreases with [\(\text{H}^+\)]. No significant effect of ionic strength and dielectric constant on the reaction rate was observed. Kinetics of oxidation of alanine and 2-amino isobutyric acid (2-AIBA) by PMS in the presence of Cu(II) ions at 308K was investigated in perchloric acid medium under pseudo-first order conditions. An autocatalytic effect was observed due to the formation copper peroxide intermediate. The rate constant for the catalyzed \((k^2_{\text{obs}})\) and uncatalyzed \((k^1_{\text{obs}})\) reactions were calculated. The kinetic data showed that both the reactions were first order with respect to [\(\text{AA}\)] and [\(\text{Cu(II)}\)] and inverse first order with respect to [\(\text{H}^+\)]. Further, \(\text{VO}^{2+}/\text{Cu}^{2+} - \text{amino acid}\) complex were synthesized and characterized by FT-IR spectroscopy. The \(\text{VO}^{2+}/\text{Cu}^{2+}\) ion – amino acid complexes are screened for their antibacterial and anticancer activity and showed good anticancer activities with high percentage of cell inhibition.